

Jand, International Conference of the POLYMER PROCESSING SOCIETY



July 25-29, 2016 LYON FRANCE



The Digital Book of Abstracts













http://pps-32.sciencesconf.org/

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* The digital Book of abstracts is edited by Dr. Khalid Lamnawar (Associate Prof.) and Prof. Abderrahim Maazouz (PPS-32 Chairman). The peer-reviewed conference proceedings will be published in PPS Proceedings and indexed by Chemical Abstracts. More details are given in the Technical program book. All accepted abstracts are included in the digital Book of Abstracts. Conference Papers are given in USB flash drive with a html access page. Archives of conference proceedings are available online. Full text archives are available to current members upon login in PPS website.

PPS[®]32

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PPS[®]32

<u>The Polymer Processing Society</u> (PPS) (<u>www.poly-eng.uakron.edu/pps/</u>) was founded in March 1985 at the University of Akron, Ohio, USA. The intent was to provide a mechanism and format for interaction and presentation of research results in the international polymer processing community. The goals are to foster scientific understanding and technical innovation in polymer processing by

providing a discussion forum for the worldwide community of Engineers and Scientists in the field. The thematic range encompasses all formulations, conversion and shaping operations applied to polymeric systems in the transformation from their monomeric forms to commercial products. Membership for the PPS is open to all researchers in the field and to all persons who feel the activities of the society advance their professional development. Membership forms are available on the PPS website.



Centre de congrès, "Cité internationale"- Lyon Conference center.

Symposia Organizers

A. General Symposia

S01. Blow Molding, Thermoforming and Rotomoulding John Vlachopolous (Canada), Kwang J. Kim (USA), Nguyen Dang Luong (Finland), Charkhtchi Abbas (France), Schmidt Fabrice (France).

S02. Nanocomposites and filled Polymers: Suprakas Sinha Ray (South Africa), Sati Bhattacharya (Australia), Sadhan Jana (USA), Tony McNelly (UK), J-F Gérard (France), Mustapha Bousmina (Morocco), Yves Grohens (France).

S03. Extrusion and Extrusion Processes: Sadhan C. Jana (USA), Maazouz A. (France), José Covas (Portugal), Hossein NAzokdast (Iran), Agassant J-F (France), Jose Maria Kenny (Italy), Philippe Coates (UK).

S04. Polymer Blend and Alloys: Kiyohito Koyama (Japan), Paula Moldenears (Belgium), Christian Carrot (France), Volker Altstädt (Germany), Françoise Fennouillot (France).

S05. Polymer Foams and Lightweight structures: Chul Park (Canada), Masahiro Ohshima (Japan), Roberto Pantani (Italy), Jannick Duchet (France).

S06. Biopolymers and Polymer from Renewable Ressources: Michel Huneault (Canada), Etienne Fleury (France), Christian Bonten (Germany), Luc Avérous (France), Patrick Navard (France).

S07. Process Modeling and Simulation: Igor Emri (Slovenia), Rahul Gupta (Australia), Patrick Anderson (Netherlands), Andrew Hrymak (Canada), Toshihisa Kajiwara (Japan), Rudy Valette (France), Amine Ammar (France).

S08. Process Monitoring, Control and Sensors: Georg Steinbichler (Germany), Jose Maria Kenny (Italy), Hossein Nazockdast (Iran), Keiji Tanaka (Japan), Didier Delaunay (France), Mhamed Boutaous (France), Clemens Holzer (Austria)

S09. Reactive Processing: Costas Tzoganakis (Canada), Jin Kon Kim (South Korea), Mohamed Taha (France), Véronique Bounor-Legaré (France), HU Guo-Hua (France).

S10. Rheology and Rheometry: Joao Maia (USA), Masayuki Yamaguchi (Japan), Jan Vermant (Switzerland), Khalid Lamnawar (France), Nadia El-Kissi (France), René Muller (France).

S11. Elastomers and thermoplastic Elastomers : Kinsuk Naskar (India), Tony McNelly (UK), Krisda Suchiva (Thailand), Liqun Zhang (China), Charoen Nakason (Thailand), Philippe Cassagnau (France).

S12. Fiber, Films, and membranes: Narongrit Sombatsompop (Thailand), Musa Kamal (Canada), Hamid Kaddami (Morocco), Alain Dufresne (France).

S13. Injection Molding and Mold: Andrew Hrymak (Canada), Shih-Jung Liu (Taiwan), Yves Bereaux (France). Michel Vincent (France).

S14. Mixing and Compounding: Tim Osswald (USA), Ica Manas-Zloczower (USA), Jozsef Karger-Kocsis (Hungary), M. Sugimoto (Japan), J-Charles Majesté (France), Bruno Vergnes (France), Gerrit Peters (Netherlands), Pierre Elemans (Netherlands)

S15. Morphology and Structure Development (with special honoring session of J-M. Haudin):Patrick C. LEE (USA), Uttandaraman Sundaraj (Canada) , Fulchiron R (France), Boyer Severine (France), Billon N (France), Abdellah Ajji (Canada), Peter Van Puyvelde (Belgium), Giuseppe Titomanlio (Italy).

B. Special Symposia

S16. Recycling and Plastic Solutions for Eco-conception: Jae Wook LEE (Korea), Hani Naguib (Canada), Valerie Massardier (France), Kim Ragaert (Belgium).

S17. High performance composite processing: Jingshen Wu (Hong-Kong), Paolo Ermanni (Switzerland), Ashok Misra (India), Zoubeida Ounaies (USA), James C. Seferis (USA), B. Defoort (France), Ph. Boisse (France), F. Chinesta (France).

S18. Additive Manufacturing for Plastic Components: Manfred Schmid (Switzerland), G. Régner G (France), JY Charmeau, C. Barrès (France), D. Drummer (Germany).

S19. Microtechnology and smart materials: Patrick C. Lee (USA), Han Meijer (Netherland), Michel Vincent (France).

S20. Biobased Plastis and Materials for Renewable Energy: Ica Manas-Zloczower (USA).





Lambla and JL White winners

Lambla Award winner for 2016 is Kinsuk Naskar of the IIT Kharagpur, India



Dr. Kinsuk Naskar was born in 1973 in Calcutta, India. He received Bachelor of Technology (B.Tech.) degree in Polymer Science and Technology in 1998 from the University of Calcutta, India. In 2000, he completed his Master in Technology (M.Tech) in Rubber Technology from Indian Institute of Technology (IIT), Kharagpur. In April 2000, he joined the University of Twente, The Netherlands as a Ph.D. employee under the supervision of Prof. Dr. Jacques Noordermeer in a project funded by Dutch Polymer Institute (DPI). He received his Ph.D. degree in June 2004. Since August 2004, he joined Rubber Technology Centre, IIT Kharagpur, India as a Faculty member. Currently he is holding the position of an *Associate Professor*. In 2005 he received DPI Patent Award from

The Netherlands for his invention in the field of multifunctional peroxides cured thermoplastic elastomers. In 2008 he received prestigious Alexander von Humboldt Research Fellowship from Germany and worked at IPF Dresden in the group of Prof. Dr. Gert Heinrich. His fields of interests are: polymer blends and composites, processing of elastomers and thermoplastic elastomers, radiation processing and cross-linking, reinforcement, green tyre technology etc. He has so far 76 papers, 4 patents and 8 books/book chapters. He has already supervised 7 PhD students and 17 Master students. He is married with Simontiny and they have two children namely, Kaustav and Rishav.



JLWhite Innovation Award for 2016 Goes to Prof. Eric Baer, the Founder of the Department of Macromolecular Science and Engineering, Case Western Reserve University



The James L. White Award will be given at PPS-32 to Eric Baer for the development of micro and nanolayered polymer systems using continuous coextrusion processing.

Professor Baer, who serves as the director of the National Science Foundation Science and Technology Center on Polymer Layered Systems (known as CLIPS), has over a period of forty years led the development of novel high value added polymeric structures and devices including novel gradient index lenses, high barrier films, and advanced films for energy storage. Recently he and his CLIPS team have developed a new nanofiber co-extrusion process with promising

applications as membrane filters. In 2010 Professor Baer founded Polymer Plus Inc., which is translating these processing technologies into several new applications including gradient index optical devices, high temperature capacitors, and advanced filters for environmental control.

Throughout his career, Professor Baer has concentrated on processing, structure, and property relationships and has published over 600 papers concerning these subjects. A fellow of various scientific and engineering societies, Professor Baer has been the recipient of many awards and has edited several technical journals in his areas of expertise.



Plenary Lectures

Structure development in Polymer Nanocomposites: From basic understanding to additive manufacturing

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In the present work, the effect of polymer-clay specific interactions, Brownian diffusion and hydrodynamics on the structure development in clay-polymer nanocomposites were studied on a model system made of PDMS-F matrix filled with 2wt% of Cloisite 30B, where F is the nature of the attached functional group with increasing intensity of polymer-C30B specific interactions. The steps of i) diffusion, ii) dispersion, iii) exfoliation and iv) clay distribution were examined using a home-modified XRD coupled with Rheomoetry and Light Scattering techniques. The simultaneous measurements allowed drawing a quantitative picture of structure development during both static and flow regimes. The obtained results were then rationalised by use of DLVO theory coupled with diffusional and rheokinetic models. The gained basic understanding is used to preserve the structure in specific additive manufacturing process.

9

Industrial Applications and Needs for Aeronautic and Space Applications

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The European Aeronautic and Space Transportation industries face strong challenges in the materials and technologies domain. For exemple, current families of civilian and military launchers will be upgraded or replaced in the next decades, and a stronc competition is on going for aeronautics.

To meet the requirements of these new developments, Airbus Defence and Space, the European prime contractor for launchers, has established a composite materials and technologies development roadmap. This roadmap is based on the main requirements of the two major applications: next generations of civil launchers and military motor cases.

It especially integrates the following objectives: to reduce the total ownership cost, to integrate environmental constraints as well as sustainable development approaches, to develop robust processes and to minimize the overall weight by designing integrated structures. Out-of-autoclave (O.o.A) technologies and associated functionalized materials are the spinal column of this roadmap.

At the same times, for planes and helicopters, Airbus operations and Airbus helicopter face challenges with regard to costs; manufacturing speed, robustness, regulation challenges, and so on, and develop also roadmaps and strategies for competitiveness.

The present lectures will present an overview of the needs and the challenges for polymer and composites in the main Airbus divisions. It will focus on the communalities and the specificities of the aeronautics and space applications requirements and development roadmaps. It will present the challenges that are to be solved for the material and processing communities in order to fae tomorrow's challenges.

Access to new properties compromise: polyolefins-based solutions are still in the race

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Even if known for a long time, polyolefins could still contribute in identification of new compromise of properties :

- The mean molecular mass and global comonomer content is well-controlled for a long time;

- However, thanks to the access to new catalyst families like metallocene catalyst, combined with appropriated polymerization process, the range of accessible polyolefins molecular structures becomes broader and broader, offering to manage the molecular weight distribution, the short chain branching content and distribution, the tacticity and the long chain branching content (and distribution). As a direct consequence, the polyolefin microstructure could significantly vary from one grade to another, with strong consequences, on viscosity, crystallization behaviour, ... At the end, creep, ductile break, sealing properties, ... could also be significantly affected. This induces profound changes in grades proposed in traditional polyolefins applications like film, pressure pipes, ... but, in several cases, this also profoundly modifies the inter-materials competition;

When arriving at the limit of product designs opportunities, additional properties change could still be induced thanks to formulation and/or by specific morphologies induced by the process. For example, combination of polyolefins with nanomaterials revolutionized conductive polymers, allowing access to various electrical conductivity levels, even with very small filler content.

Miniaturization is a trend but how does it affect the morphology development in immiscible polymer blends during shear flow?

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Abstract: For many years, polymer blending has been recognized as a method to generate materials with improved properties. These properties are highly dependent on the flow-induced phase morphology. The bulk dynamics of immiscible blends during flow is relatively well understood, especially when the system contains Newtonian components. Stimulated by the trend towards miniaturization, studies have recently focused on flow of immiscible blends in confined geometries. In that case the morphology development is not only affected by the material characteristics and the flow type, but also by the degree of confinement.

Here we present an overview on the morphology development in dilute, immiscible two-phase polymeric blends in confined shear flow. Droplet break-up and droplet coalescence are investigated systematically for a range of viscosity ratio's. For this purpose the droplets are visualized in a counter rotating shear flow cell equipped with a microscope. Concerning for break-up, it was observed that geometrical confinement promotes droplet break-up when the viscosity ratio is above 1, which implies that the critical capillary number for break-up decreases. At viscosity ratio's around one, confinement does not affect the conditions for droplet break-up whereas at viscosity ratio's below 1 the critical capillary number increases with increasing confinement, indicating that confined droplets are stabilized by the presence of the walls. Numerical simulations, using a boundary-integral method, could reproduce and explain these findings.

For coalescence, on the other hand, the effects of confinement are qualitatively similar for all viscosity ratio's: confinement decreases the coalescence angles and renders coalescence possible up to higher capillary numbers and initial offsets. Moreover, confinement induces a lower initial offset boundary below which the approaching droplets reverse flow direction without coalescence. However, the range of conditions for which coalescence occurs decreases with increasing viscosity ratio. The results are supplemented with finite element numerical simulations in 2D to explain the observations.



Polymers under topological constraints: a rheological journey from entanglements to nanocomposites

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It is known that entangled polymers exhibit plateau modulus and relax stress via distinct mechanisms (reptation, fluctuations and constraint release), depending on their size and molecular structure. The key is their ability for conformational adjustments, which is mediated by the free ends. Molecular understanding can only be achieved via synergy of targeted synthesis, characterization, physical experiment and modeling or simulations. In this spirit, after a selective presentation of the state-of-the-art, we present recent developments addressing some outstanding challenges: (i) To decode the viscoelastic response of commercial branched polymers, we use appropriately designed model comb polymers consisting of backbone and grafted chains with varying number and size. We explore their transient response in simple shear and relaxation upon flow cessation, and compare against linear and star polymers which serve as reference. We also examine their transient response to uniaxial extension. The observed features are rationalized by the tube model and recent simulations. The message is that dynamic dilution of hierarchically relaxing segments controls both linear and nonlinear viscoelasticity. (ii) In the absence of free ends (ring polymers) the rheology is very different and characterized by power-law stress relaxation. Rings can serve as effective rheology modifiers for linear polymers. (iii) Adding particles to polymers dramatically affects rheology. We use particles with known interactions as means to provide additional topological restrictions and alter the dynamics of the resulting nanocomposites. The above examples provide a framework for designing novel polymeric systems and linking rheology to processing. Acknowledgements: F. Snijkers (Lyon), G. Ianniruberto, R. Pasquino, G. Marrucci (Naples), T. Chang (Pohang), J. Roovers (Ottawa), P. Lutz (Strabourg), N. Hadjichristidis (KAUST), S. Kumar (Columbia), H. Lentzakis, S. Costanzo, Z-C. Yan, M. Kaliva (Crete).



From wall slip, extrusion instabilities to melt fracture: can nonlinear rheology of entangled polymers be useful to polymer processing?

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Polymer processing instabilities severely limit the productivity in plastics and rubbers industries. By delineating rheological responses of entangled polymeric materials without any pre-formed notion of the underlying physics, we explore the rheological origins of these difficulties in molecular terms. Specifically, this presentation summarizes a decade of intensive research carried out in my lab at Akron that has completely changed my worldview of the essence of nonlinear rheology of entangled polymers. In about sixty publications, we have collected coherent and comprehensive phenomenology [1] and proposed a molecular network paradigm [2,3] to explain the observed mechanical breakdown of polymers under large deformation. The new molecular-level understanding unified the two fields of shear and extensional rheology. It not only addresses the concept of yielding in terms of chain disentanglement but also deals with the phenomena of strain localization. In simple shear, we can predict when, how and why polymeric liquids (solutions and melts) switches from wall slip to bulk shear banding [4]. In fast uniaxial extension, we can no longer expect to reach fully developed flow state before the specimen undergoes various forms of breakup [5]. In extrusion, well-entangled melts suffer sharp shear strain discontinuity upon entry into extrusion dies that varies both spatially and temporally [6], leading to the so called gross melt fracture. It appears all types of "melt fracture" arise from some form of strain localization due to localized yielding of the entanglement network via chain disentanglement. [1] Soft Matter 11, 1454 (2015). [2] J. Chem. Phys. 127, 064903 (2007). [3] Macromolecules, 46, 3147 (2013). [4] Macromolecules, 44, 183 (2011); J. Rheol. (2016), to be published. [5] J. Rheol. 57, 223 (2013). [6] J. Rheol. 57, 349 (2013).



Abstracts

A.General Symposia

S01- Blow Molding, Thermoforming and Rotomolding

- S02- Nanocomposites and filled Polymers
- S03- Extrusion and Extrusion Processes
- S04- Polymer Blend and Alloys
- S05- Polymer Foams and Lightweight structures
- S06- Biopolymers and Polymer from Renewable Resources
- S07- Process Modeling and Simulation
- S08- Process Monitoring, Control and Sensors
- S09- Reactive Processing
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S15- Morphology and Structure Development (with special honoring session of J-M. Haudin))

B. Special Symposia

S16- Plastic Solutions for Eco-conception

- S17- High performance composite processing
- S18- Additive Manufacturing for Plastic Components
- S19- Microtechnology and smart materials
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A. General Symposia

S01- Blow Molding, Thermoforming and Rotomolding

Keynotes

S01-394

Vlachopoulos John

Particle Sintering from Rotational Molding To Additive Manufacturing

Coalescence (usually called sintering) of polymer particles is inherent in the process of rotational molding. Based originally on the coalescence of glass and ceramic particles, models were developed for the neck formation and growth. The driving force is surface tension opposed by viscosity. A model first proposed by Frenkel in 1945 (corrected by Eshelby in 1949) applies to the early stages of neck formation. This model was subsequently extended to the entire process of neck formation by the author and his co-workers (Bellehumeur, Pokluda, Kontopoulou and Takacs) in the 1990s and early 2000s . Further studies also included the role of viscoelasticity. The experimentally observed trends are fully in agreement with the model predictions. Experiments in rotational molding showed the great usefulness of the modified Frenkel/Eshelby model. Experimental studies of coalescence of just two polymer particles under the microscope in a heated chamber can provide a lot of information on the role of various parameters such as particle size, particle shape and polymer rheology. These studies have found application in the determination of rotomoldability of various resins, including recent efforts on rotational foam molding (by Emami and the author in publications that appeared in 2014 and 2015). Recently, the extended Frenkel/Eshelby model has found applications in laser sintering (LS) in which an

object is built layer-by-layer using powdered materials and a scanning laser beam. The next improvement of the model requires inclusion of temperature dependence of viscosity due to high variation in temperatures in LS. Among the benefits of accurate modeling in this area of additive manufacturing is the potential for enlarging the number of suitable materials. Of course, the properties and how they compare to parts produced by other methods is the ultimate arbiter of usefulness.

S01-764

Pop-Iliev Remon

Towards Cellular Plastic Composites Blown With Physical Blowing Agents In Rotational Molding

molding is a traditional plastic Rotational processing technology particularly useful for manufacturing large-sized and complex-shaped single-piece hollow articles. Over recent years, it has been deliberately modified into a technology that advantageously allows for creating a cellular structure, i.e., a foamed polymeric layer or core within the interior of the hollow molding that thereby encapsulates it entirely with a layer of solid polymeric skin with a desired thickness. However, the resulting extended duration of the mold-cooling segment due to the insulative effect of the developed foam layer or core within the mold represents a significant inherent disadvantage. Consequently, it becomes very difficult to effectively control the process so to retain a finecelled foam morphology and skin thickness uniformity. To address these disadvantages, an innovative extrusion-assisted rotational foam molding technology has been designed, developed and recently patented (US 8,628,704 B2; Jan. 14, 2014). It is refereed to as Rapid Rotational Foam Molding. Presently, applying chemical blowing agents is a common practice and a mandatory routine in rotational foam molding plastics processing operations due to the intrinsic atmospheric nature of the process (vented molds). However, the newly-patented rapid rotational foam molding process is expected to advance the



scientific knowledge in the field and influence the direction of thought and activity. This is so, because for the first time, it fosters engineering potentials for elimination of the blowing agent nature-related limitations in the manufacture of advanced ultralightweight multi-layered ultra low-density rotationally foam molded cellular composites. This paper attempts to identify the potentials of physical blowing agent-based foaming in low-pressurized processing settings, such as in rotational molding. The resulting new classes of ultra lightweight integral-skin rotationally foam molded cellular would be characterized with composites dramatically improved mechanical, strength-toweight, insulative, and morphological properties that are currently not achievable.



Oral

s01-19

measurements using image analysis of tomography data are performed and comparisons with the simulation results show good agreements.

S01-218

Nixon James

Biglione Jordan, Béreaux Yves, Charmeau Jean-Yves

Numerical Simulation of the Shaping of a Flask through the Injection Blow Moulding Single Stage Process

The injection blow moulding single stage process consists of producing hollow parts starting from the injection moulding of the preform shortly followed by the blow moulding of this preform. Such a process is usually available on dedicated machinery. An innovativ technology allow one to produce hollow parts on a standard injection moulding machine. Both the injection moulding stage and the blow moulding stage are being taken care of in an injection mould. Thus the dimensions of this mould are those of a conventional injection moulding mould. The fact that the two stages are located in the same mould leads to a process more constrained than the conventional one. This process temperature molecular introduces gradients, orientation, high stretch rates and high cooling rates. These constraints lead to a small processing window. In practice, the preform has to remain sufficiently melted to be blown so that the process takes place between the melting temperature and the crystallization temperature. In our numerical approach, the polymer is supposed to be blown in its molten state. Hence we identified the mechanical behaviour of the polymer in its molten state through dynamical rheology experiments. The validity of such an approach remains on the hypothesis that the crystallization does not occur before and during the blow moulding stage. To ensure this assumption, the effects of the cooling rate and the shear rate have been investigated. A viscous Cross model has been proved to be relevant to the problem. Thermal dependence is assumed by an Arrhenius law. The process is simulated through a finite element code (POLYFLOW software) in the Ansys Workbench framework. Thickness

Effect of PET moisture content during ISBM bottle formation

Since the introduction of the injection stretch blow moulding (ISBM) poly(ethylene process, terephthalate) (PET) has been the preferred material for the formation of thin-walled, light-weight containers. PET preforms injection moulded are supplied to the end user bottle manufacturer; this may be a direct link from injection moulding phase to the ISBM reheat phase, or the preform may remain in storage for an indefinite amount of time. As PET can absorb moisture form the environment (hygroscopic), the amount of time the preform is stored for may become critical. This paper investigates the effect of moisture content on the thermal properties of PET and the resultant influence on the deformation behaviour. Removing the mould and performing a free-stretch-blow analysis, the internal cavity pressure and stretchrod reaction force was recorded with an instrumented stretch-rod and the surface strain was observed using a non-contact, stereoscopic digital image correlation (DIC) technique. Thermal material transition phases as a function of moisture were investigated using differential scanning calorimetry (DSC) analysis. Results reveal that the moisture content can influence the material deformation behaviour and effectively shift the glass transition temperature and onset of thermal crystallisation. The effects of moisture level on the processability of the PET preform will undoubtedly have an influence on the formation of the bottle during ISBM and as a result the material distribution and mechanical properties of the final bottle. This knowledge is critical at various stages in PET bottle supply chain from material suppliers and preform manufacturers to converter and end users. Although there are strict criteria for handling PET granules during the preform injection moulding phase, there is currently no specific



standard for appropriate preform storage during bottle manufacturing.

S01-246

Masato Davide, Lucchetta Giovanni

Modelling and Prototyping of the Centrifugal Casting Process of Paraffin-Based Thermoplastic Polymers

Centrifugal casting is a casting technique that is used for the manufacturing of thick-walled paraffin cylinders, which are difficult to cast by other means. A permanent axisymmetric mold is continuously rotated about its longitudinal axis at high speed as the molten polymer is poured. The liquid paraffin is centrifugally thrown towards the mold wall, where it solidifies after cooling. The casting is a thick-walled cylinder with an inner circular port. The technology is used to help avoid cracking and void formation inside the solid paraffin as it cools. These voids are formed because the liquid paraffin shrinks upon cooling by 15-25% depending on the grade of wax. In this work, the centrifugal casting process for the manufacturing of paraffin cylinder was modelled and prototyped. A numerical model of growth and dissolution of bubbles during centrifugal casting was developed for the prediction of the quality of the casting. The numerical solution of the model, which captures the combined effects of buoyancy, drag and diffusion, allowed the prediction of the time required to bubbles to either dissolve into the molten polymer or to leave the region of interest. Moreover, the influence of process parameters on the mechanical properties of the final casting was firstly investigated on a small scale, and then verified on a bigger scale.

S01-541

Boztepe Sinan, De Almeida Olivier , Le Maoult Yannick , Schmidt Fabrice

Identification of the temperature-dependent relation between thermo-optical properties and

morphology of semi-crystalline thermoplastics for thermoforming process

Heating of the thermoforming of stage thermoplastics are critical as it has great effect on their formability under forming and therefore product quality. As radiation heat transfer is widely used for the heating of thermoplastic preforms, physical background of the radiation heating of bulk thermoplastic polymers has to be understood well for an accurate prediction on their temperature profile. In the past, many numerical approaches were developed based on thermo-optical characteristics of thermoplastics whereas little attention was given to the relation between their microstructure and thermo-optical parameters. Considering semi-crystalline thermoplastics the effect of microcrystalline structure is key to identify the thermo-optical properties and develop an accurate numerical radiative heat transfer model for optimization of thermoforming process. Previous studies in literature showed that there is a strong coupling between microstructure of semicrystalline thermoplastics and their thermo-optical properties in the near-infrared spectral region. In the present work, the relation between thermooptical characteristics and microstructure of polyolefin-based (PO) polymer was studied considering the change in its morphology at various temperatures. The optical characteristics of the PO were experimentally analyzed under heating conditions using an in-house developed device that is built using a Fourier Transform Infrared spectroscopy, integrating sphere and heating plate. Thanks to the analyses, the changes in the thermo-optical properties of the PO were correlated to its varying morphology under temperature. As semi-crystalline increasing thermoplastics are heated up to melting temperature to soften enough for successful forming process, their microcrystalline structure may show variation above glass transition and this temperature-dependent temperature relation cannot be neglected for building an accurate numerical model for infrared heating assisted thermoforming.



S01-553

Lison Valérie, Rul Alicia, Hurtgen Marie, De Villepin Cédric, Claes Michaël

Understanding the role of a flow modifier additive in polyethylene/carbon nanotubes-based formulations for the manufacturing by rotational molding of electrically dissipative parts at reduced CNT content

Nowadays, the most commonly used approach to produce economically hollow plastic items of any size, open or closed and of any desired shape is the rotational molding. Rotationally molded parts are used in practically every market sector including automotive, agricultural, furniture, packaging, sports and leisure, water treatment, marine or construction industries. For some applications, a discharge protection is required, for static examples; in fuel system components to prevent sparks which may cause an explosion or fires in flammable environments; in packaging to avoid damage or destroy of sensitive electronic parts,... In this purpose, carbon nanotubes (CNT) used as additives in most thermoplastics are well known to be beneficial and efficient at low content. However, unlike most of the end-converting processes (e.g. injection or extrusion), rotational molding is a shear-free process which may play an important role on the properties and quality of the final parts. Therefore, in this study, CNT-based formulations will be fine-tuned especially in terms of melt viscosity in order to enhance the sintering step and fulfill all requirements of the targeted to applications such as surface resistivity, aspect mechanical surface, layer thickness or performances. The selection of the flow modifier additive will be performed with the help of rheological measurements. The contribution will focus on polyethylene-based materials since it accounts for more than 85 % of the volume in rotational molding market. Nevertheless, the principles studied and demonstrated in this work could be used to further developments of other CNT-based formulations with tailored electrical conductivities for examples nylon, in

polypropylene, polycarbonate or polyurethane resins.

S01-628

Afzali Kamal, Keshavarzian Ali

Effect of Molecular Weight Distribution on the Thermal and Physical-Mechanical Properties of High Density Polyethylene Blow Molding Grade

High density polyethylene (HDPE) is а thermoplastic material that is characterized as a semi-crystalline polymer. Density, molecular weight and molecular weight distribution (MWD) dominate the resin properties that influence the manufacture of the polyethylene products and the subsequent performance of them. Resins with a broad range of distribution have good impact resistance and good processability. A polymer with a narrow MWD contains molecules that are nearly the same in molecular weight. Polymers can also have a bimodal shaped distribution curve. Resins having a bimodal MWD contain both very short and very long polyethylene molecules, giving the properties resin excellent physical while maintaining good processability. In this research, two blow molding grade of HDPE (BL3) with the same specifications (melt flow rate (MFI) range and density) that those produced by different manufactures were compared and studied. The MWD of the BL3 samples were studied with Gel permeation chromatography (GPC) and Capillary Rheometer (CR). Differential scanning calorimetry (DSC) was used to study the thermal properties and the Notched impact test used to study Impact Strength. The GPC results have shown that both samples, had similar bimodal shaped distribution curves, but curve of sample 2, located partially in the higher range of MWD (placed in the higher quantities on the horizontal axis (molecular weight)) than the sample 1. The CR results also showed that both samples, had similar distribution, but the sample 1 shows better processability in the blow molding shear rate range than the other sample. This was observed because the sample 1 included the lower molecular weights than the sample 2. The DSC results have shown that sample



2 had higher crystallinity and Tm than the other sample. Notched impact test results also showed that the sample 2 had higher impact resistance. Results showed that sample with the higher range MWD, had better thermal and physical-mechanical properties.

S01-736

Höfler Günther, Lin Richard J.T., Jayaraman Krishnan

Investigation of Halloysite as Reinforcement for Polyethylenes in Rotational Moulding

Rotational moulding of plastics is primarily used for the manufacture of hollow products. The predominant material used worldwide in this industry is polyethylene of various densities, most commonly in powder form. Previous studies of reinforcement materials in rotational moulding often report problems with agglomerations or inward migration of the filler. A shortcoming of rotational moulding is the difficulty of adding fillers due to the process' nature of moulding at only atmospheric pressure despite being in a closed mould. In spite of the advances in machine adaptations and mould configurations to apply internal pressure, this study focusses mainly on non-pressurized composite production. Halloysite is a natural nano-size mineral clay, occurring in different morphologies, such as tubular, platy, and spheroidal. It has an aluminol and a siloxane surface, which present different degrees of reactivity. Due the low surface charges - exfoliation or intercalation is not necessary -, halloysite is easier to process compared to other clay fillers and achieve good particle dispersion, which renders it to be a potentially suitable candidate for reinforcing rotationally moulded products. Additionally, halloysite showed to improve the thermal stability of LLDPE, which is very important as rotational moulding is usually performed close to degradation temperature. In this study, nanoparticle-reinforced composites containing halloysite with medium density or high density polyethylene are produced by rotational moulding. The influence of halloysite on the processability - melting temperature, melt flow index and internal mould temperature -, and

mechanical properties - tensile, flexural and impact -, is investigated. Keywords: Rotational moulding, halloysite, medium density polyethylene, high density polyethylene, nanoparticle-reinforced composite.

S01-9

Buffel Bart, Van Mieghem Bart, Van Bael Albert, Desplentere Frederik

Optimization Of The IR-Heating Phase In Thermoforming Of Thermoplastic Sheets: Characterization And Modelling

The goal of the heating phase in thermoforming is to obtain a uniform through-thickness temperature distribution as quickly as possible. Although the importance of the heating phase in thermoforming is clear, trial and error methods to determine the heating parameters are still common practice in industry. The current study addresses this issue by means of combined experimental and modelling efforts. The heating characteristics of two different thermoforming installations (halogen and ceramic heater elements) are experimentally determined by means of a silicone sheet with embedded thermocouples. The measurements allow to characterize the through-thickness temperature differences as a function of time. Lowering the emitted radiative power, decreases these temperature differences but also in-creases the required heating time. The experimental timetemperature data was implemented in a finite difference script to construct a framework of each thermoforming installation. In this script, heat transfer through radiation, convection and conduction are taken into account during the heating and pre-forming equilibration time. Thermal properties of the silicone sheet and various thermoplastic sheets were measured using DSC and MTPS methods. Based on the material properties and the target forming temperatures, the optimal heating settings of a thermoplastic sheet are determined. The methodology has been validated in industry by means of different case studies. Moreover the developed scripts allow to gain knowledge on the through-thickness temperature



distribution as a function of time. The results of this study lead to a more comprehensive understanding of the contact free heating of thermoplastic sheets and to the op-timization of the heating step which lowers the start-up time and cost.

S01-94

Schmidt Fabrice Mario, Le Maoult Yannick

Infrared Radiation applied to Blow Molding and thermoforming

The infrared heating of polymers is often a crucial step during Injection-Stretch Blow Molding (ISBM) or thermoforming processes, because radiative heat transfer can be very efficient in comparison to conductive or convective heat transfer. Indeed, the thermal conductivity of polymers is really low (0.1 $\leq k \leq 0.6$ W/m/K) and consequently optimising the heating and/or cooling steps remains a challenge. The results presented are based on intensive research work, conducted at the ICA Institute over the past ten years. After a brief introduction, the authors expose basic concepts dealing with radiative properties and more particularly infrared. The main radiative properties (emissivity, reflectivity, absorptivity ...) both for emitters and polymers are measured and analysed. In addition, different methods to determine relevant parameters such as filament lamps temperature are detailed. The development of accurate surface temperature measurements infrared using camera is subsequently described. This powerful non-contact measurement device can also be applied for estimating heat transfer coefficient. The infrared heating modelling of polymer preforms (tube-shape or sheet-shape), typically used in ISBM or thermoforming processes, is then presented. For many thermoplastic polymers, the assumptions of cold and non-scattering medium allow to simplify the Radiative Transfer Equation. Using previous assumptions for radiation modelling, the Beer-Lambert law together with the ray tracing method is suitable to simulate heating of semi-transparent polymers. Different results will be then presented, dealing with ISBM or thermoforming processes.



Poster

S01-479

Längauer Manuel, Zitzenbacher Gernot, Palmetshofer Matthias, Wagenknecht Tanja

Investigation of the influence of talc fillers on the infrared heating of polypropylene for thermoforming

The heating of polymeric semi-finished parts is a crucial step in the thermoforming process. The efficiency of the heating stage is influenced by several factors, with the choice of the heating method being one of them. The most prominent and economically most common selection is infrared radiation heating due to its simplicity and fairly short cycle times. Yet, the efficiency of this choice of heating for polymer thermoforming is relatively low, accounting to fewer than 20% in most cases. There are several ways to improve the heat absorption of plastic sheets. One of them is to decrease the optical transmission of the radiation with the help of inorganic filler materials. Those fillers do not only alter the optical properties, but also increase the thermal conductivity and decrease the specific enthalpy of the polymer which should lead to a more uniform temperature distribution in the semi-finished part during the heating step. This study shall reveal the influence of the concentration of a talc filler in a polypropylene matrix on the heating prior to thermoforming. The used material is PP with a talc content of 0, 10, 20 and 30% extruded to sheets of varying thickness. Three thermocouples are soldered onto the sheets from both sides. Using quartz heaters, the sheets are heated from one side only, to study the effect of the filler on the thorough heating of the material. The results of the investigations show, that with increasing amount of the talc filler, the time needed to reach the designated forming temperature decreases. Furthermore, the temperature drop from one side to the other relatively to the actual temperature also decreases when talc is added. This

leads to the conclusion, that inorganic fillers can improve the efficiency of infrared heating and lead to a more homogeneous temperature distribution.

S01-794

Agbessi Yao , Béreaux Yves , charmeau jean yves

Modelling of an innovative liquid rotational molding process

Powder rotational molding technology has little evolved until recent years because it stood alone on the market of large hollow parts, in small series. Recently, the disengagement of specific materials suppliers in rotational molding and increase of from competition blow molding and thermoforming, has motivated industrials to develop a new process of non-reactive liquid rotational molding, aiming at the use of standard injection-molding polymer grades and at reducing cycle times. In this new process, the polymer is melted beforehand in a classical injection unit and injected into the rotating mold. This method is closer to liquid coating than to the liquid/powder rotational molding process. The main part of this new process is to predict the repartition of the melted liquid layer adhering to the mold wall. Numerical approach is considered. First, modelling the thin viscous film flow with Matlab shows the hydrodynamics stability criterion of the film flow, the mean flow velocity and allows to control the viscosity parameter and the speed ratio rotation for a functional process. Then, using numerical scheme of Lax-Friedrichs, the repartition of the thin film flow with gravity is modelled. The hydrodynamic stability is respected. The lubrication approximation is considered, surface tension and the component of gravity normal to the film plane are neglected. Results are then compared with the three dimensional numerical simulation by Finite-Volume StarCCM+ code. Results show that the process time is strongly dependent on the choice of primary and secondary rotation frequencies. Keywords: Rotational molding, injection, thin film, lubrication approximation.



S02- Nanocomposites and Filled Polymers

Keynotes

S02-172

Islam Sakinul, Kao Nhol, Bhattacharya Sati N, Gupta Rahul K

Optimization and Modelling of Delignification Process for Nanocrystalline Cellulose Production from Rice Husk Biomass

Nanocrystalline cellulose (NCC) has been attributed as a noble material due to its superior properties for miscellaneous applications in medical science, pharmaceutical production and engineering fields. The major problems associated with the production of NCC are low production rate and inefficient process. Alkaline delignification plays an important role for the mass production of NCC from lignocellulosic biomass. In order to fulfill these research gaps a fractal kinetic model of alkaline delignification of rice husk biomass (RHB) was studied with process optimization. Fifteen kinetic experiments of alkaline delignification for NCC production from RHB, as designed by the Minitab® 11 software using the Box-Behnken method, were performed in a 2L jacketed glass reactor under three process parameters (time, temperature and alkali concentration) with ranges of 2-10 hours, 40-100°C and 1-4M, respectively. The nucleic growth model of fractal kinetics, developed by Nguyen & Dang (2007), has been successfully applied to the data sets available from this experimental work. The process parameters estimation for the fractal kinetic model was carried out using Matlab ® 2014b software. From this study it has been found that the most efficient delignification process with first order kinetics was obtained at 15 h, 95 °C and 2.5 M alkali

concentration. It has also been found that the kinetic rate coefficient of alkaline delignification is dependent on time instead of alkali concentration. The correlation coefficients R2 for this model was found to be 0.94, which indicated that the model can be considered with high level of confidence. From this hypothesis it can be concluded that the optimised condition gave maximum cellulose pulp for producing high quality NCC.

S02-289

Normand Guillaume, Peuvrel-Disdier Edith, Vergnes Bruno

Polypropylene/OrganoclayBasedNanocomposites:Determination of optimalconditions for dispersion

Although many studies were dedicated to the dispersion of clay in a non-polar matrix, its dispersion remains a challenge. We investigated in the past ten years the impact of the melt processing conditions on the dispersion state of organoclay in a polypropylene (PP) matrix. As evidenced by other authors, the specific mechanical energy (SME) appears to be a key parameter of the melt processing with regard to the nanocomposite structure. The dispersion state is improved by increasing the SME. However there is a critical limit beyond which the exfoliation levels off. In this work, a particular attention was paid to the effect of high SME on the nanocomposite structure in order understand the origin this limit. to of of PP, maleated Nanocomposites PPand organoclay with respective mass fraction of 85/10/5 were prepared in a co-rotating twin-screw extruder. High SME conditions were obtained via different ways by increasing the screw speed, decreasing the barrel temperature and using a more viscous PP matrix. Dead-stop experiments were performed in order to collect samples all along the screws. Samples were analyzed at different scales through SEM, TEM, X-Ray diffraction and rheology in small amplitude oscillatory shear. Extrusion conditions were analyzed using Ludovic[®] software. This allowed us to have access to local parameters along the screws. The results confirm that a higher SME



helps to improve the dispersion state. This is true unless the local temperature along the extruder is too high and induces a degradation of both the organomodifier and the polymer matrix, leading to a more difficult exfoliation. The systematic analysis combined to the calculation of local processing parameters allowed us to determine optimal processing conditions leading to the best dispersion state. The determination of the physical conditions limiting the dispersion is a key point to define specifications for the definition of twin screw extrusion profiles for dispersion purposes.

S02-290

Sundararaj Uttandaraman , Otero Navas Ivonne

Effect of MWCNT and block copolymers in the structure of polypropylene/polystyrene blends

The effect of block copolymer and multiwalled carbon nanotubes (MWCNT) incorporation on the phase morphology and electrical properties of polypropylene(PP)/polystyrene blends(PS) were investigated. The nanocomposites were prepared by melt mixing in a batch mixer. The blend morphology was characterized using scanning electron microscopy (SEM). MWCNT localization and dispersion was studied by using transmission electron microscopy (TEM) and light microscopy. The electrical conductivity of 1.0 vol. % MWCNT filled PP:PS/70:30 blend increased 5 orders of magnitude with addition of 1.0 vol% diblock and triblock copolymers. Increasing copolymer concentration more than 1.0 vol.% does not provide further improvement in electrical properties. The improvement in conductivity was correlated to the copolymer/filler localization and the morphology development in the polymer blend system.

S02-312

Zhou Shengtai, Hrymak Andrew, Kamal Musa

Microinjection molding of polystyrene/multiwalled carbon nanotubes nanocomposites

There is an ever-increasing demand for microcomponents in areas of electronics, biomedical and

microelectromechanical systems. Microinjection molding (µIM) has attracted considerable attention from both the industrial and academic spheres due to its potential for mass production of small polymeric components. However, most studies are only focused on unfilled plastics. Due to the very high shear rates present in µIM, polymer composites demonstrate issues with the filler distribution that may affect product properties depending on the filler purpose, i.e. structural, electrical or thermal conductivity. A specific mold which has a three-step configuration along the flow direction was adopted to study the effects of abrupt changes in mold geometry on filler distribution. This study is focused on the effect of high shearing conditions on the resultant properties of polystyrene/carbon nanotubes (PS/CNT) composites with special emphasis on electrical conductivity and filler distribution within the matrix. The effect of processing parameters such as injection velocity and melt temperature was investigated using design of experiments method. Results revealed that the electrical conductivity is process variable dependent and melt temperature is the dominant influencing factor. The percolation threshold of the obtained micro-components falls in the range of 5~7 wt%, with samples indicating an orientation of CNT in the flow direction, which was corroborated by morphology observation and simulation analysis.

S02-34

Pötschke Petra, Luo Jinji, Krause Beate

Polymer carbon nanotube composites for thermoelectric applications

The abundance of waste heat makes thermoelectric generators (TEGs) very attractive in harvesting low cost energy resources. Traditional TEGs made from semiconductor materials are limited to niche applications due to the high production cost, limited rare earth materials (e.g. tellurium) and brittle characteristics. In this context, there is growing interest to develop organic thermoelectric (TE) materials attributing to their low material cost, material abundance, high flexibility and scalability.



In recently years, there have been remarkable progresses in developing organic materials, in particular polymers, with high TE performance. Nevertheless, most of these studies concern conjugated polymers which are processed in solution. Here, we focus on the TE performance of polymer composites prepared from melt mixing. A cost effective and industrially widely used polymer, namely polypropylene (PP), is chosen as the matrix to fabricate electrically conductive composites. Carbon nanotubes (CNTs), the amount of which is above the percolation threshold (2 wt%), are mixed inside to construct an electrical conducting network. Single-walled CNTs, multi-walled CNTs and plasma modified CNTs are employed to study the influence of the CNT types and the functionalization on the morphology, dispersion, electrical and thermal conductivity and Seebeck processing conditions, coefficient. Melt e.g. temperature, rotation speed and time during small scale mixing are varied to find the optimum conditions for the highest ΤE performance. ionic Furthermore, liquid (IL, 1-methyl-3octylimidazolium tetrafluoroborate) is used as a processing additive during the melt mixing. It is found that IL acts as effective compatibilizer to improve the dispersion of all used CNTs in the PP correspondingly matrix and the electrical conductivity of composites. This melt mixing strategy opens new avenues for solvent-free large scale fabrication of polymer based TE materials.

S02-373

Rybak Andrzej

Modification of filler as an effective way to enhance properties of epoxy composites used in electrical devices

Filled epoxy composites are broadly used in electronic and power devices as an electrical insulation. It is of importance to achieve an efficient heat dissipation in such devices due to fact that thermal properties have a strong influence on their proper operation. For this reason, the modification of standard filler materials, such as silica or alumina, can give a promising solution. In this paper, a several methods for thermal conductivity enhancement will be discussed and experimental results will be shown, namely: a) incorporation of the hybrid fillers [1], b) use of magnetic fieldassisted filler alignment technology [2], c) synthesis and application of a novel core-shell materials [3]. The composite samples based on epoxy resin filled with the modified fillers have been investigated in determine the effective order to thermal conductivity. The obtained composite samples exhibited a significant improvement in the thermal conductivity. The results were analyzed with use of theoretical models. Additionally various the mechanical and dielectric measurements were performed showing a high potential for the composites with incorporated new modified fillers to be applied for the electrical insulation with the enhanced thermal conductivity. References: 1. K. Gaska, A. Rybak, C. Kapusta et al., Polym. Adv. Technol. 2015, 26, 26. 2. K. Gaska, G. Kmita, A. Rybak, et al., J. Mater. Sci. 2015, 50, 2510. 3. A. Rybak, K. Gaska, J. Mater. Sci. 2015, 50, 7779.

S02-43

Maxian Ondrej, Pedrazzoli Diego, Manas-Zloczower Ica

Modeling the Percolation Behavior in Bulk and Foam Polymers with Carbon Nanofillers

A new numerical model taking into account the random dispersion of nanofillers in a polymer matrix has been developed in order to predict the electrical percolation behavior of bulk and porous media incorporating 1D- carbon nanotubes (CNTs) and/or 2D- graphene nanoplatelets (GNPs). The numerical model uses applied vector calculus and linear algebra, and is able to predict the electrical percolation threshold of bulk systems assuming a perfect random dispersion and orientation of the nanofillers, resulting in a percolation volume of 0.023 and 1.628 vol% for CNTs and GNPs nanocomposites, respectively, showing а quantitative agreement with existing experimental observations [1]. CNTs were more efficient in forming a percolative network than GNPs, especially when using high aspect ratio fillers. The percolation volume was found to decrease with the



aspect ratio of CNT and GNP according to different relationships, while hybrid systems incorporating CNTs and GNPs exhibited significant synergistic effects when the two fillers were properly combined. The numerical model is also able to predict the percolation threshold in the case of porous morphology, showing a decrease in percolating volume with porosity due to filler confinement within the pore walls [2]. The parametric study of the present model can shed some light on how one can maximize the benefits arising from using different conductive fillers and tailor the polymer foam morphology to minimize the percolation threshold. Keywords: Carbon nanotubes; Graphene; Hybrid Systems; Numerical modelling; Porous materials; [1] Yue L, Pircheraghi G, Monemian SA, Manas-Zloczower I. Epoxy composites with carbon nanotubes and graphene nanoplatelets - Dispersion and synergy effects. Carbon 2014;78:268-78. [2] Ameli A, Nofar M, Park CB, Pötschke P, Rizvi G. Polypropylene/carbon nanotube nano/microcellular structures with high dielectric permittivity, low dielectric loss, and low percolation threshold. Carbon 2014;71:206-17.

S02-750

Macosko Chris

Toughening Polymers with Functionalize Graphene Oxide

Graphene oxide (GO) can be prepared economically from graphite. The epoxide and hydroxyl groups on provide many opportunities for attaching functional groups to the surface of GO. These can aid its dispersion in polymers and grafting to reactive systems. We show that very low levels of functionalized GO can increase the fracture toughness of brittle thermosets like epoxies and unsaturated polyesters. A microcrack mechanism is proposed based on microscopy of the fracture surfaces. Due to the stress concentration by graphene nanosheets, microcracks may be formed to absorb the fracture energy. However, above a certain graphene concentration, the coalescence of microcracks appears to facilitate crack propagation, lowering the fracture toughness. H. Kim, A.A.

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Oral

S02-11

Castro Jose M, Cabrera Eusebio, Zhao Yanan, Zhang Dan, Lee James

Multifunctional Nanopapers for Fiber Reinforced Polymeric Composites

In many applications, fiber reinforced polymer composites are exposed to solid particle erosion damage which reduces the performance of the material shortening the materials lifespan. In this research, novel thin nanoparticle films or nanopapers for use as a surface protective layer for composites fiber reinforced polymer are manufactured and characterized. Inclusion of these nanopapers through current manufacturing methods has shown increases in solid particle erosion protection of up to 7x and electromagnetic interference (EMI) shielding protection of 40 dB. Permeability of nanopaper is measured as an indication of difficulty of impregnation.

S02-110

SZOSTAK Marek, Walczak Rozalia

Polymer Composites with Zeolites

The article describes the investigation of the mechanical and thermal properties of polymer composite, consisting of zeolite filler and polyethylene matrix (HDPE). In the study two types of zeolites: the natural one, called Clinoptilolite originated from Lublin region in Poland and synthetic NaP1 produced from fly ash in the process of hydrothermal synthesis have been used. Zeolites have found wide applications in various fields such as chemical industry, microelectronics, optics, medicine, construction, environmental protection and agriculture. The most common zeolite is clinoptilolite, because it is the most easily accessible. The composites with 2, 5 and 10% by weight of zeolites in the HDPE matrix, have been prepared using at first the twin-screw extrusion and then injection molding methods method. The influence of the zeolite type and content on mechanical and thermal properties of obtained polymer composites has been presented. Also the structure of the composites has been studies using the SEM observations. The analysis shows that the addition of zeolite into the HDPE matrix increase Young's modulus and tensile strength together with the degree of crystallinity but decrease the impact strength and elongation. The presented preparation method and properties of obtained materials confirms the possibility of using this type of composites in production of injected parts. Keywords: polymer composites, zeolites, polyethylene, mechanical and thermal properties.

S02-113

Mighri Frej, Nafaa Athmouni, Elkoun Saïd

Effect of unfunctionalized and HNO3functionalized multiwall carbon nanotubes on the mechanical and electrical properties of cocontinuous polymeric systems

In this study, we will present our recent work on filled polymer systems made from an optimized cocontinuous mixture of Polyethylene terephthalate (PET) and polyvinylidene fluoride (PVDF) reinforced with highly conductive carbon additives composed of carbon black (CB) and synthetic graphite (GR). Multiwall carbon nanotubes (MWCNT) were functionalized then used to improve the electrical conductivity and mechanical properties of the developed systems, such as their flexural and impact strengths. It was observed that the best system was obtained using nitric acid (HNO3)-functionalized MWCNT. The latter led to the smothest samples surface, the lowest throughplane electrical resitivity (0.12 Ohm.cm) and the highest impact and flexural strengths. Theses results are attributed to the improved dispersion of the functionalized MWCNT, a result of their best compatibilization with the (PET/PVDF) polymeric phase.

S12-115



Chin Chih-Ping, Liu Jen-Yung, Cheng Kou-Bin, Chang Jing-Tang, Huang Fu-Liang

The Development of the Polyamide Filament Knitted Fabrics with Anti-mosquito, Anti UV, and Cooling Functions Using Chemical Synthesis Method

The innovation of these knitted fabrics is to use cooling fiber whose raw material is not physical compounded by traditional twin screw method, but synthesized directly by one single step chemical polymerization process. The functional powder is well-disturbed in the polymer solution while polymerization. The advantage is from the features of shorter processes, save energy and lower cost, etc. The results show that cooling additive slurry with 33% solid content and 67% DI water are directly mixed with precursors during polymerization. The best performance of cooling slurry suspension for added PPG and sodium pyrophosphate for dispersant compound ratio is 1 : 2, it has the best average particle size is 345.06nm, and -38.83mV for zeta potential measurement. Furthermore, the suspension could be conserved more than three days without sedimentation, and also the relative viscosity of polyamide 6 cooling chips is 2.184. Finally, we melt-spin the polyamide 6 filament and blend with the composite yarn with the function of anti-mosquitoes and anti-UV fiber. The product is under the test of dynamic thermal image outdoor one hour running that the ΔT is more than 0.9 °C, and static indoor 5 hours running that ΔT is more than 1.0 °C. We also got excellent cooling effect. In order to raise the color fastness to light of knitted fabric, the technique of dye select should be noticed. The composite and outdoor leisure series products were also proposed. These knitted fabrics have the cooling feeling, antimosquitoes and anti-UV function is over 50+.

S02-12

Safidine Zitouni -, Mahmoud Yasmine

Elaboration and characterization of nanostructured polyurethane rigid foams within the inclusion of oMMT: impact and fire proof behavior - 28

The aim of the present work is the elaboration of nanostructured polyurethane rigid foams within the inclusion of oMMT as a treated Nano clay(PUR/oMMT). The contents of oMMT are 2, 3, 5 and 10wt %. The nature expected by these rigid foams is the fire and impact proof behavior. The nanostructured materials were performed in two stages, firstly by the use of twin screw extruder (TSE)in contrarotative mode in which the blended polyols (CPP) were included between the MMT layers after treatment within the alkyl ammonium C18. And secondly the main urethanization reaction is performed using the combined processes:reaction injection molding (RIM) and controlled expansion to get pieces having parallelepiped shape. Both of later processes were performed by an appropriate montage. Various characterization methods toward reactants and Nano clays were used such as: FTIR, DSC, XRD and micro XRF. Adding the use of SEM and XRD behavior for the final items. The normalized inflammability test according to the UL 94 and tensile strength for the solid specimens was also performed. From the results it's found that these new materials exhibit an enhancement of tenacity and notable flame retardant character obviously for the threshold content which levels off at 2 wt. % of oMMT. Key words :nanostructured, PUR rigid foam, oMMT, TSE, RIM, impact strength, fire proof.

S02-122

Grace Landon

Projecting very long-term non-Fickian moisture absorption behavior based on short-term data

The slow approach to equilibrium concentration indicative of non-Fickian diffusion in polymer composites necessitates experimental time frames which are often of limited feasibility. As a result, experimental studies are terminated prematurely due to time constraints or incorrect identification of equilibrium. Here, the three-dimensional anisotropic diffusion behavior of a six, twelve, and forty-ply quartz-reinforced bismaleimide laminate is quantified through a five-year, full-immersion gravimetric absorption study. The applicability of the three-dimensional hindered diffusion model is



investigated, while projections of future absorption behavior made at 21 months are revisited in light of three years of additional data. The mathematical equivalency of the hindered diffusion model and a diffusion-relaxation model under certain conditions is discussed. Moisture content rises continuously throughout the five-year experiment for all samples. In the six-ply case, the standard termination criterion for the equilibrium condition is met before six months and 1.38% moisture content by weight. Actual moisture content reaches 1.56% after five years. The hindered diffusion model and associated forward projections of moisture content are found to conform well to experimental results.

S02-127

Kenig Samuel, Dodiuk Hanna, Tenne Reshef

Can Inorganic Nanotubes Replace Carbon Nanotubes in Polymer Nanocomposites?

In the advent of commercialization of inorganic nanotubes (INTs), new routes are proposed for tailoring the properties of polymer nanocomposite systems. INTs differ from multi wall carbon nanotubes (CNTs) with respect to its diameter (80nm compared to 10nm) and length (1 micron compared to a few microns). Distinctively, pristine INTs surface are rich in sulfur and tungsten elements with a small fraction of oxygen. CNTs surface is composed aromatic moieties that lead to agglomeration. The surface properties of these two classes of nanotubes effect their rheological properties and dispersion in polymers. The viscosities of CNTs containing resins (Epoxies, Polyurethanes) or melts (Polypropylenes, polyamides) are significantly higher compared to neat polymers, the respective while INTs demonstrate good dispersion in polymers and decrease the nanocomposite viscosities compared to the neat polymers. The reduced viscosities open new opportunities for INTs in liquid based processes like RTM (resin transfer molding) where the viscosity is of utmost importance. The good dispersability of INTs leads to improved mechanical as well as thermal properties. The mechanical nanocomposites properties of

containing less than 1% by weight of INTs increase the modulus by more than 50% for epoxy and polyurethane systems and toughness by more than 70%. At the same concentrations CNTs polymer systems showed an increase by only 30% in modulus and 20% in toughness. Simultaneously the glass transition temperature of INTs containing polymers showed a significant increase (more than 15oC) while equivalent CNTs containing polymers showed an increase of only a few degrees. SEM micrographs supported the experimental results indicating very good dispersion of the INTs and unique fracture mechanisms like crack bowing and cavitation. The outstanding attributes of INTs polymers compared containing to **CNTs** nanocomposites, comprise the basis for industrial applications.

S02-133

Shaayegan Vahid, Cuif Lorraine , Ameli Aboutaleb, Wang Sai, Park Chul B.

Investigation of Fiber Orientation and Displacement in High-Pressure Foam Injection Molding of Polystyrene/Carbon-Fiber Composites

We used an in-situ visualization technique to study the re-orientation and displacement of dispersed fibers in conductive polymer composites, fabricated by foam injection molding method. Composites of polystyrene/carbon-fiber were foamed using carbon dioxide. We observed that the carbon fibers, in the vicinity of cell nuclei, exhibited both rotational and translational motions under the influence of growing bubbles. Our experimental results showed that the initial cell-fiber distance plays a crucial role in the final alignment of the fibers. The shorter initial distance results in greater rotational and translational displacement of fiber during cell growth. The interaction between the cells and fibers was also modeled and validated using the experimental data. A fair agreement between the model prediction and experimental results was obtained. The results of this work, and the developed model, give a more realistic insight into the behaviour of fibers during foaming, and its influence on the functionality of the conductive polymer composites foams.



S02-140

Gong Xinhao, Shen Yucai, Wang Tingwei

Effect of OMMT on fire resistance of EVA-based ceramifying composites

EVA-based ceramifying composites, a kind of promising materials, can be widely applied in fire protection field, especially fire resistant sheaths for cables. However, the quick decomposition of the matrix has resulted in cracks and even holes in ceramic residues, which has a disastrous impact on the fire resistance of the residues. Here ceramifiable EVA composites were prepared by melt blending with wollastonite, glass frits and OMMT. Influence of OMMT on the pyrolysis behavior of the composites and properties of ceramic residues was investigated. Thermogravimetric analysis showed that the initial degradation temperature of the composite increased by 12°C and its maximum weight loss rates at the first stage and the second stage decreased by 25% and 36% respectively, when 10 phr OMMT was added. Besides, for samples heated from room temperature to 1000°C, addition of 10 phr OMMT led to a 20% increase in the flexural strength of the residues. XRD showed that an intercalated structure between EVA and OMMT was formed. Therefore, it was concluded that significant improvement in the thermal stability and the flexural strength is a result of the formation of the barrier layer.

S02-142

Deng Hua, Du Rongni, Fan Mingfeng, Fu Qiang

The Processing of Functional Polymer Nanocomposites

Various functions of polymer composites, including electrical conductive, thermo conductive, dielectric, EMI shielding, strain sensing, etc, has been extensively investigated. These functions need to be delivered by functional filler or structure. Therefore, the morphological control of these functional filler or structure should play vital role on the final properties of these functional polymer composites. Conductive polymer composites (CPCs) is used as an example. In recent years, CPCs containing large aspect ratio filler (CNT and graphene) has gained extensive attention. However, there are still two issues needs further investigation: 1. How to control the conductive network structure and their electrical property more effectively using morphological control methods as well as filler mobility; 2. How to design and fabricate special network structure for various functions. The author has carried out a series of studies focusing on "The relationship between different morphological control methods--filler network morphology & property-functionality". Through combing different processing methods and take advantage of filler mobility, new processing methods as been developed to control filler network morphology, novel multi-functional CPCs have been designed and prepared. Herein, CPCs, strain sensing polymer composites and dielectric polymer nanocomposites will be used as examples to illustrate the effect of morphology control on these functionalities.

S02-146

Jena Kishore Kumar, Alhassan Saeed M

Effects of Graphene/sulfur particles on thermal and crystallization of High density polyethylene (HDPE)

A series of novel hybrid composite were prepared from HDPE and newly synthesized Graphene / sulfur composite. Graphene / sulfur composite increased the thermal and mechanical properties of the hybrid composites. Melt compounding process was used to form thermally reduced graphenesulfur (TRG-S) composite and HDPE- thermally reduced graphene -sulfur (H-TRG-S) hybrid composite. After melt compounding of TRG-S composite, the resulted composite was characterized using Raman, XRD and FTIR to get the understanding of the composite structures. The HDPE- thermally reduced graphene-sulfur (H-TRG-S) multi hybrid composite was characterized by using FTIR, Raman, XRD TGA and DSC. FTIR and Raman show the structural conformation in the multi composites. XRD gives the sulfur and



graphene distribution in the polymer and also the nucleation behavior of polymers with increasing TRG-S concentration. DSC analysis suggests that with increasing the TRG-S concentration the crystallization was increased the in hybrid composite. The effects of nucleation and crystallization behavior on the thermal, morphology and mechanical properties of the melt compounded H-TRG-S composites are studied in this work.

S12-147

Agrawal Bhawana, Porada Monika Willert

The effect of additives on high temperature water retention, mechanical and thermal stability of polymer composites.

The high temperature water retention of new composites with PFSA (polyfluoro sulfonic acid) polymer matrix is investigated based on structural analysis of such polymers containing a mineral acid and MgF2-nanoparticles as additives. As compared to the parent polymer the temperature for water removal is increased by almost 50°C to 250°C. The thermal stability of the PFSA polymer is slightly decreased from 360 to 340°C with respect to the onset temperature of de-sulfonation and back-bone Different de-polymerization. PFSA polymer composite membranes with a fixed amount of sulfuric acid as additive and a varying amount of 3 to 15 weight % of MgF2-nanoparticles coated glass particles were investigated. Structural details of the PFSA evident from FTIR-ATR analysis of the solid membranes can be associated with two major phenomena: (1) dissociation of the proton from the sulfonic acid group in the presence of small amount of water and (2) changes in the conformation and / or the degree of the crystallinity of the PTFE hydrophobic domains composite membranes in the PFSA as a function of the polymer and the weight ratio of the solid additive. From these results evidence is given that sulfuric acid acts as bridging agent to facilitate direct bonding between the sulfonic acid groups of the PFSA polymer and MgF2-nanoparticles, which are deposited as coating on the surface of micron-size glass particles used for mechanical strengthening of the polymer. The

significantly increased water retention capability is attributed to the intimate bonding between the PFSA polymer and the solid inorganic additive. References: (1) Di Noto V.; Gliubizzi, R.; Negro, E.; Pace, G. J. Phys. Chem. B 110, 2006, 24972. (2) Di Noto V.; Gliubizzi, R.; Negro, E.; Vittadello, M.; Pace, G. Electrochim. Acta 53, 2007, 1618. (3) Di Noto V.; Piga, M.; Piga, L.; Polizzi, S.; Negro, E. J. Power Sources 178, 2008, 561. (4) Di Noto, V.; Piga, M.; Negro, E.; Giffin, G. A.; Polizzi, S.; Zawodzinski, T. A. RSC, Adv., 2013, 3, 18960. (5) Di Noto, V.; Piga, M.; Giffin, G. A.; Keti, V.; Zawodzinski, T. A. J. Am. Chem. Soc. 134, 2012, 19099.

S02-152

Mieth Florian, Heim Hans-Peter, Sauer Viola

Influence of artificial aging on the thermal conductivity of graphite and ceramic filled compounds

Thermally conductive modified materials are being increasingly applied in different fields of industry. Some of these applications have long lifecycles of 10 years or above. Due to that it has to be ensured that the thermal conductivity of the used materials is remaining at least about the same period of time. Usually the increase of the thermal conductivity is achieved by adding thermally conductive filler materials. Carbon or ceramic fillers are the most common types. In the last years several investigations in the field of thermally conductive materials analyzed the influence of different filler materials, filler content and processing conditions. Also the aging behavior of commonly used polymers is widely described. But studies on the aging behavior of thermally conductive composites are still missing. Existing studies on fiber reinforced composites are just poorly comparable. Besides the fact that they differ in terms of filler type and filler content, these investigations usually focus on mechanical rather than thermal properties. To fill this gap different matrix materials are compounded with typical ceramic and carbon based fillers. After processing in injection molding the specimen are subjected to artificial aging cycles and their thermal conductivity is determined. Finally the results are



discussed according to several aging based changes in the material, like cristallinity, moisture, fillermatrix interaction or thermo oxidative degradation using microscopy and thermal analysis.

S02-166

Kavianiboroujeni Azam, Cloutier Alain, Rodrigue Denis

Determination of the optimum coupling agent content for composites based on hemp and high density polyethylene

It is well known that for polymer composites based on natural fibers, the addition of a coupling is necessary to improve fiber dispersion and adhesion with the matrix. Nevertheless, an optimum content must be found which is related to the total surface area created between the fibers and the matrix. But in most cases reported in the literature, a single property (like tensile strength or flexural modulus) is used to determine this optimum value. In this work, high density polyethylene (HDPE) was reinforced with hemp fibers as a typical system. In particular, the addition of a coupling agent based on maleated polyethylene (MAPE) was studied to determine its optimum content. To better detect the specific effect of the selected coupling agent, reinforcement content was limited to 10% wt., while the MAPE content was controlled at different levels (0, 5, 7, 9 and 11% wt. based on total hemp content). Compounding was performed in a twin-screw extruder and the samples were produced by compression molding. From the composites obtained, a complete characterization in terms of morphology (SEM), mechanical properties (tension, torsion, flexion and impact), and density (pycnometry) was made. From all the results obtained, it was shown that 9% wt. MAPE was the optimum content to maximize all the mechanical properties (including density), with the only exception being the notched Charpy impact strength. These results indicate that any physical property besides impact strength can be used to determine the optimum coupling agent content.

S02-167

JAHAN NUSRAT, Ajji Abdellah , Mighri Frej, Rodrigue Denis

Development of piezoelectric properties in PVDF: Effect of particle concentration and stretching variables

Polyvinylidene fluoride (PVDF) has relatively high thermal stability (~120°C) with moderate piezoelectric coefficient (d33~30 pC/N), while cellular polymers such as polypropylene (PP) have higher d33 values (120-600 pC/N) with poor thermal stability (up to around 50°C) which limit their applications in high temperature transduction. Therefore, a three-phase composite was studied where organoclay was added to enhance the polar β phase and CaCO3 to introduce a cellular structure in PVDF to get a combined effect from both source of piezoelectricity with thermal stability. The samples were prepared by mixing PVDF with an organically modified nanoclay (1-12 wt%) and CaCO3 (30-40 wt%) into a Brabender mixer and subsequent hot pressing with thickness around 160 um. Fourier transform infrared spectroscopy (FTIR) results showed that although the supplied CaCO3 was not surface modified, it still results in around 30% of β phase in PVDF in absence of nanoclay and a gradual increase was observed in β phase with increasing amount of CaCO3. This increase was further improved by adding surface modified organoclay. Although various percentages of clay were used, 2 wt% led to maximum β phase (~55%) due to better dispersion. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) confirmed the results further. A maximum of 87% ß phase was found in PVDF/40 wt% CaCO3/2 wt% nanoclay sample after stretching at a ratio (R) of 4.5 at 90°C. Additionally, while the PVDF/CaCO3 composite was brittle enough to stretch beyond R=2, only 1 wt% of nanoclay in PVDF/CaCO3 made it stretchable above R=5. On the other hand, scanning electron microscopy (SEM) of the stretched films showed the presence of lens-shaped voids inside the film. With increasing stretching ratio and CaCO3 concentration, the percentage of porosity increased along with the length and height of the voids with homogenous distribution. A maximum 55% porosity was found for the samples studied with 40% CaCO3.



S02-184

Knorr Roland, Leuteritz Andreas, Boldt Regine, Kühnert Ines, Wang DeYi, Wagenknecht Udo

The role of process induced platelet orientation in layered flame retardants

Platelet shaped minerals like layered silicates and layered double hydroxides can play an important role in flame retardant compositions for polymers, if the minerals are dispersed in nano scale. Previous research was focused on chemical composition of the minerals, the modifiers and the role of the minerals in multicomponent flame retardant composites. One of the supposed mechanisms of flame retarding effects of layered nano minerals is to act as diffusion barrier for both combustible pyrolysis gases in one direction and oxygen in the opposite direction. Theoretically, these effects depend from orientation of the platelets, which will be tested with nanocomposites in practice. Nanocomposites of montmorillonite/polyamide-6 with different montmorillonite contents were prepared via melt compounding. These nanocomposites were shaped in standard samples for cone calorimeter tests. Tuned orientations of the platelets were set using different shaping methods like flat film extrusion, injection moulding compression moulding and combinations of them. The gas diffusion properties depending from orientation were measured. The burning behaviour of the samples was tested using a cone calorimeter. The measured burning parameters will be discussion regarding the influence of platelet different orientation caused by processing techniques. A future outlook will be given.

S02-211

Taguet Aurélie, Otazaghine Belkacem

How can the localization of nanoparticles (silica nanospheres or kaolin nanoplatelets) into PS/PA6 blends influence the final properties?

Dispersion of nanoparticles (NPs) in polymeric media is a key issue for all attended final properties [1]. It is well-known that dispersion depends on the affinity between the NP and the matrix but also on groups). Scanning Electron Microscopy showed that these two types of functionalization lead to different localization and orientation of the nanoplatelets in the 80/20 PS/PA6 blend, leading to different rheological, thermal and mechanical properties. Moreover, a gel-like behavior was noted for a PS/PA6 co-continuous system in which nanoplatelets were localized at the interface. [1] J. Jancar, et al., Polymer, 2010, 51, 3321-3343 ; [2] R. Bahrami, et al., ACS Nano, 2014, 8, 10048-10056 ; [3]

Polymer, 2014, 55, 2704-2715.

S02-214

Calorimeter.

by

or

Krause Beate, Cohnen Andreas, Pötschke Petra, Hickmann Thorsten, Koppler Dagmar, Proksch Bettina, Kersting T., Hopmann CH

T. Parpaite, B. Otazaghine, A. Taguet, et al.,

the processing conditions. Moreover, recent studies have shown that by functionalizing a NP it is

possible to control its localization in a polymer

blend [2]. However, very little works deal with the influence of this final localization of NPs into a

polymer blend onto properties [3]. In this work,

raw and functionalized silica nanospheres or kaolin nanoplatelets were incorporated into PS/PA6

(80/20) polymer blends by melt processing in order

to tailor their dispersion, their localization and the

final properties of the blends. In a first example,

silica nanospheres were dispersed either in the PA6

dispersed phase (raw silica NPs) or at the interface

silica NPs). This leads to different thermal

degradation behavior of the nanocomposites that

were measured by Pyrolysis-Combustion Flow

functionalization of kaolin has been achieved using

their asymmetric surface chemistry. Indeed, they

were functionalized by "grafting onto" of either

polystyrene-based silane copolymers (that can react

with both silanols and aluminols groups of kaolin)

copolymers (that reacts only with the aluminols

second

phosphonic

example,

acid

the

In

polystyrene-based

(γ-Méthacryloxypropyltriméthoxysilane-modified

Influence of Graphite and SEBS Addition to Polypropylene Composites on Thermal and Electrical Conductivity and Mechanical Properties 33



The incorporation of electrical and thermal conductive fillers in polymers is of great interest for electrochemical applications such as bipolar plates to replace metals in the fuel cell technology. The durability of bipolar plates based on thermoplastic composites and their production are not yet satisfactory due to the high proportion of the conductive filler and the resulting embrittlement. Therefore there is a need to reduce the proportion of the conductive filler on a high level (e.g. single or hybrid filler systems of carbon based fillers) and to improve the mechanical properties by blending with a suitable impact modifier. In this study, composites based on polypropylene (PP) and different filler systems were melt mixed using small scale microcompounder Xplore DSM15 as well as lab scale co-rotating twin-screw extruder Coperion ZSK26Mc. The measurements of the electrical and thermal conductivity as well as mechanical properties of the composites were performed on pressed plates. It was found that the addition of synthetic graphite powders having different particle size distributions leads to different increases of the thermal conductivity. The highest value was measured for composites containing TIMCAL Timrex® KS500. The electrical volume conductivity was detected around 5 S/cm at 80 wt.-% graphite. Furthermore, the influence of styreneethylene-butylene-styrene block copolymer (SEBS) based impact modifier on the mechanical properties of PP filled with 80 wt.-% of different synthetic graphite was investigated. For that the proportion of SEBS in the PP component was varied systematically. The conductivities were influenced by the kind of graphite and the content of impact modifier. The results indicate that the impact strength of the composite containing TIMCAL Timrex® KS500 can be increased by approx. 100% when replacing 50 wt.-% of the PP component by SEBS.

S02-227

Clarke Ashley, Vasileiou Alexandros A, Kontopoulou Marianna

Crystalline Nanocellulose in Biodegradable Polyester nanocomposites prepared by in situ polymerization Significant research has focused in recent years on how to integrate CNCs into polymeric materials. The polar and hydrophilic nature of CNCs makes incompatible with them most polymers. Furthermore, the high specific surface area of the nanosized particles promotes aggregation and results in inefficient dispersion and weak interfacial interactions. Chemical modification of the surface of the nanocrystals to improve compatibility in most cases leads to a loss of their inherent properties. Thus, melt compounding methods have been met with limited success. In this work, in situ polymerization is investigated as an efficient method for dispersing CNC in condensation polymer matrices. Poly(ethylene succinate) (PESu) is a biodegradable aliphatic polyester with similar mechanical properties to linear low-density polyethylene. However, low crystallization rates limit its processability. Effective dispersion of CNCs within PESu is investigated here as a way to improve the crystallization properties without detrimentally affecting degradability. The addition of CNCs directly into the PESu polymerization mixture using in situ polymerization dispersed the nanoparticles efficiently, as individual particles, without visible cluster formation. The were polymerization kinetics altered with increasing CNC content, causing a decrease in the polymer molecular weight. The addition of small amounts of CNCs, up to 0.25 wt%, resulted in a slight decrease in viscosity, whereas significant increases in the zero shear viscosity were observed at 1 wt% CNC. PESu containing well-dispersed 0.25 wt% CNC maintained the tensile properties of the matrix, while demonstrating significantly improved crystallization kinetics and reduced haze due to the formation of smaller crystallites. CNC acted as a very efficient nucleating agent, while biodegradability remained unimpeded. Nanocomposites of PESu and CNC with improved crystallization kinetics may provide а "green" biodegradable alternative to plastics commonly used for general purpose biodegradable containers and food packaging.

S02-228

Sousa Jose Alexandrino



Influence of Nanoclay on Mechanical Properties of Glass Fiber Reinforced Polypropylene Composites

Hybrid filler reinforced thermoplastics composed with short glass fiber (GF) and different particulate fillers, such as calcium carbonate, talc and glass spheres, present special interest for engineering applications, as substantial reductions in mechanical properties anisotropy and molding warpage are expected from these systems, as compared to the same characteristics inherent to with GF only. These binary composites improvements are achieved by the partial substitution of GF by particulate fillers and are attained at the cost of minor reductions in rigidity, strength and toughness properties of these ternary composites. However, when nanoscale fillers such as nanoclay (NC) are incorporated in GF-reinforced thermoplastics, the mechanical strength properties of these systems are severely affected, even at very low NC content. Literature data concerning the phenomena that cause the deterioration of the tensile, flexural and impact properties of thermoplastics with hybridized reinforcement of short GF with NC are scarce and require to be sufficiently understood so as to overcome this limitation. Thus in this work, using model GFreinforced polypropylene (PP) composites with varying total and relative concentrations of GF and organophilic montmorillonite clay (O-MMT) along with maleated PP as compatibilizer were twinscrew extrusion compounded with three different mixing protocols, in order to identify the factors leading to the observed loss in mechanical strength properties. Using tensile, flexural, izod impact and dynamic-mechanical (DMTA) characterization tests electron microscopy (SEM and and TEM) elucidation of the fiber-matrix interface/interphase microstructure, it is concluded that the physical presence of NC particles at the interface contributes towards substantial reduction of shear stress transfer at the fiber-polymer interface.

S02-233

Arjmand Mohammad, Mirkhani Seyyed Alireza, Krause Beate, Pötschke Petra, Sundararaj Uttandaraman

Impact of Synthesis Temperature on Structure of Carbon Nanotubes and Morphological and Electrical Characterization of Their Polymeric Nanocomposites

Carbon nanotubes (CNTs) were synthesized by a chemical vapor deposition technique at a broad range of temperatures, i.e. 550°C to 950°C (at 100°C intervals). CNTs were synthesized by flowing source and carrier gases (ethane, argon, and hydrogen) over Fe catalyst in a quartz tubular reactor. **CNTs** were melt-mixed with а polyvinylidene fluoride (PVDF) matrix in the 2mL APAM mixer. The resulting nanocomposites were then compression molded, and electrically and morphologically characterized. Moreover, a wide characterization techniques range of were employed to obtain detailed information about the physical and morphological characteristics of CNTs. It was surprisingly observed that, despite the ascending trend of powder conductivity with synthesis temperature (11.0 - 40.3S·cm-1), the nanocomposites made with (CNT)650°C had significantly lower percolation threshold (around 0.5wt.%) and higher electromagnetic interference shielding (20.3dB over the X-band for 1.1mm thickness), compared to the other temperatures. The characterization of nanofillers showed that the synthesis yield and quality of (CNTs)650°C were superior to CNTs synthesized at 550°C. At 750°C and higher, most of the carbonaceous materials synthesized had planar rather than tubular graphitic structure. These findings were attributed to sintering and coalescence of catalyst particles at high synthesis temperatures. It was also observed that dispersion state of (CNT)650°C within the PVDF matrix was much better than that of CNTs made at the other temperatures. Superior electrical properties of (CNT)650°C can be attributed to a combination of high synthesis yield, aspect ratio, and crystallinity of CNTs coupled with good state of dispersion within the PVDF matrix. Moreover, it was found that the inferior electrical properties of the nanocomposites made with planar graphitic materials synthesized at high temperatures were due to lack of intercalation and exfoliation of the more platelet-like nanomaterials.

S02-249


Domurath Jan, Saphiannikova Marina, Ausias Gilles, Férec Julien, Heinrich Gert

Viscosity amplification in dilute suspensions of non-spherical particles in a non-Newtonian matrix fluid

When non-spherical particles, like rods or discs, are added to a liquid the increase in viscosity of the mixture is often described by the Lipscomb model. One important result of Lipscomb's model is that it predicts a strong increase in the viscosity of the suspension with increasing aspect ratio of the filler particles. Despite the fact that this model was originally proposed for a Newtonian matrix fluid it is also applied to polymer melts filled with nonspherical particles. Such an approach completely decouples the influence of the particle shape from the non-linear properties of the suspending fluid. Yet, since polymer melts often exhibit strong non-Newtonian behaviour, e.g. shear thinning, it is to be expected that such a superposition will give a wrong prediction of the suspension viscosity. To investigate this problem we performed a numerical study of a suspension based on a non-Newtonian matrix fluid and rigid spheroidal particles. In particular, we simulated an elongational flow of a Bird-Carreau fluid around spheroidal particles and used numerical homogenization to obtain the intrinsic viscosity of the suspension as function of applied rate of deformation, thinning exponent and aspect ratio. In the Newtonian regime we also compare with results from literature. In the transition region from Newtonian to non-Newtonian behaviour we obtained lower values of the intrinsic viscosity. In the power-law regime of the Bird-Carreau model, i.e. at high deformation rates, we found that the intrinsic viscosity of the suspension is independent of the applied rate of deformation. Further we obtained from the simulations that the intrinsic viscosity at high deformation rates strongly depends not only on the aspect ratio of the particles but also one the thinning exponent in the Bird-Carreau model, implying that the superposition approach in fact leads to a wrong prediction of the suspension viscosity at high deformation rates.

S02-261

PAZAT Alice, BEYOU Emmanuel, BARRÈS Claire, BRUNO Florence, JANIN Claude

Chemical Modification of Graphite Oxide Sheets and Their Uses in Polyisoprene-based Nanocomposites

Recently, graphene-based materials have attracted much interest due to their remarkable mechanical, thermal, electrical and barrier properties ensuring promising applications such as flexible electronics, energy storage devices and nanocomposites. From an industrial application point of view, the best method for large scale production of graphene is based on the oxidation of graphite leading to graphite oxide (GO), which can subsequently be functionalized, followed by its chemical reduction to restore electrical conductivity. Herein, the preparation of polyisoprene/graphite oxide composites was accomplished through the use of polyisoprene-grafted GO. First, the hydrolysisreaction of condensation acryloxypropyl trimethoxysilane (APTMS) or allyltrimethoxysilane onto GO led to the derivatization of both the edge carboxyl and surface hydroxyl functional groups. Then, the dangling vinyl groups of APTMS or allyltrimethoxysilane were used for in-situ modified polymerization The of isoprene. nanofillers were characterized by thermogravimetric analysis, infrared spectroscopy, differential scanning calorimetry and solid-state nuclear magnetic resonance. Then, the polyisoprene-grafted graphene oxide platelets were dispersed in a polyisoprene matrix at various contents and the corresponding composites were studied through rheological measurements and electron microscopy observations.

S12-273

Chang Hong-Ming, Lue Shing-jiang

Preparation of PBI/Reduced-Graphene Oxide Composite Membranes by blending Method for Alkaline Direct Alcohol Fuel Cells

This research focused on improving direct methanol alkaline fuel cell (DMAFC) performance using hydroxide-potassium-doped polybenzimidazole /reduced-graphene oxide



(PBI/RGO/KOH) electrolytes. The RGO was prepared using hydrazine/sodium borohydride from GO and functionalized with C-N functional groups. The RGO composite had higher ionic conductivity and decreased methanol permeability than the pristine PBI. A power density (Pmax) of 240 mW/cm² was obtained for a DMAFC employing PBI/0.1 wt% RGO/KOH electrolyte at 80 °C with 2 M methanol and 6 M KOH as the anode feed, much higher than the Pmax using PBI film (172 mW/cm²). To the best of our knowledge, this Pmax is among the highest reported values in the literature for DMAFCs.

S02-276

Kamal Musa R., Abdallah Wissam, Tan Victor

The Properties of Polyethylene Nanocomposites Incorporating Cellulose Nano Crystals (CNC)

Cellulose nanocrystals (CNC), derived from large renewable forest and other biosources, have been of growing interest in the formation of polymer nanocomposites. Recently, we reported that the quality of dispersion of CNC in PLA systems is enhanced substantially by the use of spray freeze dried CNC (CNCSFD). This enhancement is attributed to the observed high porosity and network structure of CNCSFD. The presentation will report the results of studies to evaluate the characteristics and behavior of nanocomposites obtained by the incorporation of CNCSFD in low and high density polyethylene resins. The effect of CNCSFD on the quality of dispersion and on the crystallinity and thermal and mechanical properties of the resins will be discussed. These characteristics will be compared to the behavior of composites prepared with the same polyethylene resins using clay and other commercial CNC particles.

S02-287

Kuester Scheyla, Barra Guilherme M. O., Demarquette Nicole R.

Carbon-based thermoplastic elastomer composites for electromagnetic shielding

In recent years, problems related to electromagnetic interferences, originated by communication devices and electronic equipments, have become an and development important issue the of electromagnetic shielding materials has become of both social and scientific interest. In order to substitute dense metals that are normally used as electromagnetic shielding materials, it is possible to use conductive polymer composites. In this study, we prepared carbon-based thermoplastic elastomer composites of poly (styrene-b-ethylene-ranbutylene-b-styrene) (SEBS) and four different carbon fillers, graphene (GR), expanded graphite (EG), carbon black (CB), and carbon nanotubes (CNT), for electromagnetic interference (EMI) shielding applications. The electrical conductivity and EMI-SE of the composites were strongly dependent of the type and amount of carbon filler used. For both the electrical conductivity and EMI-SE the composites ranked in the following order of GR < EG < CB < CNT. The composite with CNT presented superior values in both analysis, probably due the higher aspect ratio of the CNT compared to the other fillers. For concentrations above 8 wt. % of CNT, the composite presented an electrical conductivity increase of 17 orders of magnitude, and EMI-SE higher than the minimum required for commercial applications (< 20 dB, < 99 %).

S02-296

Santos João Paulo Ferreira, Terzic Ivan, Loos Katja, Bretas Rosario Elida Suman

Polystyrene functionalized multi-walled carbon nanotubes for SEBS nanocomposites with improved conductivity

In this work, multi-walled carbon nanotubes (MWCNTs) were functionalized with azideterminated polystyrene (PS). The functionalized MWCNTs were mixed with styrene-b-(ethylene-cobutylene)-b-styrene (SEBS), a triblock copolymer, to produce electrical conductive nanocomposites. SEBS block copolymers consist of polystyrene (PS) hard domains and ethylene and butylene soft Therefore, the combination of segments. the **MWCNTs** and SEBS in well-mixed а



32nd PPS International Conference 2016, Lyon, France nanocomposite with stable morphology may lead to a material with new and interesting properties electronic devices. The PSfor for the functionalization with designed molecular weight (Mn) and narrow molecular weight distribution (Mw/Mn) was synthesized by atom transfer radical polymerization (ATRP) of styrene followed by end group transformation from bromide to azide and then reaction with the MWCNTs. Mn~2500g/mol and Mw/Mn~1.1 were measured by gel permeation chromatography (GPC) The functionalization was confirmed by infrared spectroscopy (IR) and thermogravimetric analyses (TGA). To produce the nanocomposites the functionalized MWCNTs were mixed with SEBS using tetrahydroxyfuran (THF) as a solvent and then precipitated in methanol, a nonsolvent. Films of these nanocomposites were produced by melt-pressing. The macroscopic dispersion of the MWCNTs through the polymer matrix was analyzed by optical microscopy. The electrical AC conductivity of the nanocomposites was measured by impedance method. The results showed that films containing 0.1 and 0.5 % (v/v) of PS-functionalized MWCNTs exhibited significantly improved electrical conductivity compared to SEBS films containing pristine MWCNTs. Optical micrographs showed a better dispersion of the functionalized MWCNTs compared with the pristine MWCNTs.

S02-30

Grady Brian, Guo Jiaxi

Use of Polymer Blends to Reduce Carbon Nanotube Breakage during Melt Processing

In order to adequately disperse carbon nanotubes into a polymer via twin-screw extrusion, requires forces that have been shown to reduce multi-walled carbon nanotube (MWCNT) contour length by 30-90%, depending on starting contour length and the specifics of processing. For the case where the MWCNTs remain in the continuous phase, we show that the addition of a small amount of a second polymer, in this case 20%, leads to a much smaller reduction in contour length under the same processing conditions which in turn leads to ~3 reduction in the percolation threshold. For the case where the MWCNTs partition to the dispersed phase, we find that the length does not reduce at all, within the limits of our experimental measurement. Further, in this latter case, the morphology of the blend can change substantially if the end-to-end distance of the tubes is longer than the diameter of the dispersed phase.

S02-311

Wilkinson Arthur

Low viscosity processing to form electrically conductive epoxy resin composites using novel hybrid cnt- coated silica particles

Hybrid silica- MWCNT particles were produced by the growth of nanotubes onto spherical, mesoporous silica gel particles using CVD. The aims were to develop CNT-based particles that disperse easily in polymers to form stable electrically-conductive networks without anv significant increases in viscosity. Epoxy resin suspensions of these hybrid particles (SG6_3) were studied compared to suspensions of discrete (nongrafted) CNTs (NC) in the same resin Visual observation revealed striking differences between the SG6_3 and NC suspensions. For example, the former flowed easily from the jars in which they were mixed even when the loading was increased to 5 wt.% (equivalent to 1.68 wt. % of CNT). These suspensions were also quite stable and upon tilting the jars after standing for 24 hours no obvious sedimentation was observed. In contrast, a spatula was required to transfer all of the NC suspensions, even the lowest loading of 0.17 wt. %. The rheological properties of the suspension were studied using rotational and dynamic shear tests using a Thermo Scientific MARS II rheometer. The complex viscosity of suspensions containing up to 5 wt.% of SG6_3 (containing 1.68 wt.% of grafted CNT) remained essentially unchanged, whereas an increase of up to five orders of magnitude resulted upon the addition of 1.68 wt.% of non-grafted CNTs. Whilst rheological studies indicated that SG6_3 did not form a percolated network at addition levels of 5 wt.%, addition of only 2 wt.% (0.66 wt.% CNT) was found to form an electrically -



conductive percolated network in an epoxy resin composite with conductivity ~ 10-4 S/m.

S02-339

Jeddi Javad, Katbab Ali Asghar

AC Electrical Conductivity, Shielding Effectiveness and viscoelastic characteristics of Nanocomposites based on RTV Silicon Rubber and Nano Graphite Sheets/Carbon Black hybrid system

Highly flexible nanocomposites based on room temperature vulcanizing (RTV) silicon rubber, and conductive nano system comprised of high structure carbon black (CB) and graphite nano by plates (GNP) were fabricated solution processing method. The synergistic characteristic of this nano system upon involved the electromagnetic interference shielding mechanisms of prepared composites was investigated. Electrical properties and EMI shielding efficiency of nanocomposites generated by various ratios of CB/GNP were measured and compared with the binary nanocomposites based on SR/CB and SR/GNP. The composites prepared by SR/CB showed higher electrical conductivity and lower percolation threshold than composites based on SR/GNP. However, despite of higher aspect ratio of GNP, the electrical properties of the hybrid based composites showed to be governed by the major filler phase and synergistic characteristic was not exhibited by hybrid filled nanocomposites. AC electrical conductivity and dielectric characteristic of the all prepared nanocomposites were evaluated as a function of fillers ratio within frequency range of 100-105Hz. For all binary and ternary nanocomposites ac conductivity showed increasing by frequency below percolation threshold without plateau (nonohmic conduction) , whereas above percolation threshold ac conductivity showed plateau within low frequency region, but sudden increase within high frequency region indicating nonohmic conductivity. Dielectric and electrical analysis suggested that, above percolation threshold direct contact plays as the main mechanism for electric charge current throughout SR phase for all nanocomposites. EMI shielding

effectiveness measurement results within X-band frequency revealed that absorption loss is dominant mechanism for the attenuation of the intensity of incident electromagnetic wave in all nanocomposites generated by SR/CB, SR/GN and SR/CB/GN nano systems.

S02-346

Silva de Lima Carlos Alberto, Amurin Leice G, David Eric, Demarquette Nicole R

Rheological and electrical properties of SEBS/MWCNT nanocomposites

For the last few years poly(styrene-b-ethylene-cobutylene-b-styrene)/multi-walled carbon nanotubes (SEBS/MWCNT) nanocomposites have gained attention as these materials can present interesting properties, and be used in different applications, coating, such as antistatic EMI shielding, artificial temperature sensor, muscle, flame retardant, etc. MWCNT have remarkable electrical, thermal and mechanical properties, and the block copolymer (SEBS) can provide a template to tailor the morphology and therefore the engineering properties of the nanocomposites. In this work, SEBS/MWCNT nanocomposites with different concentrations of MWCNT were obtained by melt mixing in a twin-screw extruder. The morphology was characterized using small amplitude oscillatory shear (SAOS) and small angle X-ray Scattering (SAXS). The electrical and dielectric properties of the samples were also evaluated. Rheological and SAXS results indicated that SEBS block copolymers presented a morphology of PS cylinders within a EB matrix. The state of dispersion of CNT was accessed using SAOS measurements. Different methodologies were applied to investigate the rheological and electrical percolation threshold, for example, power law theory, Van-Gurp Plot, etc. A rheological percolation low threshold was achieved. When only 0.25wt% of CNT was added to SEBS, the slope changed of G'=f(0.1-0.01) from 0.29 to 0.05. The electrical percolation threshold was achieved at lower concentration than 1.00wt% of CNT: when 1.00 wt% of CNT was added to SEBS, the composite became electrically conductive.



S02-347

Wang Jianfeng, Wu Hong, Guo Shaoyun

Simultaneous toughening and reinforcement in melt-processed polycarbonate-graphene composites with extremely low grapheme loading

Two different commercial graphene materials were incorporated into polycarbonate (PC) by melt compounding. In this work, PC was chosen as the polymer matrix due to its distinct notch sensitivity, which greatly limits the current and potential application of PC. The toughening and reinforcement effect of graphene on melt-processed PC were investigated. A maximum toughness at loading as low as 0.03 wt% or 0.07 wt% was observed in the two PC/graphene nanocomposites studied. As opposed to neat PC, the notched impacted strength increased 48% with 0.07 wt% graphene loading, the elongation at break increased 75% with 0.03 wt% graphene loading. Fortunately, the yield strength of these novel materials at such low graphene loading increased around 11% as well. These simultaneously toughened and reinforced polymer/graphene nanocomposites, which were fabricated via melt processing with extremely low graphene loading, may open the door to downstream industrial application of largescale manufactured graphene-type materials. Deflection, pinning and termination of crack, formation of microcrack and layer breakage of graphene were observed via microscopy of fracture surface and proposed to be toughening mechanism.

S02-359

Upadhyaya Madhab, Kakati Dilip Kumar

SurfactantMediatedSynthesisofPolyaniline/MontmorilloniteClayNanocomposites and Their Characterization

Abstract Polyaniline/Clay nanocomposites are in the forefront of academic and industrial research in recent times. Polyaniline (PANI) is an extensively studied conducting polymer because of its economic viability, easy processability, good stability and controllable electrical conductivity which makes it suitable candidate for various applications. Among the large number of layered solids, montmorillonite clay (MMT) is the most suitable candidate for the synthesis of polymer nanocomposites, because it possesses a unique structure and reactivity together with high strength, stiffness and high aspect ratio of each platelet. MMT is also known for good swelling and ion exchange properties, low cost and attractive features such as a large surface area and ionexchange properties. Here, in this work, synthesis and characterization of PANI/MMT nanocomposites has been reported. PANI/MMT nanocomposites were synthesized by emulsion polymerization method. Dodecylsulphuric acid (DSA) served the dual purpose of dopant and emulsifier. Analysis of X-ray diffraction results demonstrated the intercalation of PANI-DSA between the clay layers at the nanoscale level. The interaction between the intercalated PANI-DSA and clay layers was observed from FTIR spectra. The dc conductivity was observed in the range 0.033-3.214 Scm-1 at room temperature which found to be dependent on the loading of clay and dopant concentration. The morphology of the composite was investigated by scanning electron microscope and the morphology changed with the variation of MMT loading.

S02-361

Alimoradi Younes, Nazockdast Hossein, Javadi Azizeh

Effect of shear flow induced Nano orientation on
the crystallization kinetics of
polypropylene/MWCNT Nano composites

The flow induced Nano orientation on crystallization of Nano composites has always been a challenging issue. The main objective of the present work was to study the crystallization behavior of PP/MWCNT Nano composites by using rheological technique. In this study Nano composites PP/MWCNT melt blending method with mixing 20min, 190 0C & 90rpm in combination with different percentages of carbon nanotubes prepared. were То the incorporation of nanoparticles, in all cases 10Phr, PP-g-MA was used. Viscoelastic studies and sample's crystallinity is done by the rheological techniques and tools of



RMS and check dispersion and orientation distribution of nanoparticles the with transmission electron microscope TEM. The results of temperature sweep tests (G'-T) showed a Nano induced increase in crystallization temperature which could be attributed to nucleation mechanism. That, this results were found to be agreement with DSC results. However, the flow induced Nano orientation did not have a considerable effect on changing the crystallization temperature. The isothermal rheological measurements (G'-time) performed on the sample under different shear rate or shearing time showed a significant increasing effect on crystallization rate but, with little total effect on the total crystallinity. This results could be explained in terms of amplification effect of shear induced orientation.

S02-364

Hosseinpour Ali, Katbab Aliasghar, Mehranpour Milad, Nazockdast Hossein, Ghiassinejad Sina

Localization of MWCNTs in EOC/COC blends

The aim of this work was to study the localization of MWCNTs in the immiscible blend of ethylene 1octene copolymer (EOC) and cyclic olefin copolymer (COC) 80/20. The samples were prepared by different feeding sequences using melt compounding in an internal mixer. The results of the melt linear viscoelastic analysis, FESEM observations and electrical conductivity measurements showed that the MWNTs localized either in the COC droplets or accumulated in the interface even for the hybrid samples in which MWNTs was initially melt mixed with EOC matrix as a thermodynamically unfavorable phase. The results were found to be in good agreement with the predicted results based on wettability. Interestingly the results of the rheological as well as electrical conductivity showed a percolation thresholds in the same range as those reported for the other hybrid systems in which MWNTs localized in the matrix and formed three dimensional network. This was attributed to the migration of MWNTs from unfavorable EOC phase to the interface and forming a MWNTs interconnected network.

S02-377

Patti Antonella, Acierno Domenico, Russo Pietro

Influence of Filler Dispersion and Interfacial Resistance on Thermal Conductivity of Polypropylene/Carbon Nanotubes Systems

Carbon nanotubes effectiveness, as thermally conductor, in polymer/CNTs nanocomposites, is related to main aspects as dispersion, interfacial thermal resistance and thermal contact resistance. Features of raw materials and processes parameters for the realization of nanotube/polymer composites, can affect simultaneously the above critical issues, also in adverse way. In this contribution, polypropylene based-composites, containing multi walled carbon nanotubes (MWNTs), are prepared by melt-blending and then characterized prevalently in term of thermal transport behavior, choosing different matrix grades, filler functionalization and process conditions. In more details, the influence on properties of products of both commercial polypropylene two resins, different in MFI and the addition of а compatibilizer, as maleic anydryde grafted polypropylene (Ma-g-PP), is verified. Moreover, three different commercial MWNTs with the same aspect ratio, one neat and two chemically modified with carboxyl -COOH and amino -NH2 groups, respectively, are chosen to prove effects of on thermal conductivity functionalization of Finally, different meltnanocomposites. compounding and molding conditions in terms of temperature, time, screw speed, pressure, filler drying and so on, are considered to optimize them for enhanced thermal conductivity.

S02-407

Tokumitsu Katsuhisa, Terakura Kosuke, Yamada Masahiro, Sugimoto Masayuki

Mechanical and Thermal Properties of Poly(Lactic Acid) with Cellulose Nanofiber Modified by Bisphenol fluorene diglycidyl ether (BPFG)

Mechanical and thermal properties of poly(lactic acid) (PLA) with cellulose nanofiber (CNF) treated by Bisphenol fluorene diglycidyl ether (BPFG), B-



CNF, was investigated. When using neat CNF to obtain PLA/CNF composite, the CNFs were aggregated together and the average dispersed size was about 1 µm. When using B-CNF to obtain PLA/B-CNF composite, however, B-CNF can be dispersed homogeneously in PLA matrix and the size of B-CNF was getting smaller than that of CNF about several hundred nm. Furthermore, when employed master batch (MB) procedure, which is the method that PLA/B-CNF with high concentration of B-CNF (20 wt%) was prepared in advance, then it was blended with PLA to produce PLA/B-CNF (MB) composite at а given concentration of B-CNF, the CNFs can be dispersed much smaller and the size reached about 100 nm in PLA matrix. When comparing the storage modulus (E') of PLA/CNF, PLA/B-CNF, and PLA/B-CNF (MB) at the plateau region above Tg, of PLA, the value of E' of PLA/B-CNF (MB) was the largest, then PLA/B-CNF composite was the second, and PLA/CNF composite was the third, but the values of them were larger than that of neat PLA. On the other hand, when comparing the peak intensity of tand at the temperature region of Tg of PLA of these composites, it arranged in ascending in order: PLA/B-CNF (MB), PLA/B-CNF, PLA/CNF, and the largest one for neat PLA. These results suggested that B-CNF can play a role to restrict the molecular motion of PLA in comparison with neat CNF, especially B-CNF in PLA/B-CNF (MB) composite did much restrict the molecular motion of PLA. Besides, from the result of Coefficient of Thermal Expansion (CTE) of the composites, we estimated volume fraction of the interaction phase in PLA/CNF, PLA/B-CNF, and PLA/B-CNF (MB) by means of mixtures rule. As a result, it was found that the interaction phase in PLA matrix was the largest for PLA/B-CNF (MB), the second for PLA/B-CNF, and the third for PLA/CNF. There was a good relationship between the inten

S02-414

Shen Yucai, Zhang Yuwei, Shi Kunxiang, Wang Tingwei

Effect of modified graphene oxide on the thermal conductivity of epoxy composites

Manipulating interfacial thermal transport is technologies important for many including nanoelectronics, solid-state lighting and energy generation. Organic/inorganic interfaces are often become the heat transport bottlenecks. In this study graphene oxide (GO) was modified by different strategies like non-covalent and covalent, organic and inorganic. Modified GO was then mixed and cured with epoxy. Different GO/epoxy interfaces and GO dispersion were observed. Morphological characterization was achieved by scanning electron microscopy. The effect of modified GO on the thermal conductivity and mechanical properties of epoxy composites will be measured. It is expected to identify the optimal GO/epoxy interface for enhancing thermal conductivity of epoxy composites. The mechanism to improve the thermal conductivity of GO filled composites will be discussed. This will open effective methods in designing thermal conductive composites.

S02-434

Sundararaj Uttandaraman, Arjmand Mohammad, Sadeghi Soheil

Nitrogen	Doped	Carbon
Nanotube/Polyvinylidene		Fluoride
Nanocomposites:	Synthesis,	Morphology,
Rheology, and Electrical Properties		

Nitrogen-doped carbon nanotubes (N-CNTs) were synthesized by a chemical vapor deposition technique, wherein source and carrier gases (ethane, and ammonia, and argon) were passed over alumina-supported metallic catalysts in a quartz tubular reactor. Three different catalysts were used to synthesize N-CNTs: namely Co, Fe, and Ni; and nitrogen content, and nitrogen bonding type of N-CNTs aspect ratio, synthesis yield were determined. Synthesized N-CNTs were mixed with PVDF using an APAM mixer at 240C and 235rpm, and the morphology, electrical conductivity and electromagnetic interference (EMI) shielding of were resulting nanocomposites investigated. Substantial differences were observed in the synthesis yield, and the morphological, rheological, and electrical properties of the generated materials depending on catalyst type. The N-CNT aspect



32nd PPS International Conference 2016, Lyon, France ratio was the highest for the Co catalyst, followed by Ni and Fe, whereas nitrogen content was the highest for Ni. Raman spectroscopy showed the lowest defect number and highest N-CNT crystallinity for the Fe catalyst. We observed superior dispersion of N-CNTs within the PVDF matrix for N-CNTs synthesized over Co and Fe as compared to Ni. Differential scanning calorimetry showed similar PVDF matrix crystallinity for the generated nanocomposites. Moreover, the N-CNT network superstructure formed in the PVDF matrix was drastically impacted by synthesis conditions and choice of catalyst. Non-ergodic features of rheological behavior, such as solid-like behavior, ultraslow low-frequency relaxation, and thixotropy, showed significant differences due to synthesis procedure. Electrical characterization demonstrated the following order of electrical conductivity and EMI shielding (from high to low): Co > Fe > Ni. Superior electrical properties of (N-CNT)_Co nanocomposites were due to a combination of high synthesis yield, high aspect ratio, low nitrogen content and high crystallinity of N-CNTs combined with a good state of N-CNT dispersion.

S02-478

Icduygu Mehmet Galip, Asilturk Meltem, Altan Mustafa Cengiz

Preparation and characterization of poly(methyl metharcylate) microcapsules containing epoxy resin and carbon nanotubes

Aim of this study was to prepare microcapsules for self-healing applications in polymers and composites. Microcapsules containing epoxy carbon nanotube dispersion were prepared by solidification of Poly(methyl methacrylate) [PMMA] between resin and water interface. Dichloromethane (DCM) was selected as solvent for epoxy and PMMA. Similar systems have already been used by various groups without carbon nanotubes which revealed that two parameters have significant effect on microcapsule formation and morphology. If the first parameter epoxy/PMMA (core/shell) weight ratio exceeds 6/1, then fractured microcapsules start to appear. The second parameter is evaporation temperature of

evaporation temperature is raised over 40oC. Therefore, 40oC was selected in the current study as evaporation temperature. Preliminary results showed that microcapsules tend to stick each other and form agglomorates over 1:1 w/w epoxy/PMMA ratio. Hence, 1:1 w/w epoxy/PMMA ratio was used for rest of the experiments. Four different mixing speeds (300, 500, 800, 1000 rpm) and carbon nanotube content (0.25, 0.50, 1.00, 2.00 w/w %) were employed during the encapsulation process. The microcapsules were characterized by FTIR, SEM, thermal confocal microscopy and analysis techniques. Microcapsules having 55-10 micron average diameters were obtained by increasing mixing speed from 300 to 1000 rpm. Increasing mixing speed caused a decrease in particle size distribution, while it also gives rise to a more homogeneous nanotube distribution inside the microcapsules. Roughness of microcapsule surface increased with increasing nanotube content and mixing speed. SEM images of microcapsules showed that microcapsules with various types of core-shell morphology are formed during the encapsulation process. Thermal analysis results showed that epoxy content of microcapsules varies independent of the reaction parameters.

DMC. It was shown that a porous capsule surface is

formed during encapsulation process if

S02-481

Altstädt Volker, Breu Josef

Improvement of the Mechanical and Electrical Properties of Technical Thermoplastics by Utilizing 2nd Generation Layered Silicates

In this study a novel kind of reinforcing polymethylmethacrylate (PMMA) and improving the electrical properties of polyetherimide (PEI) with a 2nd generation of layered silicates is shown. The potential of commercially available natural layered silicates seems to have reached their limitations due to small lateral dimensions and a high heterogeneity of surface charge. For example, melt compounding results mostly in incomplete delamination of the tactoids, which further reduces the maximal possible aspect ratio and therefore the desired properties. Also the incorporation of



the

commercially available natural organo-clay in PMMA by melt-compounding leads to an increase of the stiffness, but an unsatisfactory dispersion quality of the nanoclay in the PMMA matrix leads to an decrease in toughness. Therefore reasons a newly developed kind of synthetic layered silicate was used in a transfer batch moulding process to create a PMMA-nanocomposite. With these synthetic layered silicates which have aspect ratios of up to 600, it was possible to significantly increase the young's modulus of about 55% and the fracture toughness of about 70 %, without any decrease in tensile strength. Furthermore analysis of the corresponding fracture surfaces by scanning electron microscopy show in case of the novel filler an additional energy dissipating mechanisms like crack deflection, crack bridging as well as debonding effects with platelets pull-out leading to enhanced fracture toughness. In addition to the improvement of the mechanical behavior, the layered silicates possess the ability to decrease the coefficient of thermal expansion (CTE) of the matrix material. Therefore layered silicates provide the possibility of utilizing thermoplastic materials for applications which require a lower CTE, e.g. polymer-metal-hybrids.

S02-529

Ryabenkova Yulia, Pattinson Andrew, Coates Phil, Twigg Peter

Functionally gradient polyvinyl alcohol based nano-hydroxypatite loaded material for osteochondral defect treatment

Current treatment of osteoarthritis and traumatic lesions of articular cartilage employs the usage of osteochondral implants made of biocompatible polymers. Synthetic scaffolds based on polyvinyl alcohol (PVA) hydrogels have been used to repair or replace damaged tissue, with varying degrees of success. Nano-hydroxyapatite (nano-HA), in turn, is the main hard component of bone and has potential to be used to promote osseointegration of implants. This study investigates the possibility of creating a cell-conducting functionally gradient material made of PVA and nano-HA with excellent biomechanical exceptional parameters and

biocompatibility properties. While the polymer has the closest characteristics of the articular cartilage, the presence of the ceramic component as a filler mimics the osseous structure thus making the material an excellent choice for the treatment of osteochondral defects. The material composition was evaluated using infrared attenuated total reflectance spectroscopy (ATR-FTIR) as well as thermogravimetric analysis (TGA) and X-Ray Powder Diffraction (XRPD), whereas biomechanical characteristics while undergoing deformations were tested using Dynamical Mechanical Analysis (DMA). As a result, we have shown that by varying the ratio of a polymer and filler it was possible to achieve the desired parameters for the storage and loss moduli which are close to the ones measured for various parts of the cartilage and bone.

S02-555

Lison Valérie, Hurtgen Marie, Rul Alicia, De Villepin Cédric, Claes Michaël

New insights to produce by tubing extrusion electrically conductive multi-layer fuel lines based on polyamide 612/carbon nanotubes formulations

For more than 20 years, the automotive industry has been setting higher safety and environmental standards. However, the substitution of metals for plastics parts in tubing and other fuel pathways has induced a risk of explosion in fuel systems due to electrostatic discharge (ESD). Indeed, liquid fuels flowing through the fuel delivery system to the engine can generate static charges which are more likely to build up to dangerous levels if there are not dissipated by the tubing material. To prevent ESD in fuel lines, electrically dissipative materials containing carbon nanotubes are used in fuel pumps, fuel filter housings, fuel line connectors, fuel line clips, fuel reservoirs, fuel filler pockets and related electronic housings. In this context, we will present our latest product developments by multilayer extrusion process of fuel lines which the inner dissipative layer is composed of polyamide 612/carbon nanotubes - based formulations. The first part of the work will highlight the influence of extrusion compounding parameters and/or the



viscosity of polymer grades on the dispersion and distribution of carbon nanotubes agglomerates. The second part will consist on the optimization of multi-layer extrusion process parameters in order to fulfill all requirements of the application such as the targeted ESD properties (according to SAE J1645 – Surface resistivity should not exceed 104 -106 Ohms/square) at reduced CNT content and minimum thickness layer; an efficient chemicals resistance combined to a low permeation to diesel, petrol, methanol, ethanol or biofuel; and a high quality surface finish without visual defects. Moreover, the resistances for long-term fuel exposure and high temperature conditions of the components will be evaluated.

S02-577

SLIWA Fabien, LEONARDI Frédéric, MERCADER Célia, ANDRE Sandrine, CHARMAN Maxime

Twin-screw extrusion of Cellulose NanoCrystals (CNC) and poly(ethylene) after dispersion of CNC in poly(ethylene glycol) : Effects of PEO/CNC content on rheological, mechanical and thermal properties of theses ternary blends.

Recently, many works have been published on the use of CNC as polymer reinforcement for nanocomposite applications [1,2] but these methods of elaboration of CNC composites at a laboratory scale are often based on solvent dispersion. In order to extrapolate to an industrial scale, extrusion processes are required. Nevertheless, two points have to be considered to produce thermoplastic composite by melt-processing: - a low thermal stability of CNC (below 200°C) - a strong tendency of CNC to agglomerate when dried Direct extrusion of CNC leads to a very poor dispersion whatever extrusion processing conditions used. A two step methods have been selected [3]: a first dispersion of CNC in the water-soluble polymer in order to obtain a composite PEO/CNC, then this concentrate product is dispersed by melt-blending in polymers matrix of LDPE [4]. We have chosen this method to elaborate our composites and we have tried to improve the dispersion of CNC at a pre-industrial scale by an optimization of material parameters that can be tune to enhance dispersion of CNC

Rheological measurements, optical and MEB observations have been done on these ternary blends (PEO, CNC, and LDPE) to select best conditions leading to well dispersed CNC composites: • For a 5w% of CNC in the blend, what is the optimal CNC/PEO ratio in order to have a good re-dispersion in a LDPE matrix ? • We continue by playing with the molecular weight of the PEO used and we have seen an important effect of this parameter on the CNC dispersion • Finally, we have made a rheological percolation curve by varying the CNC content in the optimized blend. The rheological percolation threshold found on this optimized blends is in agreement with a theoretical value derived from L/D value which is below 10 in our case. Other final physical properties of the optimized blends have been characterized to select possible industrial applications. 1. Aspler J et al. Biopolym. Nanocomposites. John Wiley, 461-508 (2013) 2. Mariano M et al . J Polym Sci Part B 52:791-806 (2014) 3. Ben Azouz K et al .Macro Lett 1:236-240 (2012) 4. Pereda M et al., Appl Mater Interfaces 6:9365-9375 (2014)

S02-58

Chiu Fang-Chyou, Chen Ying-Jing, Yeh Shih-Chang

Carbon Nanotube- and Graphene Nanoplateletadded PVDF/PMMA Blend-based Nanocomposites

Multi-walled carbon nanotube (MWNT) and graphene nanoplatelet (GNP) were, individually, incorporated into poly(vinylidene fluoride) (PVDF), and PVDF/poly(methyl methacrylate) (PMMA) blends achieve binary and to ternary nanocomposites. MWNT and GNP were more compatible with the PVDF matrix than with the PMMA-containing matrices. Addition of respective nanofiller did not alter the development of á-form PVDF crystals in the composites. Crystallization rate of PVDF was enhanced by the presence of MWNT or GNP, and the enhancements observed were optimal in the binary composites. The melting temperature (Tm) of PVDF increased in the binary composites, but the blends showed similar Tm values to the formed ternary composites. Thermal stability of PVDF was enhanced in the composites



with the inclusions of individual MWNT and GNP. Rheological data confirmed the formation of MWNT/GNP (pseudo)network structure in the composite systems. It was also noted that the intensely entangled chains of high-molecular weight PVDF would dominate the rheological response of PVDF-included samples in the melt state. The rigidity of neat componets and the blends increased after the formation of binary/ternary composites. Electrical percolation threshold between 1 phr and 2 phr MWNT/GNP respective loading was identified for the composite systems.

S02-592

Kazemi Yasamin, Kakroodi Adel Ramezani, Wang Sai, Ameli Aboutaleb , Filleter Tobin , Park Chul B

Electrical Conductivity and Crystallization Behavior of Polypropylene in the Presence of Supercritical Carbon Dioxide and Multiwalled Carbon Nanotubes

Over the last decades, carbon nanotube (CNT)filled conductive polymer composites (CPCs) have demonstrated great potential as a highly desired class of advanced functional materials. The CNT content required for achieving the percolation threshold in the CPCs depends on several factors including the type and intrinsic electrical conductivity of the CNTs, the aspect ratio, the degree of alignment, the level of dispersion, and the interconnectivity of the CNTs in the polymeric matrix. Among these parameters, the level of dispersion and the interconnectivity of CNTs have a crucial effect on the electrical conductivity. It is believed that the contact resistance of the conductive network and the dielectric properties of the CPCs can be dramatically altered via slight geometrical changes in the local contact regions between the nanotubes. The current research work is focused on studying the effects of the type and content of polypropylene (PP) crystals on the electrical properties of PP/CNT composites. The isothermal crystallizations of PP/CNT composites were performed at different temperatures (135-150 ^oC) under atmospheric and supercritical carbon dioxide (scCO2) conditions. The experimental results indicate that the γ -form of PP crystals was

formed under scCO2 atmosphere at elevated temperature. Transformations of the PP crystals, from α -form to γ -form crystals, caused by the differences in the isothermal crystallization conditions, were shown to have remarkable effects on the electrical conductivity and the dielectric properties of the PP/CNT composites.

S02-594

Ahmadi Hamid, Hosseini Seyed mohammad, Javadi Azizeh, Nazockdast Hossein

Dielectric Properties of PC/PVDF/MWCNT nanocomposites: Effect of Nanoparticle Localization

In this study Polycarbonate (PC)/ Poly (Vinylidene (PVDF) Fluoride) (50/50)w/wblend nanocomposites containing 0-3.2 wt. % of MWCNTs were prepared via melt mixing. The Electrical and Dielectric properties of samples were measured in the frequency range of 10-1-106 Hz. The results showed a co-continuous morphology for this blend and localizing the MWCNTs in the PC phase, which is due to the more attendance of nano tubes to this phase. In the other hand, it was found that by controlling the kinetic parameters including the sequence of feeding, the CNTs were forced to localize in the thermodynamically unfavorable PVDF phase. This was evidenced by rheological results like relaxation time spectrum. The results of AC conductivity measurement revealed the much higher dielectric constant for these nanocomposite samples compared to those ones which the MWCNTs were localized in the PC phase. This was explained in terms of beta crystalline phase of PVDF and higher dielectric constant of it.

S02-603

Paiva Maria C, Cunha Eunice P, Voigt Oliver, Liebscher Marco, Simon Frank, Pionteck Jurgen, Pötschke Petra

Melt mixing functionalized graphite nanoplates into PC/SAN blends

The present work focusses on the analysis of the combined effect of chemical functionalization of

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graphite nanoplates (GNP) and the melt mixing conditions on the dispersion and localization of the GNP PC/SAN blends, composite in the morphology, and the resulting electrical and mechanical properties. The GNP modification was performed using a mild functionalization method based on the dipolar cycloaddition reaction of azomethyne ylides to the GNP aromatic carbon surface [1]. The functionalization reaction was performed at 250°C, and its effectiveness was assessed by thermogravimetric analysis, showing a weight loss approximately 10% higher than the corresponding pristine material, at 800°C when heating the GNP under N2(g) at 10 °C/min. The Raman spectra of the functionalized GNP (f-GNP) presented a larger area of the D band relative to the original GNP, characteristic of structural modifications induced by covalent functionalization of the sp2 carbon surface. X-ray photoelectron spectroscopy demonstrated the presence of nitrogen at f-GNP surface that may be assigned to pyrrolidine-type functional groups. Previous work performed with carbon nanotubes has shown that their pyrrolidine-functionalized surface react with ester groups (for example in PLA), and carbonate groups in PC, under melt mixing conditions. GNP and f-GNP were melt mixed into PC/SAN = 60/40 wt% blends using a two-step approach with premixing first graphite nanoplates into PC followed by blending with SAN resulting in 1-8 wt% loading of (f-)GNP. Mixing was performed using a small scale twin-screw compounder and plates were obtained by compression molding. Dispersion of (f-)GNP was assessed using light microscopy on the extruded strands; the localization was examined by TEM. In addition, electrical and mechanical properties of the composites were studied and compared to those of the polymer blend. 1. M. Paiva et al. 2010. ASC Nano, 4, 12, 7379.

S02-609

Bhattacharyya Arup R., Parija Suchitra

Multiwalled Carbon Nanotubes Based Polypropylene Composites: Role of Interfacial Interaction The study was aimed to investigate the improved interaction of polypropylene (PP) matrix and multiwalled carbon nanotubes (MWNTs) via the use of a non-covalent modifier, Lithium salt of 6-amino hexanoic acid (Li-AHA) and a compatibilizer, polypropylene grafted maleic anhydride (PP-g-MA). Composites of PP and MWNTs were prepared with pristine as well as Li-AHA modified MWNTs with PP-g-MA by melt-mixing in a conical twin-screw micro-compounder. MWNTs were further extracted from pristine as well as modified PP/MWNTs composites. X-ray diffraction analysis (XRD) showed characteristic diffraction peaks of α crystalline phase of PP for MWNTs extracted from modified PP/MWNTs composites with MWNTs: Li-AHA ratio of 1:2 and 1:4 (wt/wt). However, extracted MWNTs corresponding to PP/MWNTs composites of pristine did not show any crystallization peak corresponding to the PP phase. Differential scanning calorimetric analysis showed the crystallization peak of the PP phase for MWNTs extracted from PP/MWNTs composites with Li-AHA modified MWNTs (1:4 wt/wt) indicating the presence of crystallizable PP phase. Thermoanalysis showed gravimetric degradation behaviour corresponding to the PP phase, which was not visible in the pristine MWNTs indicating the presence of the PP phase. FTIR spectroscopic analysis also could detect the melt-interfacial reaction between maleic anhydride functionality of PP-g-MA and amine functional group of Li-AHA, which could improve the interfacial interaction between PP chains and the MWNTs

S02-612

Gassiot-Talabot Alix, Desse Melinda, Sanchez Jean-Yves, Carrot Christian

Reinforcing a Poly(ethylene oxide) using Nanocrystalline Cellulose : dispersion of the filler in a melt process

The development of high-performance battery separators using solid electrolyte polymers in a continuous industrial process is a promising field of research when considering economical and ecological aspects. These solid polymer electrolytes should be permeable to ionic current but electrically



insulating, all the while maintaining sufficient mechanical resistance. To enhance mechanical dispersion of nanometrics properties, fillers (nanocrystalline cellulose) in a polymer is the chosen pathway. Nanocrystalline cellulose is a type of filler with lengths between 100 and 300 nm and diameters between 5 and 20 nm. They are obtained after acid hydrolysis which removes the amorphous parts of the cellulose elementary fibril. Thus, nanocrystalline cellulose has a high crystallinity which leads to a high elastic modulus. A homogeneous dispersion of these fillers allows the formation of a percolating network at low concentrations (thanks to their high form factor), which greatly enhances the mechanical properties of the matrix. The goal is to carry out this dispersion in molten polymer through extrusion, as opposed the well-established solvent to evaporation process. The main difficulties are the aggregation of cellulose whiskers which occurs through hydrogen bonding and the concentrated medium in which these fillers are dispersed. To achieve dispersion, both the internal mixer and a miniextruder have been used. Different protocols as well as a copolymer have been tested to promote dispersion. Results have shown that there is orientation of the fillers thus increasing the concentration necessary to obtain a percolating network. In this presentation we will show that we have found a way to overcome the orientation issue and have managed to disperse nanocrystalline cellulose with no modification of the surface or addition of plasticizer.

S02-62

El Mabrouk Khalil, Risite Heriarivelo , Bousmina Mostapha, Fassi-Fehri Omar

The Effect of 3-aminopropyltriethoxysilane on rheological and mechanical properties of polyamide 11/clay nanocomposites

Polyamide-11 (PA11)/organoclay nanocomposites were prepared via melt compounding using silane grafted montmorillonites and Cloisite 20A. Two graft procedures were used for clay modification. The first one provided a grafted 3aminopropyltriethoxysilane (APTES) at clay surfaces, whereas the second led to intercalated structure in addition to grafted APTES at clay surface. X-ray diffraction and transmission electron microscopy confirmed the formation of the exfoliated nanocomposites at low clay loading (2 wt. %) and a mixture of exfoliated and intercalated structures at higher clay contents. Thermogravimetric analysis, melt rheology as well as tensile tests showed that the degree of dispersion of clay within polymer matrix plays a vital role in property improvement. In addition, elongation at break was considerably enhanced in the case of silane grafted clay. This was attributed to hydrogen bonding between clay surfaces and PA11 via APTES.

S02-622

Gonzalez Mauricio, Shahbikian Shant, Huneault Michel A

Effect of different mineral fillers on rheological and mechanical properties of Polylactide/Poly(methyl methacrylate) blends

Expanding the use of PLA through polymer blending technologies to tackle a wider range of engineering applications would have several key benefits for society. There has been a tremendous effort in immiscible polymer blends involving PLA, typically with PLA as the major phase. In this study, the focus has rather been placed on miscible blends of PLA with PMMA where only a few studies have been carried out up to now. In particular, we had examined the miscibility window, the rheology, the thermal and the mechanical behavior of these blends. In order to produce composites of interest for a wider range of applications, the effect of different filled version of these blends has also been investigated. Four different polymer blends of PLA and acrylic resins prepared by melt processing. were Three reinforcing minerals were used as well: clay, quartz and calcium carbonate. To examine if the crystallization could be modified by changing the PLA chain mobility, a castor oil plasticizer was also used in selected blends. Experimental results for unfilled blends showed in all cases, a single glass transition indicating that there was no observable



phase separation. In addition, the glass transition data exhibits a slightly negative deviation as expected from the Fox theoretical relationship and the ability of PLA to crystallize was strongly restricted by the presence of the amorphous PMMA. The blends rheology was investigated by oscillatory shear rheology. All binary blends showed a typical viscoelastic behavior with a Newtonian plateau at low frequency range. As expected from theoretical relationships such as the Krieger-Dougherty equation, the viscosity increased with quartz and clay concentration as a solid network developed in the material at low frequency typical of materials exhibiting a yield stress. At 53 vol%, the complex viscosity of the blend was increased by three orders of magnitude. Surprisingly, addition of calcium carbonate leads to a significant drop in viscosity.

S02-629

Carreau Pierre J

Properties of polymer /CNC nanocomposites

Key results of our recent investigations on the development of polymer/cellulose nanocrystal (CNC) nanocomposites will be presented and discussed. The base polymers were polypropylene (PP) containing a malleated PP (PPMA), PP containing poly(ethylene-co-vinyl alcohol) (PVOH), used as a compatibilizer, as well as polylactide (PLA). A much finer dispersion, at the nanoscale, of the CNCs in the polymer matrix could be achieved using solution-cast methods. The rheological properties of these nanocomposites were shown to exhibit solid-like behavior and an apparent yield stress at very contents of CNCs. For PPs with two different molecular weights and prepared in the molten state using different temperatures, the tensile modulus of composites containing PPMA and 2 wt% CNCs was improved by about 30% and the tensile strength was increased by 10% in comparison with the unfilled matrices. The tensile PP/PVOH nanocomposites modulus of the containing 5 wt% CNCs was increased up to 47 % compared to the neat PP. However, the best mechanical properties were obtained for PLA/CNC nano-composites using a solution preparation method based on N,N-dimethylformamide (DMF). In dynamic mechanical thermal analysis (DMTA), the storage modulus of PLA containing 6 wt% CNCs increased up to 74% in the glassy region and to 490% in the rubbery region. However, the elongation at break decreased for all PP or PLA/CNC nanocomposites. The Halpin-Tsai model was used to predict the Young moduli of nanocomposites and good agreement with the experimental data was observed for both PP and PLA composites

S02-651

Rigail-Cedeño Andres F, Schmidt Daniel F

BIO-BASED EPOXY CLAY NANOCOMPOSITES

The present research focuses on the study of a new family of bio-based aliphatic epoxy nanocomposites and other high performance for coatings applications. A sorbitol glycidyl ether (SGE) epoxy resin has been cured with three polyamines, a diamine poly(ethylene oxide) (PEO) poly(propylene oxide) diamine (PPO), as well as triethylenetetraamine (TETA). The degree of dispersion of an organically modified montmorillonite (OMMT) clay was assessed via xray diffraction (XRD) in both the neat resin components and cured films. In general, the compatibility of both diamines with the organoclay was found to be good. While this would seem to imply enhanced dispersion, in practice low molecular polyetherdiamines will intercalate but not exfoliate montmorillonite layers due to their inability to screen interactions between adjacent layers. Both the neat resin components and the cured materials display multiple diffraction peaks.Nevertheless, the nanocomposite films showed excellent transparency, consistent with the degree of dispersion implied by the XRD patterns derived from these materials. The curing behavior of all samples was followed by near-IR (NIR) spectroscopy. The extent of epoxy conversion was high for neat and filled systems. The effect of the OMMT in the systems is related to interactions between the curing agents and the clay modifier as



well as the silicate layers themselves. SGE/PEO and SGE/TETA systems gave earlier gelation times compared to SGE/PPO systems as observed by viscosity measurements. In addition to cure kinetics, mechanical properties were also studied. The SGE/TETA/OMMT system displayed a larger increase in Young's modulus (as measured via tensile testing) compared to all other nanocomposites, consistent with the idea that this system should display more hydrogen bonding and stronger interactions than the other systems studied. Similar results were observed via Shore D hardness measurements. These results demonstrate the possibility to prepare, process and cured biobased epoxy clay nanocomposites with enhanced performance. Ongoing work is focused on a broader range of bio-based formulations with enhanced hydrophobicity.

S02-657

Heydarnejad Moghadam Mohammad, Goharpey Fatemeh, Nazockdast Hosein, Kazem Farahzadi Setareh

Nanocomposites based on poly(styrene-b-(ethylene-co-butylene)-b-styrene) triblock copolymer and carbon nanotube-graphene nanoplatelet hybrids: Rheological and electrical study

ovel nanocomposites based on poly(styrene-btriblock (ethylene-co-butylene)-b-styrene) copolymer with hexagonally packed cylindrical (HEX) microdomains, and CNT-GNP hybrids has made it possible to achieve stretchable electrically conductive materials at very low loadings of nanoadditives. nanocomposites were prepared by solution mixing. Appropriate surface modification of hybrid components and sequence of mixing results in well dispersion of nanoadditives in SEBS. XRD results showed a better dispersion of GNPs in presence of CNTs. Rheological data indicated that the storage modulus increased considerably with addition of hybrids of nanoparticles, due to formation 3-Dimensional of network of nanoadditives. Rheological measurements were also used to determine the effect of hybrid nanoparticles on micro phase separated structures, orientation and recovery of cylindrical PS domains.

nanoparticles exhibit two distinct effects on phase separation: modified GNPs boost phase separation acting as bases for formation of PS domains while aggregations and randomly oriented nanoparticles lead in confinements and disorderliness which decreases phase separation. Electrical conductivity measurements using CNT and GNP simultaneously, demonstrates synergistic transport GNP-CNT-GNP effect due to physically interconnected conductive network structure formed throughout the rubbery phase of the matrix.

S02-673

Wang Yong

How to efficiently Enhance the Thermal Conductivity of Poly(vinylidene fluoride)-based Composites?

Poly(vinylidene fluoride) (PVDF) is a typical semicrystalline polymer with good processing ability and exciting properties, including superior piezoelectric and pyroelectric properties. It has many applications ranging from supercapacitors, transducers, actuators to batteries. Due to the fact that the PVDF-based electronic devices become slimmer and more integrated today, improving the thermal conductivity of PVDF-based material becomes very significant today. The traditional methods that developed to enhance the thermal conductivity of polymer materials are usually related to the use of a large amount of conductive fillers. This results in not only the deterioration of processing ability and mechanical properties but also the rising of product cost. In the present work, several kinds of PVDF-based composites were prepared, including PVDF/carbon nanotubes (CNTs), PVDF/boron nitride (BN) and PVDF/graphene (GE). To efficiently enhance the thermal conductivity of these composites, a few polyvinylpyrrolidone (PVP), graphene oxide (GO) or other components, were introduced into these composites, respectively. The results showed that compared with the binary PVDF-based composites, the presence of the third component largely enhanced the thermal conductivity of these composites. The dispersion of fillers, the crystallization of PVDF matrix and the interfacial



interaction between PVDF and fillers were systematically investigated. The denser filler network structure and the improved interfacial interaction were suggested the main mechanisms for the largely enhanced thermal conductivity of PVDF-based composites.

S02-681

Mehranpour Milad, Mohammadi Seyed Ali , Ghasemi Ismail

Effect of Carbon Nano Tube (CNT) on PA/PE base Shape memory alloy

Shape memory polymers (SMPs) are new class of smart materials which their main characteristics is to recover its initial form after undergoing a large recoverable deformation via stimulation by heat, electricity , magnetic field and light . Nonconductive nature of polymers hinders the effect of stimulus such as heat and electricity to stimulate the shape recovery process. Shape memory polymers have two parts of soft and hard phase . That soft phase cause the deformation ability and other part is the harder phase and retentive initial form that called fixing phase. Having high rate of conductivity by conductive fillers such as MWCNT particles would be utilized in shape memory polymer alloys. Adding MWCNT particles to SMPs not only dramatically boosts their conductivity and accelerate the rate of shape recovery process but also MWCNTs at hard phase of SMPs reinforces the hard phase and increase the fixity and therefor recovery rate of SMPs . At the present work the PE/PA6 alloy compatibilized by polyethylene grafted maleic anhydride was blended by functionalized MWCNTs through acid treatment and was used as a shape memory material. In order to having selective localization of carbon nano tubes, two mixing procedure were selected. Thermal programing for inducing of shape memory properties considered using general tensile testing machine equipped with hot oven. The localized MWCNT in the well distributed polyamide phase might be causes to improve conductivity and better stimulate of SMP. The rheological properties and morphology of the samples were investigated by RMS and SEM. The results showed that well mixing

of two phases as well as Nano filler. Finally the SMP properties of the composite showed improvement because of better conductivity and performed morphology.

S02-701

Derdouri Abdessalem, Martinez-Rubi Yadienka, Simard Benoit

Melt-mixing preparation and characterization of polycarbonate / boron nitride nanotube nanocomposites

Abstract Nanocomposites based on unfunctionalized boron nitride nanotubes (BNNT) and polycarbonate (PC) were investigated. BNNT are novel nanoparticles having a tubular structure similar to that of carbon nanotubes except that alternating B and N atoms supersede the C atom. Preparation of the PC/BNNT nanocomposites was carried out at the small scale using dry pre-mixing PC powder and BNNT followed by melt mixing using twin-screw extrusion. The nominal concentration range of BNNT in the PC matrix spans from 0.1 to 5 % in weight. Characterization tasks were carried out on the PC/BNNT samples: morphology observation by electron microscopy (SEM; TEM), rheological measurements (SAOS), thermal characterization (DSC; TGA), tensile mechanical testing, and optical transmittance in the visible range. The rheology data reveal a transition from fluid-like behaviour to a solid like-behaviour at low frequencies as the BNNT content is increased. This result suggests the formation of a percolating structural network of BN nanotubes within the matrix. The interconnected BNNT network results in an apparent yield stress as demonstrated by a plot of viscosity versus shear stress. Linear correlations between optical transmittance, glass transition temperature and loss tangent are demonstrated but need to be investigated further. These correlations may be related to the fact that these properties are all affected by the state of BNNT dispersion and their interaction with the polycarbonate matrix. These and other results will be presented and discussed.

S02-71



Moritzer Elmar, Heiderich Gilmar

Fiber Length Reduction during Shearing in Polymer Processing

In recent years a continuously rising demand of short-fiber-reinforced thermoplastics has been noted. The reason for the rising demand are the excellent weight specific mechanical properties compared to non-reinforced thermoplastics. The mechanical properties of the compound of highstrength fibers and the ductile matrix polymer is based on complex physical relations in which the fiber length is a major influencing factor. When processing short fiber reinforced thermoplastics with screw machines (injection molding, extrusion) the fiber length is a resulting material property that is, to some extent, influenced by the process parameters. The extent of the influence and the effects of the process parameters have been carried out in many different studies, mainly with parameter variations. Nevertheless, the influence of the shearing stress on the fiber breaking is also physically modelled. However, the influences of different fiber contents are not taken into account. To investigate the correlation between the fiber content of the thermoplastic polymer and the fiber length degradation a defined flow field is necessary. For this purpose, a test stand with a heated rotating piston and a stationary outer cylinder is used. In the gap between the piston and the outer cylinder the melted material faces shear stress depending on different rotational speeds. For the investigation different short-fiber-reinforced thermoplastics (polypropylene matrix) with different fiber content are used. By measuring the fiber length after different shearing times the timevarying fiber length is determined. With these results the influences of the fiber content and shear stress on the fiber length can be identified.

S02-713

Ghahramani Nikoo, Seyed Esfahani Seyed Armin, Mehranpour Milad, Nazockdast Hossein

The rheological and thermal conductivity study on PA/COC blend filled by Boron Nitride

Thermally conductive and electrically insulating polymer/boron nitride (BN) composites are highly attractive for various applications in many thermal management fields. However, the preparation methods for polymer/BN composites with prescribed performance have usually caused difficulties in the material post processing. Therefore, using polymer blends with selective localization can be utilized as a solution for this problem. The effect of selective localization of boron nitride (BN) particles on the thermal conductivity of immiscible PA/COC blends is studied. The aim of the present work is to use PA/COC blend with co-continuous morphology in order produce PA/COC/BN thermally to conductive composites with minimum volume fraction of fillers. The efficiency of this method is evaluated through a comparison between thermal conductivity of PA/BN and PA/COC/BN systems. The rheological results and scanning electron microscopy (SEM) images reveal a greater affinity of BN with PA compared to COC phase. It is also shown that in order to form a thermal path and obtain an appropriate thermal conductivity, high concentrations of BN (≥30 wt. %) are needed. Thermal conductivity measurements show that the thermal conductivity of PA/COC/BN composites are lower than what expected based on the mixture law for polymer blends in comparison with PA/BN composites with the same concentration of BN in PA. The cooling rate is found to affect the thermal conductivity of the composite samples which is explained in terms of the crystallinity of PA.

S02-731

Kulkarni Aditya, Mukhopadhyay Nabaneeta, Bhattacharyya Arup, Panwar Ajay Singh

Effects of dispersant concentration and solution pH on the dispersion of non-covalently modified graphene in aqueous medium: A molecular dynamics simulation study

Non-covalent modification of graphene surfaces is a versatile strategy for improving dispersion of CNTs in polymer matrices. The sodium salt of 6amino hexanoic acid (Na-AHA) is a reactive modifier for CNTs that leads to both improved

CNT dispersion in water and exfoliated nanotube networks in PA6 polymer-blend systems during subsequent polymer melt-mixing. However, the dispersion mechanism of Na-AHA modified CNTs in aqueous media is not well understood. The first issue is related to the partitioning of the Na-AHA molecules onto the CNT surface from the solution. Another unknown is whether the CNTs are stabilized primarily via electrostatic or steric interactions. Also, Na-AHA has both carboxyl and amino groups, and either could be ionized depending on solution pH. Molecular dynamics simulations are utilized in conjunction with the thermodynamic perturbation method to explore the effect of Na-AHA concentration and pH on the dispersion of two graphene sheets. Our main result is that the potential of mean force (PMF) changes from a short-range strong attraction for bare graphene surfaces, to an increasingly long-range repulsion upon addition of Na-AHA which adsorbs onto the graphene surfaces. Further, we find that the long-range repulsion is electrostatic in origin which clearly points to an electrostatic stabilization of Na-AHA-modified graphene (or equivalently CNT) dispersions. To the best of our knowledge, evidence of electrostatic stabilization of noncovalently modified hydrophobic nanoparticles has not been previously reported in the simulation literature. In addition, we also use molecular dynamics to simulate the effect of solution pH on the dispersion of Na-AHA modified graphene surfaces. The simulations indicate that the repulsive interaction between graphene sheets is maximum for intermediate pH values. These results are in line with experimental observations which clearly show that Na-AHA modified CNTs are best dispersed at intermediate pH values.

S02-747

Serghei Anatoli, David Laurent, Boiteux Gisèle, Xu Weiqing

Coupled electrical-mechanical investigations on polymer composite materials: anisotropy in the conductivity evolution upon mechanical stretching In the current contribution, we present a recent experimental development that allows one to carryout coupled electrical-mechanical investigations of polymer composite materials upon mechanical stretching. Our approach enables one to characterize the evolution of the electrical properties of the samples in the elastic and in the plastic regime of mechanical deformation. Two orthogonal directions are accessible for the electrical investigations: parallel and perpendicular to the direction of the mechanical stretching. For the perpendicular direction, а non-conventional approach to measure conductivity values without employing a direct contact between the electrodes and the samples under investigation has been developed and implemented. The method was based on establishing the mathematical relation between the value of the conductivity and the frequency position of the Maxwell-Wagner-Sillars interfacial polarization peak observed in dielectric spectra of composite materials. For composite materials based on polyethylene filled with carbon black, a pronounced anisotropy in the evolution of upon mechanical conductivity stretching is observed: the conductivity varies by 5-6 orders of magnitude along the parallel direction and only 1-2 decades along the perpendicular direction. This behavior is attributed to а morphological anisotropy induced by stretching.

S02-428

Auscher Marie-Camille, Cassagnau Philippe, Fulchiron René, Périé Thomas

Effect of Stearic Acid on the yield stress and relative viscosity – from low filler content to highly filled zirconia suspensions.

Highly filled suspensions have attracted much interest in the past decades since they may be required for specific applications involving for example thermal conductivity or mechanical strength. Their processing may need to be adapted since an increase in filler concentration generally comes along with an increased viscosity up to a critical content at which the viscosity diverges. In addition a "stable" and homogeneous dispersion is often a must. Understanding the mechanisms

32nd PPS International Conference 2016, Lyon, France



governing the stability of highly filled suspensions in the case of submicron zirconia powders in polyolefins is the aim of the present study. In particular, the processing method Ceramic Injection Molding (CIM) is one of the applications and requires both a high solid content and a stable, finely dispersed suspension even under high shear rates. Powder-matrix interactions are to be well understood to control both the rheology and the dispersion state. Powders agglomeration must be prohibited and increasing the solid contents already yields beneficial effects thanks to hydrodynamics forces. Steric stabilization using fatty acids is another effective method widely reported in literature. The beneficial effect upon the dispersion is generally supported by a decrease in the suspension viscosity and storage modulus. The present study discusses the dispersion mechanisms of stearic acid. For this purpose the relative viscosity and yield stress are more deeply studied. Both are measured using a plate-plate geometry of a stress-controlled rheometer. The viscosity is obtained at a given frequency. Yield stress values are extrapolated from stress-strain curves as the minimum stress required to bring the suspensions into motion. Contrary to what is generally claimed, adding stearic acid to a suspension can increase both the viscosity and yield stress. This has been observed at solid contents below a critical value. Discussion about the physical significance and practical consequences will be provided.

Poster

S02-168

Kashi Sima, Gupta Rahul K, Kao Nhol, Bhattacharya Sati N

Rheology and Physical Characterisation of Graphene Nanoplatelet/ Poly (butylene adipateco-terephthalate) Nanocomposites

Graphene nanoplatelets (GNPs) were dispersed in poly(butylene adipate-co-terephthalate) (PBAT) by melt mixing. Morphological studies were carried out via scanning electron microscopy and X-ray diffraction. Results showed good dispersion of GNPs in PBAT at low filler loadings. SEM images showed establishment of physical contact between GNPs above 9 wt% which was also detected in electrical conductivity measurements where a sharper increase in conductivity was observed beyond this GNP loading. Interestingly, thermal stability of PBAT was also found to enhance as the GNP loading was raised to 9 wt% and higher. Melt flow behaviours of the prepared nanocomposites were characterized by dynamic and steady shear rate tests. Viscoelastic properties exhibited significant enhancement with increasing GNP loading. The effect of GNPs was more pronounced in storage modulus which exhibited less frequency dependency in the low frequency region. Rheological percolation threshold of GNPs in PBAT was determined to be in vicinity of 9 wt% at 140 °C which is in good agreement with SEM and electrical conductivity results. However, percolation was found to be temperature sensitive, occurring at lower GNP concentrations as the temperature was increased further from the system's melting point.

S02-126

Lee Chia-Fen

The Morphology and Control Release Behavior of Thermosensitive Poly(N-Isopropylacrylamide-Methylacrylic acid)/Au Semi-hollow Composite Latex Particles

In this work, the poly(methyl methacrylate-coacid)/poly(methacrylic methacrylic acid-co-Nisopropylacrylamide) thermosensitive composite semi-hollow latex particles were synthesized by three processes. The first process was to synthesize the poly(methyl methacrylate-co-methacrylic acid) (poly(MMA-MAA)) copolymer latex particles by the method of soapless emulsion polymerization. The second process was to polymerize methacrylic acid (MAA), N-isopropylacrylamide (NIPAAm) and crosslinking agent, N,N'-Methylenebisacrylamide (MBA), in the presence of poly(MMA-MAA) latex particles to form the linear poly(MMA-MAA)/crosslinking poly(MAA-NIPAAm) core-shell latex particles with solid structure. In the third process, part of the linear poly(MMA-MAA) core of core-shell latex particles was dissolved by ammonia to form the thermosensitive poly(MMA-MAA)/poly(MAA-NIPAAm) semi-hollow latex particles. The morphologies of the semi-hollow latex particles show that there is a hollow zone between the linear poly(MMA-MAA) core and the crosslinked poly(MAA-NIPAAm) shell. The crosslinking agent and shell composition significantly influenced the lower critical solution temperature (LCST) of poly(MMA-MAA)/poly(MAA-NIPAAm) semihollow latex particles. Besides, the gold nanoparticles (Au NP) were produced by the method of condensation, and wrapped in the poly(MMA-MAA)/poly(MAAthermosensitive NIPAAm) semi-hollow latex particles to form the poly(MMA-MAA)/poly(MAA-NIPAAm)/Au semihollow composite latex particles, and then the composite latex particles were used as carriers to load with Arbutin. The morphologies and the behavior of control release of the composite latex particles were investigated.

S02-157

Tuccar Kilic Nilay , Turgut Gizem, Boyacioglu Seyhan, Yogurtcu Ozge, Yildirim Aysun, Kodal Mehmet, Ozkoc Guralp



32nd PPS International Conference 2016, Lyon, France

Synthesis and Properties of POSS modified PS Microbeads

Polymeric microbeads are known as spherical particles that are 1-1,000 microns in diameter. Monodisperse polymeric particles are widely used in scientific and technological applications such as diagnosis of illness, electronics, catalyst carriers, coatings, biological sensors, etc. In general, microbeads are synthesized by using different techniques solvent polymerization such as emulsion evaporation, and dispersion polymerization. However, dispersion polymerization is one of the common techniques to synthesis monodisperse particles. In this project, polyhedral oligomeric silsesquioxanes (POSS) containing polystyrene (PS) based monodisperse microbeads were prepared by using dispersion polymerization. The function of different functional POSS nanoparticles (i.e. amino, epoxy) is to modifiy the surface properties of PS microbeads. Fourier Infrared (FTIR) Spectroscopy showed that the surface of microbeads were functionalized.X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were proved the presence of POSS particles on the surface of PS microbeads. Gel permeation chromatography (GPC) results showed that the molecular weight of PS microbeads was increased with of POSS incorporation nanoparticles. It was revealed from thermogravimetric analysis (TGA) data that percent char yields of POSS/PS microbeads are higher than that of neat PS microbeads. In addition, scanning electron microscopy (SEM) and optical microscope images were clearly exhibited the mono-sized distribution of microbeads. Keywords: Polymeric microbeads, dispersion polymerization, PS, POSS

S02-180

Dhahri Abdelwaheb, Beyou Emmanuel, Baouab Mohammed Hassen V

Electrical conductivity of Au-immobilazed onto polysaccharides reduced graphite oxide sheets

Graphene typically refers to a monolayer of carbon atoms packed into a honeycomb crystal structure, which are one-atom thick of sp2 bonded carbon, thus yielding a two-dimensional array of carbon arranged in a hexagonal structure. Functionalising the carbon substrate with polymers includes the well known 'grafting to' and 'grafting from' approaches. The classical approach first involves aggressive oxidation of graphite according to the Hummers' method leading to the formation of graphite oxide (GO). For example, we have demonstrated that the treatment of graphite oxide with organic alkoxy silanes (e.g., acryloxy propyl trimethoxysilane (APTMS) and triethoxysilaneterminated PDMS) and radical initiators can lead to the derivatization of both the edge carboxyl and surface hydroxyl functional groups. Cellulose is a polysaccharide exhibiting excellent properties such as nontoxicity, hydrophilicity, biocompatibility, and biodegradability so that can be used in the functionalization of graphene for potential applications in the biocomposites, areas of biomedical areas, and biosensors. In addition, Au nanoparticles are often employed in electronic materials, the detection of heavy metal ions, and catalysis. However, nanoparticles tend to aggregate when fabricated alone and therefore a supporting material is needed to grow and anchor the metal nanoparticles that is why GO has been used as a support material for many types of NPs including Au, Pd, Pt. Experiments reported here for cellulose assess the ethylenediamine nucleophilic addition onto carboxylic acid and epoxide groups located on the GO sheets' surface. Then, chloro-cellulose and chitosan were grafted onto the formed aminografted graphite oxide sheets and doped by gold nanoparticles. In the case of chitosan the grafting procedure involves an amide linkage with GO. The powder electrical conductivity of the resulting materials were studied as function а

S02-182

temperature.

Pinto Camila P., Saade Wesley A., Pachekoski Wagner M., Dalmolin Carla, Becker Daniela

Organic Modification Of Mmt Clay With Polyaniline: Effect On Electrical And Morphological Properties



MMT Clay was modified by replacement of Na+ with anilinium ion (An+) followed by chemical oxidation with ammonium persulfate in order to produce polyaniline in a rigid structure. This MMT-Pani composite was, then, tested as conducting filler for polystyrene films, processed in a Haake torque rheometer and hot pressed. MMT-Pani filler PS/MMT-Pani and nanocomposites were characterized by XDR, FT-IR, UV-vis, TG and DSC, showing Pani intercalation inside the clay platelets and improved interactions of the conducting polymers with clay. Ac and Dc electrical conductivity of fillers and nanocomposites were analised by two probe methodology and electrochemical impedance spectroscopy (EIS), respectively. Pani alone presented a high electrical conductivity, whereas the presence of the insulanting clay affects all electrical conducting mechanism. The morphology of the nanocomposites were analysed by SEM and TEM and showed improved clay exfoliation when higher quantities of MMT-Pani filler were added.

S02-201

Müller Michael Thomas, Krause Beate, Kretzschmar Bernd, Jahn Ivonne, Pötschke Petra

Thermal Conductivity of Hybrid Filled HDPE Nanocomposites

Managing heat dissipation is for example in electronic applications a great issue in context with the ongoing size reduction of electronics devices. To achieve enhanced thermal conductivity in polymer based electronic packaging currently metallic particles or mineral materials are used. As metallic particles have the disadvantage to promote thermo-oxidative polymer degradation alternatives have to be found. One approach is the use of carbon fillers like Vapour Grown Carbon Fibers (VGCF), multiwalled carbon nanotubes (MWCNT)or expanded graphite (EG). Such polymer nanocomposites combine improvements in heat transport with established plastics processing methods. In this contribution, composite materials based on high-density polyethylene containing nanostructured fillers were prepared. To test the effects of VGCF, MWCNT, anthracite powder,

microsilica, organoclay, and expanded graphite as well as mixtures of these fillers, small scale mixing using a DSM Xplore 15 twin screw compounder was performed. The amount and mixing ratios of the fillers were varied to determine the effect on the achievable level of thermal conductivity. Due to the orientation of rod-like filler particles leading to anisotropic heat flow, the thermal conductivity measurements were carried out in the throughplane direction as this direction is most interesting for industrial applications. In order to improve filler dispersion and induce chemical interactions between the polymer and the filler, the use of maleic anhydride-grafted polyethylene and aminofunctionalized MWCNT were investigated. As reported before, covalent matrix filler bonding can benefit the thermal transfer between the nanotubes and the polymer matrix. The filler dispersion and phase adhesion were studied using scanning electron microscopy. When limiting the maximum filler content to 10 wt%, the highest enhancement in thermal conductivity by 166% was found for VGCF followed by a 1:1 filler combination of VGCF with EG (148%).

S02-203

Krause Beate, Carval Jérôme, Pötschke Petra

Influence of Mixing Conditions on Carbon Nanotube Shortening and Curling in Polycarbonate Composites

Composites of polymers with carbon nanotubes (CNTs) combine the excellent electrical and mechanical properties of CNTs with the properties and the flexible shaping of polymers. Electrical percolation at low filling grades is connected with the very high aspect ratio of CNTs requiring that the high initial CNT length is preserved to large extent after melt mixing. As shown before, shortening happens during melt mixing [1-3]. In this work, composites of polycarbonate and 0.25-2.0 wt% multiwalled CNT (Nanocyl NC7000) were melt mixed in a small-scale microcompounder by varying the mixing conditions (time, rotation speed). The electrical properties were measured and the CNT macrodispersion was examined by light microscopy. Furthermore, the length



shortening and the changes in the curling state of the CNTs due to melt mixing were investigated in comparison to the as-grown nanotubes [1]. For these investigations composites containing 0.75 wt% CNTs were dissolved in chloroform and the single tubes were imaged using transmission electron microscopy. On such images, the length and the curling value of CNTs were quantified and correlated to the mixing conditions. The curling value was defined as the ratio of total to effective length of the individual nanotube. It was found that the CNT macrodispersion improved with increasing specific mechanical energy (SME) input. Additionally, the electrical percolation threshold increased with increasing SME input which correlated well with the more pronounced CNT shortening. Comparing the mean curling value at different mixing conditions, a decrease of the curling with increasing SME can be seen. Generally, the curling value lowered with decreasing CNT length. It is assumed that the nanotubes break at the defect sites and the remaining nanotube parts have a lower defect density and are straighter and more similar to an ideal nanotube. [1] Carbon 2011, 49: 1243-1247 [2] Comp Sci Technol 2011, 71(8): 1145-1153 [3] Polymer 2012, 53(2): 495-5

S02-204

Krause Beate, Predtechensky Mikhael, Ilyin Evgeny, Pötschke Petra

PP/SWCNT Composites Modified With Ionic Liquid

Carbon nanotubes (CNTs) have been shown in the last years as versatile filler to influence several polymer properties favorably. This concerns especially the electrical conductivity of single- and multiwalled CNTs which can be transferred to insulating matrices by establishing a percolated filler network. Melt mixing was shown to be a highly convenient method to produce thermoplastic composites containing CNTs. One crucial point in producing such nanocomposites is the filler dispersion, which is difficult to achieve strong due to van-der-Waals forces and entanglements between the tubes. For that the addition of dispersion agent is a common way. In

this study, polypropylene (PP) based composites with singlewalled CNTs (SWCNTs) were prepared by masterbatch dilution using a small-scale As Xplore DSM15. **SWCNTs** compounder unfunctionalised Tuball® (OCSiAl S.a r.l., Luxembourg) materials were used. To improve the SWCNT dispersion as well as to decrease the electrical percolation threshold an ionic liquid (IL, 1-Methxl-3-octylimidazolium tetrafluoroborate) was added. Different CNT : ionic liquid ratios were selected. Furthermore, the SWCNT concentration in the masterbatch was varied between 1 and 3 wt%. The CNT macrodispersion was characterized using light microscopy and the electrical resistivity was investigated. It was found that the electrical percolation threshold of the Tuball® filled PP composites prepared with a 2 wt% masterbatch and modified by the ionic liquid (CNT : IL=1:1) occurred at 0.05-0.07 wt%, whereas without the ionic liquid it was at 0.1 wt%. The electrical percolation threshold increased when using a higher concentrated masterbatch or a lower content of the ionic liquid.

S02-205

Kodal Mehmet, Şirin Hümeyra, Özkoç Güralp

Relationship between Crystallization Kinetics and Interfacial Interactions in PLA/POSS Nanocomposites

In this study, the relationship between crystallization rate and surface chemistry of polyhedral oligomeric silsesquioxanes (POSS) in poly(lactic acid) (PLA)/POSS nanocomposites was investigated. Four different kinds of POSS particles having different chemical structures were used. The composites were processed in a Xplore microcompounder at a screw speed of 100 rpm and 180°C barrel temperature. The POSS content was varied as 1, 3, 7 and 10 wt%. Common kinetic models such as Avrami, Ozawa and Dobreva and Gutzow were non-isothermal used to determine the crystallization behaviour of PLA/POSS nanocomposites by using the thermal data obtained from differantial scanning calorimetry (DSC). The morphology during the crystal growth was investigated by a polarized optical microscope (POM) equipped with a hot-stage. Thermodynamic



work of adhesion approach was adopted using the experimentally determined surface energies to investigate the interfacial interactions between POSS particles and PLA. A strong correlation was obtained between interfacial chemistry and the nucleation rate in PLA/POSS nanocomposites. It was found that the polar interactions are the dominating factor which determines the nucleation activity of the POSS particles. Keywords: PLA, POSS, nanocomposites, non-isothermal crystallization kinetic, interfacial interactions Acknowledgement: This study is granted by The Scientific and Technological Research Council of Turkey (Project No: 111M514).

S02-206

Filizgök Selen, Kodal Mehmet, Özkoç Güralp

Non-isothermal Crystallization Kinetics of Carbonaceous Nanofiller Reinforced Poly(butylene succinate) Nanocomposite

In the recent years, biodegradable products have raised great interest since the non-biodegradability of the commercially available plastics has caused many environmental problems associated with their solid waste pollution. Poly(butylene succinate) (PBS), a biodegradable biopolyester, has many applications such as food packaging, mulch films, nonwovens, fiber/textile, consumer goods, electrics and electronics, automotive interior and others. In this study, we have focused on the influence of the carbon-based nanofillers (carbon nanotubes (CNT) and fullerene (F)) on the non-isothermal crystallization kinetis of poly(butylene succinate). Biodegradable PBS composites based on carbonaceous nanofiller containing 0.5 and 1.0 wt % nanoparticles were prepared by melt compounding in a Xplore microcompounder. The data for nonisothermal crystallization kinetics studies were obtained using differential scanning calorimetry (DSC). The combined Avrami-Ozawa method could adequately describe the primary stage of nonisothermal crystallization kinetics of the neat PBS and PBS nanocomposites. The spherulitic morphology and growth were observed with hot stage polorized optical microscopy at 95 °C. The structure of nanocomposites in the nanometer scale

was characterized using transmission electron microscopy (TEM) observations. The results indicated that the nanocomposite samples exhibited enhanced crystallinity and nucleation density significantly, along with smaller spherulite size. There was a strong dependence of the rate of crystallization and extent of crystallinity of PBS on nanofiller loading and its shape. CNTs were found to be more effective nucleating agent for PBS under experimental conditions. Keywords: Poly(butylene succinate), carbonaceous nanofiller, nonisothermal crystallization kinetics

S02-215

Qi Xiaodong, Dong Peng, Fu Qiang

Observation of multi-shape memory and temperature memory effect via tuning distributed architecture of graphene oxide in poly(propylene carbonate)

А novel biodegradable polymer-based nanocomposites with tunable multi-shape memory effect and temperature memory effect based on poly(propylene carbonate) (PPC)/graphene oxide (GO) was prepared. By using a solvent-exchange and solution co-precipitation approach, a highcontent GO was incorporated into PPC matrix up to 20 wt% with excellent dispersion. The distributed architecture of GO could be tuned from a 'GO dotted dispersion' and 'GO network' to 'GO compact layered structure' with increasing GO content. GO sheets acted as cross-linking points, which confined the movement of PPC chains and increased the glass transition temperature (Tg) of PPC. The most eye-catching features were the appearance of two improved Tg with GO content over 10wt%, the one was corresponding to the slightly confined PPC, and the other could be attributed to the highly confined PPC. As a result, triple shape memory effect (TSME) was achieved via deformation at the two distinct Tg. In addition, experiments were designed to establish а temperature memory effect (TME) based on the stress free strain recovery, and it was found that the temperature corresponded to the maximum strain recovery rate could be quantitatively related to the deformation temperature. To the best of our



knowledge, this is the first effort to take advantage of strong 'nano-effect' via formation of two separated Tg to access TSME and a broad Tg to access TME simultaneously. Our work suggests a controllable approach to design a tunable multishape memory and temperature memory polymer, which could expand to a broad range of polymer composites.

S02-220

Şirin Hümeyra, Kodal Mehmet, Karaagac Bagdagul, Özkoç Güralp

Investigation of the Correlation between Adhesion Strength and Thermodynamic Work of Adhesion

The poly(hedral oligomeric silsesquioxane) (POSS)/silicone rubber (SR) crosslinked rubber composites reinforced were prepared by using laboratory type internal mixer at pre-optimized conditions. The POSs was used to enhance the adhesion properties of SR to reinforcing fibers such as Kevlar and Rayon. Three different POSS types including different functional groups were selected. These functional groups were expected to provide crosslinking with SR and grafting to fiber surfaces. The POSS type and the POSS loading level and reinforcing the fiber type (Kevlar and Rayon) were experimental handled as parameters. The fiber/silicone adhesion was investigated by Hadhesion tests. In addition the thermodynamic work of adhesion (TWA) was determined by using the surface free energy components of the compounds and fibers. The correlation between adhesion strength values and the TWA was investigated to understand the adhesion mechanism. It was found that H- adhesion tests showed an increased adhesion values by the addition of POSS particles. It was seen that there is a linear correlation between H-adhesion values and TWA. Keywords: Silicone Rubber, POSS, Reinforcing Fiber, H-Adhesion, Thermodynamic Work Adhesion Acknowledgement: This study is granted by The Scientific and Technological Research Council of Turkey (TUBITAK) (Project No: 113M258).

S02-225

Sanchez-Solis Antonio, Perez Ricardo, Ponce Aurora, Moreno Leonardo, Manero Octavio

Graphene, Nanographite By Ultrasound And Their Polypropylene Nanocomposites

In this work is presented the study of graphene and nanographite yield from an aqueous mixture of graphite and acrylic associative thickener, HASE (Hyper Alkali swellable emulsion), by ultrasound from the exfoliation of graphite. HASE function is to prevent coalescence of nanographite particles and exfoliated graphene sheets. Treatment times for graphite ultrasonic exfoliation were up to 21 days with sweep of frequencies and amplitudes. Once graphene sheets and nanographite particles were obtained, it was carried out processing of nanocomposites from graphene-nanographite, chemically modified bentonite clay by L-lysine aminoacid salt and carbon nanotubes using polypropylene as thermoplastic matrix, through a twin-screw extrusion process. At the end of the extruder was coupled a static mixing head which generates elongational flows and it is equipped with six piezoelectric elements 50 Watts each, located radially in the head, for developing ultrasonic waves. The results of parallel plate rheometry of the nanocomposites showed the complex viscosity was increased by threefold compared to the viscosity of virgin polypropylene. Nanocomposites tensile mechanical properties were improved and fracture deformation increases up to 100% pointed out excellent dispersion and distribution of nanoparticles on the whole polymer matrix. By Raman spectroscopy was determined the yield of nanographite tactoids and graphene sheets within the graphite ultrasound exfoliation process. Thermogravimetry assay showed HASE 5% weight in compounding made nanocomposites exhibited degradation rate of 1.9 %/°C, lower than that of pristine polypropylene, 2.6 %/°C, making these materials more thermally stable. In addition, these materials had dielectric constants up to 5 times higher that of polypropylene, which make them susceptible to be use in electronic components because the electrostatic charge dissipation



property or as electromagnetic shielding radiation materials.

S02-280

Schawe Jürgen E.K.

A new crystallization process in polypropylene filled with calcium carbonate

The influence of calcium carbonate filler on the crystallization behavior of PP is investigated by DSC and fast scanning DSC measurements. The non-isothermal crystallization process at industrially relevant cooling rates of about 100 K/s is significantly influenced by the calcium carbonate filler. Isothermal crystallization measurements indicate a new crystallization process in the temperature range between 45 °C and 80 °C caused by the filler. The CaCO3 content dependence of this additional process is studied. To find an explanation for the origin of this process we have analyzed the interaction between polymer and filler, crystalline structure the and the crystallization kinetics. From the experimental results we conclude that the newly observed crystallization process is driven by an additional nucleation process for the growth of á-phase crystals.

S02-283

Biçer Ezgi, Bahçeci Melis, Özbalaban Tugçe , Kemaloğlu Doğan Şebnem, Kodal Mehmet, Özkoç Güralp

Comparison of PP/TALC with PLA/TPU/TALC Composites: "Mechanical, Morphological and Thermal Properties"

As a renewable resource derived from an aliphatic polyester with good biocompatibility and degradability, polylactide (PLA) has been used for many applications and is widely considered a potential alternative to conventional petroleumbased materials. Polypropylene (PP)/talc composites are widely used in automotive applications such as instrument panel, dashboard and so on. Due to its brittle nature of PLA, its usage is limited to rigid and inflexible products. The aim of this project is to produce an environmentally

friendly alternative to talc-filled PP composites from PLA based compounds. In order to provide a polyester based biodegradable toughness, thermoplastic (TPU) polyurethane was incorporated to PLA. Talc was used to improve the heat resistance of the PLA/TPU blends. PLA/TPU/talc compounds were prepared with different weight ratios in a laboratory twin-screw extruder. The injection-molded samples were characterized by means of electron microscopy, static and dynamical mechanical tests and calorimetry. It was found that the addition of TPU to PLA improved the impact strength and elongation at break but decreased the tensile strength and modulus. The addition of talc balanced the toughness and stiffness of the PLA/TPU blends. The study showed that talc filled PLA/TPU blends can be an alternative to talc filled PP in terms of mechanical and thermal properties. Keywords: PLA, thermoplastic polyurethane, talc, blending, toughening

S02-301

Liu Huili, Bai Hongwei, Fu Qiang

Preparation of poly(L-lactide)/multi-walled carbon nanotubes nanocomposites with tunable matrix crystallization rate and mechanical strength

In this work, poly(L-lactide)/multi-walled carbon nanotubes (PLLA/MWCNTs) nanocomposites with tunable matrix crystallization rate and mechanical strength have been prepared by modifying MWCNTs with different chain length of poly(Dlactide) (PDLA). The PDLA grafted MWCNTs (MWCNTs-g-PDLA) nanohybrids with different weights of PDLA molecular chains were successfully synthesized by altering the reaction time in the ring-opening polymerization of Dlactide monomers on the MWCNTs surface. During subsequent melt-mixing of PLLA with the asprepared MWCNTs-g-PDLA, the grafted PDLA chains and PLLA matrix chains could co-crystallize into stereocomplex (SC) crystallites (confirmed by TEM, WAXD, and DSC) at the nanocomposites interface. The results reveal that with the increment of grafted PDLA chain length, the dispersion of



MWCNTs in the PLLA matrix as well as the tensile strength of PLLA/MWCNTs nanocomposites gets improved obviously, which mainly attributes to the strong interfacial adhesion imparted by the interface-localized SC structure. Moreover, the addition of MWCNTs-g-PDLA nanohybrids leads to an evidently enhanced matrix crystallization rate and the enhancement of the crystallization rate increases apparently with the length of the grafted PDLA chains, confirming the strong heterogeneous nucleating effect of the interface-localized SC crystallites on PLLA matrix crystallization. This work demonstrates the important role of grafted PDLA chain length in tailoring the interfacial adhesion and matrix crystallization rate of PLLAbased nanocomposite

S02-32

Hsu Feng-Hao, Wu Tzong-Ming

Investigation of Polypyrrole/Molybdenum trioxide/Graphene nanoribbon nanocomposite with high electrochemical capacity performance for electrode material of supercapacitor

А of nanocomposite ternary polypyrrole/molybdenum trioxide/graphene nanoribbon (PPy/MoO3/GNR) was successfully synthesized in situ oxidation by using polymerization method. The Fourier transform infrared (FTIR) spectra shows the metal oxide of MoO3 is successfully combined with GNR. The morphology is observed by using field emission scanning electron microscope (FESEM) and transmission electron microscopy (TEM). The electrochemical analysis, which is investigated by using electrochemical analysis instrument, shows the highest specific capacitance of 844 F g-1 and good cycle stability after 1000 cycles for PPy/MoO3/GNR ternary nanocomposite. These results demonstrate that the combination of each component can efficiently enhance the electrochemical capacity performance.

S02-323

Cha Sang Hoon , Kim Jae Ik, Bae Han Na, Sung Dae Hyun, Ryu Sung Hun

Rheological and crystallization behavior of glass fiber reinforced nylon composite

Fillers, such as glass fiber or carbon fiber, have been widely used to enhance the properties of polymer matrix. Reinforced polymer composite is a useful structural material to replace metal or ceramic structures. Lightweight structural material is one of key issues to make energy efficient vehicle and reinforced polymer composite is one of strong candidates to achieve this purpose. In real application, it is not easy to make thin, large or complicate structures due to high viscosity of polymer composite, especially high filler content. Crystallization behavior also affects the interfacial property between filler and polymer matrix. High content of short and/or long glass fiber reinforced nylon-6,6 is investigated to replace the metal structure in vehicle which requires high flexural strength and modulus. High content of glass fiber results in low melt viscosity and sometimes it causes poor mechanical properties due to poor wettability between glass fiber and polymer matrix. The use of viscosity improver has been reported, but in general poor mechanical properties were obtained. Newly synthesized chemicals from laboratory and some commercial materials are used to improve the melt viscosity. Effect of viscosity improver, filler content and processing conditions on the melt viscosity and crystallization behavior of composite is investigated. Compatibility of chemicals and polymer, size distribution of glass fiber are also investigated. Rheometer is used to measure the melt viscosity and morphology of composite are analyzed using X-ray and scanning Differential electron microscopy. scanning calorimetry is used to analyze crystallization behavior of composite under isothermal and nonisothermal conditions. Mechanical properties are obtained using universal tensile tester.

S02-328

fu sirui, zhang jun, yu bowen, chen feng, fu qiang

Effect of ball milling and hosphoric acid treatment on the properties of short Kevlar fiber reinforced polypropylene



As a traditional industry plastic, polypropylene(PP) shows a tremendous application potential in many areas. However, the practical use of PP is mainly restricted to the low load-bearing environments because of its poor low-strain mechanical strength and stiffness. In this work, short kevlar fiber was introduced into PP matrix to improve its mechanical properties. In order to improve the dispersion of the fiber and enhance the interfacial interaction between fiber and matrix, a combination of ball milling and hosphoric acid treatment was used in this work. Pre-dried Kevlar fibers were soaked in hosphoric acid aqueous(0wt.%, 10wt.%, 20wt.%, 30wt.%) and milled for different time with various roller speed. It is interesting to observe that kevlar fiber can be easily exfoliated into several microfibers during ball milling, and the exfoliation has evident effect on the reinforcement effect because of the increase of interfacial adhesive area between the newly-formed microfibers and the PP matrix. Our work demonstrates that mechanical performance of short fiber reinforced plastic composites could be significantly improved by enhancing interfacial strength and fiber exfoliation using a facile surface modification strategy and conventional melt-processing technology.

S02-329

Hamidi Youssef K., Aktas Levent, Altan M. Cengiz

Thermal History Effects on Moisture Absorption of Fiber-Reinforced Polymer Composites

Fiber-reinforced polymer composites may offer numerous attractive features such as low cost, high specific performance and ease of production. However, there are concerns about the overall durability of these materials, especially for sustained performance under severe and changing environmental conditions. Moisture is known to have detrimental effect on the mechanical properties of composite components. However, there is a general lack of data on the effects of lifecycle thermal history on moisture absorption in fiber-reinforced polymer composites. This work

investigates the effect of previous life-cycle thermal history on moisture absorption in resin transfer molded glass/epoxy composites. Disk-shaped parts (D=152.4 mm) are fabricated using EPON 815C and EPICURE 3282 curing resin agent. Reinforcement is provided by six layers of randomly oriented planar glass fiber performs with 0.459 kg/m2 surface density, vielding approximately 32 % fiber volume fraction. Samples cut from the molded disks are initially immersed in water at room temperature for 48 hours. Then, these samples are divided into three groups which are subjected to 0°C, -25°C or liquid nitrogen for another 48 hours, thus imparting various levels of life-cycle damage. A set of specimen undergoes the same absorption cycle at room temperature to characterize the baseline behavior of the composite samples. Afterwards, all samples undergo a desorption cycle. Specimen are subsequently immersed in water at room temperature for 18 months. Their masses are measured at periodic intervals to quantify the amount of water absorbed. Moisture intake is found to increase considerably with harsher environmental/thermal history of the different composite parts. In addition, stiffness reduction after freezing and after moisture absorption is also measured. Stiffness is found to drop for all composite parts considerably after moisture absorption. The stiffness drop is observed

S02-337

Deng Sha, Fu Qiang

before moisture absorption.

A rapid and scalable filler-treatment method to enhance thermal conductivity of polyvinylidene fluoride/expanded graphite composite

to be much more significant for the samples that were exposed to lower freezing temperatures

In the current work, we illustrate a facile strategy to improve thermal conductivity of polyvinylidene fluoride/expanded graphite (PVDF/EG) composites by pre-treatment of EG via the newly explored ball milling. Before conventional melt processing, EG powders were treated by shear-force-dominated ball milling. In this way, the loose and porous vermicular structure of EG could be effectively 63



destroyed and partly exfoliated to graphite nanosheets (GNSs), the size of which can be simply controlled by adjusting milling time. As a result, the PVDF/GNSs composites show improved thermal conductivity owing to better dispersion. Filler content fixed at 15%, the thermal conductivity of PVDF/GNSs composites can reach 1.29 Wm-1K-1, 42.5% higher than that of PVDF/EG (0.90 Wm-1K-1). More importantly, the electromagnetic interference (EMI) shielding and tensile strength of PVDF/CNSs composites is also improved. Our work provides a simple and scalable method for filler treatment and has great potential for improving thermal conductivity of polymer composites in the fields of engineering.

S02-348

Yang Weixing, Wu Kai, Chen Feng, Fu Qiang

A ultrathin flexible, high electrical conductivity of graphene/cellulose nanofiber film for efficient electromagnetic interference shielding

Reduced graphene oxide (RGO) have been used as nanofillers to improve the electrical and mechanical properties of polymers, in which the RGO content is usually low due to the serious agglomeration. For composites, full exploitation of these the extraordinary properties of graphene is limited by low RGO loading. In this work, We report the preparation of ultrathin flexible, highly conductive nanofiber reduced graphene oxide/cellulose (RGO/CNF) composite films with high RGO content through a simple vacuum-assisted selfassembly technique followed by a post-reduction treatment procedure. By adjusting the GO content, various RGO/CNF nanocomposite films with 5-50 wt% content of graphene were obtained. The crosssectional scanning electron microscopy(SEM) images reveal the graphene nanosheets were homogeneously distributed in the CNF matrix with a layered structure. the oriented layered structure of RGO/CNF nanocomposite film is formed in the vacuum-assisted filtration process. The unique layered structure that incorporate cellulose nanofibers for the graphene nanosheets dramatically increases the electrical conductivity of RGO/CNF nanocomposite films. with 50wt% of graphene ,The electrical conductivity of the resulting RGO/CNF nanocomposite films from this study is 2093.3 S m - 1. Further investigation demonstrates that the resulting lightweight and flexible RGO/CNF nanocomposite films show superior shielding effectiveness (SE) of electromagnetic interference in the X-band even under the thin thickness of samples.

S02-35

Chen Yi-An, Wu Tzong-Ming

Crystallization kinetics of poly (1, 4-butylene adipate)/organically-modified layered zinc phenylphosphonate nanocomposites

The organically-modified layered zinc phenylphosphonate (m-PPZn) were prepared by a facile chemical intercalation method. Poly(1,4butylene adipate) (PBA) belonged to biodegradable polymers and was friendly to environment. Thus, the solution-casting method was used to obtain the new PBA/m-PPZn nanocomposites. Crystallization kinetics and morphology of PBA and 0.5wt% PBA/m-PPZn nanocomposites were studied using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), transmission electron (TEM), and wide-angle microscopy X-ray diffraction (WAXD). Both WAXD and TEM results illustrated that most of the layered materials of partial delamination are randomly dispersed in the PBA matrix. The crystallization time increased with increase in crystallization temperature for neat PBA and 0.5wt% PBA/m-PPZn nanocomposites. When compared to neat PBA, the t1/2 of the fabricated 0.5 wt% PBA/m-PPZn nanocomposites demonstrated significant decreased under the same isothermal crystallization conditions. This indicates that the incorporation of the m-PPZn content into PBA significantly enhances the crystallization rate of PBA. With the presence of m-PPZn, the nuclei number of PBA increases and the spherulite size significantly reduces. Therefore, the addition of m-PPZn to PBA induces heterogeneous nucleation.

S02-37

Wang Ching-Yuan, Wu Tzong-Ming

Synthesis of graphene nanoribbon/reduced graphene oxide/polypyrrole nanocomposites as electrode for supercapacitor

A high performance electrode material for a supercapacitor has been developed based on graphene nanoribbon (GNR), reduced graphene oxide (rGO) and polypyrrole (PPy) nanocomposites (GNR/rGO/PPy) synthesized via in-situ chemical polymerization. The morphology and molecular structure of the nanocomposites are characterized field-emission by using scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and Fourier transform infrared (FTIR). Electrochemical spectroscopy characterization of the electrode materials have been carried out by using cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. GNR/rGO/PPy nanocomposite reveals that the highest specific capacitance of 591 F/g at a scan rate of 5 mV/s, which is better than these of PPy and PPy/GNR nanocopmposite. Furthermore, GNR/rGO/PPv nanocomposite shows a high rate capacity and good cycle stability after 1000 cycles. The excellent electrochemical performance demonstrates that the GNR/rGO/PPy nanocomposite has a great potential in energy storage devices.

S02-379

Tsai Gang-Shian, Chen Yi-An, Chen Erh-Chiang, Wu Tzong-Ming

Isothermal crystallization behavior and microstructure of poly(butylene succinate-coadipate)/modified layered double hydroxides nanocomposites

A biodegradable poly[(butylene succinate)-coadipate] (PBSA) synthesized by polycondensation reaction is solution-mixed with organicallymodified layered double hydroxide (m-LDH) to

fabricate the PBSA/m-LDH nanocomposite. The crystallization behavior and microstructure of PBSA/m-LDH nanocomposite are studied by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and small-angle X-ray scattering (SAXS). Both WAXD and TEM results demonstrate that most of the layered materials are exfoliated and randomly distributed in the PBSA matrix. With the addition of 3 wt % m-LDH into PBSA, the half-time for crystallization of PBSA/m-LDH nanocomposite decreased by 47-76% for isothermal crystallization at 48-56 °C compared with that of neat PBSA. The microstructure of PBSA/m-LDH nanocomposites identified by SAXS shows higher crystal layer thickness is achieved with the presence of 3 wt % m-LDH.

S02-382

Deng Sha

A rapid and scalable filler-treatment method to enhance thermal conductivity of polyvinylidene fluoride/expanded graphite composite

In the current work, we illustrate a facile strategy to improve thermal conductivity of polyvinylidene fluoride/expanded graphite (PVDF/EG) composites by pre-treatment of EG via the newly explored ball milling. Before conventional melt processing, EG powders was treated by shear-force-dominated ball milling. In this way, the loose and porous vermicular structure of EG could be effectively destroyed and partly exfoliated to graphite nanosheets (GNSs), the size of which can be simply controlled by adjusting milling time. As a result, the PVDF/GNSs composites show improved thermal conductivity owing to better dispersion. Filler content fixed at 15%, the thermal conductivity of treated PVDF/GNSs composites can reach 1.29 Wm-1K-1, 42.5% higher than that of PVDF/EG (0.90 Wm-1K-1). More importantly, the electromagnetic interference (EMI) shielding and tensile strength of PVDF/CNSs composites is also improved. Our work provides a simple and scalable method to improve thermal conductivity of polymer composites .



S02-383

Xi Shuting, Kong Miqiu, Yang Qi , Li Guangxian, Huang Yajiang

The efficiency of reactive solid-state epoxy and nonreactive silica nanoparticles in compatibilizing a commercial polyester blend, namely poly(methyl methacrylate) /polycarbonate (PMMA/PC) blend, were evaluated and compared in terms of morphology, thermal and mechanical properties. The significantly refined morphology and largely enhanced mechanical properties evidenced that both the epoxy and silica nanoparticles possessed superior compatibilization efficiencies to the PMMA/PC blend. More importantly, these improvements were achieved without sacrificing their thermal stability and causing noticeable degradation of macromolecular chains, which are usually unavoidable when using conventional transesterification catalysts as the compatibilizers. Finally, the underlying compatibilization mechanisms involved, advantages and disadvantages of these compatibilization strategies were discussed. It is believed that the strategies proposed may be also applicable in designing other high-performance polyester blends with balanced mechanical and thermal properties.

S02-385

Yin Bo, Dou Rui, Yang Mingbo

Excellent electromagnetic interference shielding via tri-continuous structure with MWCNTs selective dispersion

Compared with the random distribution of nanofillers in polymer matrix, selective distribution of nanofillers in one phase, especially in the interfacial phase, is proposed to be the ideal scenario to achieve the special functional application in multiphase polymer composites. For CNTs, which have larger aspect ratios, selective distribution at the interfacial phase of immiscible polymer blends is very difficult. Here we introduce a method to selectively disperse CNTs into interfacial PS phase in PVDF/PS/HDPE ternary blends by the control of interfacial tension and

phase viscosity. It is found that ternary composites with tri-continuous structure has the best effect to improve the electromagnetic interference shielding (EMI SE) with the same MWCNTs content compared with other comparison samples. The results show that the average EMI SE of PS/MWCNTs composite is 15 dB, indicating that ≈95% of the electromagnetic radiation is blocked by the shielding material. And for PVDF/PS-MWCNTs composite, the average EMI SE is about 18 dB which is still lower than the basic requirement value (~20 dB) for commercially application. However, PVDF/PS/HDPE-MWCNTs for composite, the EMI SE increases to about 30 dB, which indicates that ≈99.9% of the electromagnetic radiation is shielded. To clarify the EMI shielding the PVDF/PS/HDPE-MWCNTs mechanism in composites, the result indicates that the contribution of SER is negligible. The SEtotal, SEA, and SER at 9.5 GHz of the PVDF/PS/HDPE-MWCNTs composite with 1.6 vol.% MWCNTs are 31.7, 29.1, and 2.6 dB, respectively, which indicates that the contribution of absorption to the total EMI SE (91.8%) is much larger than that from reflection (8.2%), indicating an absorption dominant shielding mechanism rather than reflection

S02-391

Xu Liyang, Yin Bo, Yang Mingbo, Feng Jianming, Xie Banghu

The Impact of Alkylated Graphene Oxide on the Crystallization Behavior of Poly (4-methyl-1pentene) under Stretching at High Temperature

In this work, we studied the relationship between microstructure and macroscopic deformation and the impact of alkylated graphene oxide (GO-ODA) on the change of microstructure in the stretching process at high temperature. The nanocomposites are obtained via introducing GO-ODA to poly(4methy-1-pentene) (PMP or TPX) using a solution approach. It is found that melting points of two with the strain samples rise increasing accompanied crystal orientation during stretching process. Differential scanning calorimeter (DSC) results show that the melting points of TPX/GO-ODA (0.5 wt%) are higher than that of TPX and



they all have a constant melting point at high strain. Crystallinity trends of two samples were somewhat similar with the changes of melting point. It is worth noting that the added GO-ODA makes samples reach the plateau region of the crystallinity at a greater strain than TPX. With wide-angle X-ray scattering (WAXD) analysis, crystal was destroyed in the stretching process of two samples. Smallangle X-ray scattering (SAXS) results show that the calculating fibrils diameter of TPX/GO-ODA are smaller than that of TPX. From analyzing the change process of internal structure, GO-ODA is the role of barrier and delay the molecular response to tension in the drawing process. In this work, GO, as a kind of nanofiller, is used to study the impact on crystallization behavior of polymer/filler composites during stretching process, which obviously is great significance to widen the application of GO. College of Polymer Science and Engineering, Sichuan University, Chengdu, 610065, People's Republic of China. Address: Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu, China, 610065. E-mail: vinbo@scu.edu.cn

S02-396

ENOMOTO Kazuki, TAKAHASHI Yukiya

Oxidization of carbon nanofiber and its effect on tensile properties of PA11 matrix composite reinforced with carbon nanofiber

In order to improve interfacial adhesion between the thermoplastic matrix and the carbon nanofibers (CNFs), two-step oxidization by using mixed acid and hydrogen peroxide was performed on the CNFs. Moreover, polyamide 11 (PA11) based composites reinforced with the oxidized CNFs were fabricated, and tensile properties of the composite were evaluated. The effect of oxidization on the tensile properties was discussed by comparing the experimental results to the rule of mixture. From the results of the X-ray diffraction and XPS, the carboxyl groups were introduced to the surface of CNFs by oxidization process. However, the oxidization by using strong mixed acid destroyed the structure of CNFs excessively. On the other hand, when the mild oxidization by using hydrogen peroxide was carried out after strong oxidization in short time, the structure of CNFs was not destroyed and was able to give functional groups including oxygen effectively. As the result, tensile property of the composites reinforced with CNF improved.

S02-397

Vargas Maria Angeles, Vazquez Humbert

Non-isothermal curing kinetics and physical properties of MMT-reinforced unsaturated polyester (UP) resins

Cure behavior of unsaturated polyester (UP)/montmorillonite (MMT)/methyl ethyl ketone peroxide (MEKP)/cobalt octoate intercalated nanocomposites with various MMT loadings was investigated by dynamic differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Transmission electron microscopy (TEM). UP/MMT nanocomposites were prepared by sequential mixing. Non-isothermal DSC curves were obtained by applying heating rates ranging from 5 to 20 C/min. They presented two exothermic peaks, which should correspond to two independent cure reactions. The effective activation energy Ea, was determined by applying both the Kissinger's and Starink's methods. The results showed slightly higher activation energy for nanocomposites, except for UP/10-MMT. It was found that the dependence of Ea on a is complex. All the systems in this study fitted Sesták-Berggren (SB)model in overall reaction controlled kinetics and the corresponding model parameters, n,m, A were obtained, but it was insufficient in depicting complex reaction kinetics. Transmission the electron microscopy data support the formation of a partially delaminated nanocomposite material. UP and nanocomposites showed similar behavior on thermal stability.

S02-399

Wu Kai, Liu Xiaohui, Chen Feng, Fu Qiang

Preparation of functionalized h-BN encapsulated by graphene oxide

67



Hexagonal boron nitride (h-BN) has a similar layered structure with good thermal conductivity to graphite, but conversely electrically insulating. So h-BN is popular in preparing thermally conducting but electrically insulating materials for dieattachments, encapsulations, dielectrics and substrates used in electronic packaging. However h-BN has generally poor compatibility with most polymer matrix, resulting in weak interaction between surfaces of h-BN and matrix. Interface associated with the surface chemistry of fillers is a critical factor in affecting the properties of filled polymers, including both thermal conductivity and mechanical properties. In this study, we prepared functionalized h-BNencapsulated by graphene oxide through electrostatic self-assembly and added this modified filler into epoxy resin. Fouriertransforminfrared (FT-IR), scanning electron microscope (SEM), Raman spectroscopy and Energy Spectroscopy X-Ray Dispersive (EDX) are characterized to highly prove the encapsulation of graphene oxide. Owing to the rich oxygencontaining functional groups of graphene oxide on the surface of the h-BN, both the thermal conductivity and mechanical properties show obvious enhancement.Meanwhile, the thermal conductivity of polystyrenefilled by h-BN reduced graphene oxide (rGO) also largely increased. Moreover, the content of encapsulated graphene oxide or graphene was extremely little (less than 0.2 wt %), so good electrically insulation and low dielectric loss was maintained.

S02-40

Oliani Washington Luiz, Ferreto Helio Fernando Rodrigues, Komatsu Luiz Gustavo Hiroki, Lugao Ademar Benevolo, Rangari Vijaya Kumar, Lincopan Nilton, Parra Duclerc Fernandes

Preparation and Characterization of Polyethylene Nanocomposites with Clay and Silver Nanoparticles

Polyethylene is widely used for packing applications. From the different grades of polyethylene, LLDPE and LDPE play a major role in the film blowing industry. The use of nanoclay in polymer matrices (non-polar) requires the use of a compatibilizer agent, ethylene graft maleic anhydride copolymer (PE-g-MA), which acts as a bridge for nanoclay-matrix-interaction. In our study, blown films of LLDPE, LDPE, and their blends were produced using a twin screw extruder. The combination of PE as matrix, montmorillonite (MMT) and silver nanoparticles (AgNPs) intended to improve mechanical and thermal properties. with wt% Nanocomposites films 1 of montmorillonite and 0.5 to 1.0 wt% silver nanoparticles were prepared by blow extrusion and evaluated. Nanoclay intercalation/exfoliation degree was investigated by X-ray diffraction spectroscopy (XRD) and scanning electron microscopy (SEM). Mechanical and thermal properties were evaluated. The results showed optimum dispersion at intercalation/exfoliation levels for PEs:MMT:AgNPs, slight increasing in mechanical and especially improvement in thermal properties.

S02-476

Socher Robert, Pötschke Petra, Krause Beate

Effect of additives on MWCNT dispersion and electrical percolation in polyamide 12 composites

For the preparation of electrical conductive thermoplastic composites by incorporation of carbon nanotubes (CNTs) melt compounding is a suitable and scalable method. During the process of of as produced dispersion primary CNT agglomerates into the matrix, the wetting and infiltration of the matrix polymer chains into the agglomerate structures are important initial steps, followed by the dispersion steps involving rupture and erosion of agglomerates. Low viscous additives can help to facilitate such steps e.g. by reducing the interfacial tension between CNTs and matrix. Also additives which interact with the π -system of the seem to be promising to stabilize CNTs individualized CNTs. The aim of this study was to improve the dispersion of multiwalled CNTs in and decrease the polyamide 12 electrical percolation threshold by the use of additives. Different kinds of additive were selected which either interact with the π -system of the CNTs (iImidazolium based ionic liquid (IL) and 3,4,9,10-



pervlenetetracarboxylic dianhydride (PTCDA)) or improve the CNT wettability (cyclic butylene terephthalate, CBT). The composites were melt mixed using a DACA microcompounder. The CNT macrodispersion was analysed using transmission light microscopy on thin sections. The electrical percolation threshold for PA12/MWCNT, measured on compression molded plates, was found at 2-2.25 wt%. The addition of CBT leads to a decrease towards 1 - 1.5wt% whereas the CNT macrodispersion was not improved. A slightly higher percolation threshold of 1.5 wt% was found for PTCDA as additive, whereby the CNT macrodispersion did not improve. The lowest percolation threshold was achieved with IL at 1-1.25 wt% CNT. At the same time, the CNT macrodispersion was improved as indicated by the presence of a lower number and lower size of remaining CNT agglomerates. This illustrates that the use of such additives may improve the performance of PA12 based CNT nanocomposites.

S02-487

Cruz Heidy, Son Younggon

A Study on the Effects of Aspect Ratio and Bulk Density on the Electrical Properties of Polycarbonate/MWCNT nanocomposite

Since the discovery of carbon nanotubes (CNT), significant research works have been directed to its use as conductive filler to polymer nanocomposites since it exhibits high potential application in several fields such as electrostatic dissipation (ESD), electrostatic painting and electromagnetic interference shielding (EMI-shielding). To date, most experimental results about the electrical properties of polymer-CNT composites have been produced using simple, laboratory-scale process such as compression molding which can lead to results that may not be comparable to more complex, industrial-scale process like injection molding. The main challenge, however, is the poor electrical performance of the polymer nanocomposites produced by injection molding compared to compression molded nanocomposites. In this work, the influence of CNT length to the electrical injection-molded performance of

polycarbonate/multiwall CNT composites was studied. Three types of multiwall carbon nanotubes with different lengths were melt-mixed with polycarbonate in a twin screw extruder followed by injection and compression molding. Results show that nanocomposites with higher CNT aspect ratio exhibit better electrical conductivity. Longer nanotubes tend to form a stronger conductive network during secondary agglomeration which can withstand the high shear forces during injection molding.

S02-491

Ren Penggang, Ren Fang, Xie RuiHong

Preparation and properties of graphene oxideregenerated cellulose/polyvinyl alcohol hydrogel with pH-sensitive behavior

Graphene oxide reinforced regenerated cellulose/polyvinyl alcohol(GO-RCE/PVA) ternary hydrogels were successfully prepared via a repeated freezing and thawing method in NaOH/urea aqueous solution. The effect of GO content on the mechanical properties, swelling behavior, water content of composite hydrogels was investigated. It was found that the mechanical properties of GO-RCE/PVA hydrogels were largely enhanced relative to RCE/PVA hydrogels. With the addition of 1.0wt% GO, the tensile strength was increased by 40.4% from 0.52 MPa to 0.73MPa, accompanied by the increase of the elongation at break (from 103% to 238%). Meanwhile, GOternary hydrogels performed RCE/PVA the excellent pH-sensitivity, and the higher pH leaded to higher swelling ratio. With 0.8wt% GO loading, the swelling ratio of GO-RCE/PVA ternary hydrogel was improved from 150% (pH=2) to 310% (pH=14). In addition, a slight increase in the water content of the ternary hydrogel was achieved with increasing concentrations of GO. It is believed that this novel ternary hydrogels is a promising material in the application of biomedical engineering and intelligent devices.

S02-497

Osada Yu, Nishitani Yosuke, Kitano Takeshi



Effect of Processing Sequence on the Mechanical and Tribological Properties of Ternary Nanocomposites (VGCF-X/PA6/HDPE)

The aim of this study is to develop the new tribomaterials for mechanical sliding parts with sufficient balance of mechanical and tribological properties. The effect of processing sequence on the mechanical and tribological properties of ternary nanocomposites (VGCF-X/PA6/HDPE) was investigated: the polymer blends of polyamide 6 (PA6) and high density polyethylene (HDPE) filled with vapor grown carbon fiber (VGCF-X) which is one of the carbon nanofiber and has 15nm diameter 3µm length. Five different processing and sequences, (1) VGCF-X, PA6 and HDPE were mixed simultaneously (Process A), (2) Re-mixing (Second compounding) of the materials prepared by Process A (Process AR), (3) VGCF-X was mixed with PA6 (VGCF-X/PA6 blends) and then these composites were blended with HDPE (Process B), (4) HDPE was blended with PA6 (PA6/HDPE blends) and then these blends were mixed with VGCF-X (Process C), (5) VGCF-X were mixed with HDPE (VGCF-X/HDPE blends) and then these composites were blended with PA6 (Process D) were attempted for preparing of the ternaery nanocomposites (VGCF-X/PA6/HDPE). These ternary polymer nanocomposites were melt mixed by a twin screw extruder and injection-molded. Their mechanical properties such as tensile, Izod impact and Durometer hardness, and tribological properties were evaluated. Tribological properties were measured by a ring on plate type sliding wear tester dry condition. The mechanical under and tribological properties changed in according with the processing sequence of ternary nanocomposites (VGCF-X/PA6/HDPE). These may be attributed to the change of the internal structure formation of ternary nanocomposites (VGCF-X/PA6/HDPE).

S02-501

Dong-Lin Kuo, Tzong-Ming Wu

Characterization of organically modified layered zinc phenylphosphonate/ Poly(butylene succinate/adipate) nanocomposites In this study, the organically-modified layered zinc phenylphosphonate (m-PPZn) prepared using coprecipitation method sucessfully were synthesized to intercalate hexadecylamine into the interlayer spacing of PPZn. The interlayer spacing of m-PPZn determined by wide-angle X-ray diffraction (WAXD) was increased from 14.5 Å for PPZn to 27.9 Å for m-PPZn. These results suggest hexadecylamine that the were successfully exchanged and intercalated into the interlayer spacing of PPZn. The poly(butylene succinate/adipate)(PBSA)/m-PPZn nanocomposites were then prepared by melt-mixing. The structure, morphology, and crystallization behavior of the PBSA/m-PPZn nanocomposites were characterized using WAXD, transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). Both WAXD and TEM results demonstrate that most of the partial-delamination m-PPZn was randomly dispersed in the PBSA matrix. With the addition of 5wt% m-PPZn, the crystallization temperature (Tc) of the PBSA/m-PPZn nanocomposites was increased about 3.84 oC compared with that of neat PBSA using nonisothermal crystallization method. It has been shown that m-PPZn containes an effective nucleating effect for PBSA.

S02-537

Garnier Audrey, Brendle Jocelyne, Bounor-legare Veronique, Michelin Laure, Rigolet Severinne, Melis Flavien

Innovative fillers for polymers: Functional talclike organic-inorganic hybrids prepared by sol-gel route

Several studies have shown the interest of organomodified 2:1 phyllosilicates as fillers for polymers to enhance thermal, mechanical or barrier properties. Montmorillonite were particularly investigated whereas only a few studies deals with talc like structures. Organic-inorganic talc like hybrids (TLH) can be prepared by a process based on sol-gel chemistry which enables the formation of the materials under mild conditions in a one-step method. In this case, the organic groups are linked directly to the inorganic framework by covalent



bonds whereas, in the case of montmorillonite only low energy bonds are obtained between the silicate layers and the organic moieties or surfactants. This method allows the production of a variety of TLH based compound with different organic moities bringing specific properties. In this study, the solgel synthesis of organic-inorganic talc like hybrids having the following chemical formula: Mg3(RSi)4O8(OH)2 (where R stands for the organic part) starting from diethylphosphatoethyltriethoxysilane (SiP) and an ethanolic solution of magnesium nitrate hexahydrate was optimised. It was shown that by using short aging times (5 min to 1 day) and low volume of solvent at room temperature, it is possible to form a range of lamellar structures as confirmed by XRD. FTIR, TGA 13C, 31P and 29Si NMR analysis confirmed the integrity of organic moieties in the TLH structure and enables gathering information degree on the of polycondensation of the silicon species

S02-554

Cermak Michal, Kadlec Petr, Polansky Radek

Mechanical properties and fire retardancy of LLDPE based compounds with two different phyllosilicates nanofillers

Currently, the physical endurance of fire retardant cable materials classified for nuclear Loss of Coolant Accident has been gradually improved since its first introduction after the fire accident at the Browns Ferry Nuclear Plant in 1975. However, the Fukushima Daiichi disaster showed still insufficient performance of the fire retardancy and radiation resistance of those materials, which certainly did not help the situation during the most critical moments of this major accident. Therefore, the tightening of the requirements for LOCA cables at the currently constructed reactors (e.g. Mochovce NPP, units 3, 4; Novovoronezh NPP II, units 1, 2; Rostov, units 3, 4, etc.) was an obvious and necessary step for the safety improvement. The current state of the art in this field of multicomponent polymer compounds does not provide a completely suitable solution for those requirements providing more realistic conditions

during the loss of coolant accident. Therefore, the motivation of this article is to provide an investigation of mechanical and thermal responses of the core-cable insulation compounds filled by two different phyllosilicates - halloysite nanotubes (HNT) and montmorillonite (MMT) modified by salt with quaternary ammonium different fulfilment (1, 3 and 7 wt%). Mechanical testing showed, that Young Modulus has been improved according of the loading level of HNT. On the contrary, an opposite impact of Montmorillonite on the same parameters have been recorded. Thermogravimetry showed, that testing compound filled by 7 wt% of HNT has a significant suppression of the maximum heat flow by 70 %. It indicates a significant reduction of the maximal intensity of the combustion of the experimental compound. Impact of MMT were behind the expectation. Probably, the thermal degradation of the quaternary ammonium salt and subsequent ignition of created radicals caused a higher maximum of heat flow than the reference pure polymer (LLDPE) containing only stabilization.

S02-583

Kadlec Petr

Comparison analysis of dielectric properties of LLDPE based compounds filled by halloysite nanotubes and montmorillonite

The motivation of this described research is to provide a comparative analysis of dielectric properties two different phyllosilicates of intercalated into the polyolefine based composites. For this investigation, halloysite nanotubes and montmorillonite modified with quaternary ammonium salt have been used as a nanofiller. Developed composites may find application as an insulation materials of power cables. Therefore, the proper investigation of the dielectric influences is crucial. In the first part of the paper, the structural description of used composites with different loading level of nanofiller (1, 3 and 7 wt%) and pure polymer matrix are provided. The major section of this paper is dedicated to the dielectric properties of composites in the DC and AC field. Results of measurement under DC field are


described primarily by values of volume resistivity and polarization indexes. Results of DC analysis were in most of parameters conclusive, because of order of magnitude. the changes in one Nevertheless, polarization and depolarization current characteristics showed а certain improvement in terms of charging/discharging rate, which can indicate an entrapping of electric charge behavior of both nanofillers. Evaluation of composites behaviour in AC field is based on temperature and frequency dependences of dielectric constant and loss factor. These dependences are obtained by Broadband dielectric spectroscopy. Results show that halloysite nanotubes exhibits different dielectric polarization phenomena compared to montmorillonite. In particular, dielectric losses of composites with halloysite nanotubes are lower at high and expected working temperatures than dielectric losses of compound with montmorillonite. Incorporation of halloysite nanotubes into composites causes more significant relaxation polarizations. The experiment confirmed the influence of different chemical structures and incorporation of water molecules in nanofillers on the dielectric properties.

S02-599

Silva Josiane Aparecida da, Pachekoski Wagner Mauricio, Becker Daniela

Influence of Graphene Nanoplatelets on the Properties of Plasticized Poly (lactic acid) Nanocomposites

Poly (lactic acid) (PLA) is biodegradable and compostable polymer with great potential for of non-biodegradable substitution polymers, particularly those that are applied in products with quick shelf live. PLA fulfils the packaging industry's requirements for most of the rigid objects but the polymer needs to be plasticized to be used as soft films. In this paper, the aim was evaluate the effect of plasticizer and graphene dispersion in PLA properties. The plasticizers used were polyethylene glycol (PEG) and dibutyl sebacate (DBS). Plasticizers have been used as diluents in graphene nanoplatelets pre-dispersion via sonication and then this mixture was added in melted PLA.

Thermal properties were evaluated by differential calorimetry and thermogravimetric scanning analysis and water vapor permeability test were carried out by ASTM method E96. The DBS addition decreased glass transition temperature (Tg) and PLA water vapor permeability in approximately 50%. It is also observed PEG addition decreased thermal stability and accelerates PLA The water degradation. graphene nanoplatelets addition improve water vapor barrier properties up to 40%. Besides, an increase in crystallinity degree was also observed with graphene addition.

S02-615

Oliveira Amanda Dantas, Beatrice César Augusto , Passador Fabio Roberto, Pessan Luiz Antonio

Characterization of Nanocomposites for Hydrogen Storage

The use of hydrogen as an energy carrier suitable to replace gasoline and other fossil fuels has been widely discussed as a way to sustainably fuel our civilization. However, hydrogen storage is a major barrier in the establishment of infrastructure for hydrogen technology. The incorporation of nanoparticles to the polymer matrix may be an alternative to obtain materials with promising properties for hydrogen storage. In this work, polyetherimide-based Nanocomposites were prepared using carbon nanotubes doped with sodium alanate (NaAlH4) as filler. The sodium alanate content was fixed at 30 wt% and were studied three carbon nanotubes concentrations: 5, 10 and 20 wt%. The nanocomposites were characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Hydrogen sorption measurements.

S02-643

Mertz Alex, Graham Alan L. , Gelb Lev, Ingber Marc S. , Redondo Antonio

Permeability in Fractal Aggregates: Application to Unstable Colloidal Gels



In unstable colloidal gels, the viscous flow through non-neutrally buoyant colloidal network the determines the initial rate of collapse. The resistance to this flow through the network is characterized by the permeability. The permeability is generally accepted to be a power-law function of volume fraction, where the power is dependent on the fractal dimension of the network. However, in high-volume-fraction gels the "fractal" nature of the gel structure is questionable, and dependence of the permeability on finer structural details of the gel network is as yet unknown. We investigate permeability in model gel structures using coarsegrained numerical simulations. Our approach is based on assigning a "local" permeability to each point in the volume based on geometric considerations, in particular a geometrically defined local pore size and the distance to the nearest point on the gel network. The relationship between permeability and local pore size is established with supplementary finite-element simulations of pressure-driven flow past an array of cylinders. In calculations on model gel structures generated by diffusion-limited cluster aggregation (DLCA), this approach is found to be insensitive to the "coarse" grid size used, and reasonable agreement with available experimental data is obtained over a wide range of gel volume fraction. Subsequent calculations consider the effects of gel connectivity, polydispersity and pore size distribution on permeability, as investigated using model gel networks prepared using several different simulation algorithms.

S02-645

Beatrice Cesar A G, Oliveira Amanda D, Passador Fabio R, Pessan Luiz A

Polymer Nanocomposites for Hydrogen Storage

Hydrogen as an energy source is quite attractive because it prevents air pollution and greenhouse emissions. However, one of the main problems with the utilization of hydrogen is its on-board storage. The purpose of this work was to develop a new hybrid material consisting of a sulfonated polyetherimide matrix with aluminum nanoparticles and faujasite type zeolite. Dilute solutions were first prepared under stirring at room temperature and the solutions were dried under vacuum. The hybrids were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Transmission Electron Microscopy (TEM) and Hydrogen sorption measurements. The addition of aluminum decreased the glass transition temperature of the hybrids when compared to the sulfonated polymer. TEM analysis was performed to identify the morphology of the hybrid material and it was observed that simply physically mixture occurred between polymer matrix and metallic nanoparticles.

S02-648

Pötschke Petra, Gültner Marén , Häußler Liane

Influence of matrix crystallinity on electrical percolation of multiwalled carbon nanotubes in polypropylene

In polymer composites containing carbon nanotubes (CNTs) the influence the matrix crystallinity on electrical percolation and conductivity is under intensive and controversy discussion. Whereas some authors describe the formation of crystalline layers around the nanotubes, which hinders electrical percolation, others report lower percolation threshold in partially crystalline polymers due to the effect of selective localization of fillers inside the amorphous phase. This study aims to contribute to this discussion by using three different polypropylenes (PPs) having different crystallinities. Whereas the industrial PP (HP500N) showed a crystallinity of 49%, two products from ALDRICH named as "amorphous" (PPa) and "isotactic" PP (PPi) had crystallinities of 17% and 52%, respectively. The ALDRICH PPs had comparable molecular weights of 14,000 and 12,000 g/mol and similar melt viscosities at the processing temperature of 180°C, whereas HP500N shows much higher molecular weight and melt viscosity. Multiwalled CNTs Baytubes C70P (1-5 wt%) were added by melt mixing performed using a DSM Xplore 15 ccm microcompounder and plates were compression molded. Dispersion as assessed by light microscopy was the best for HP500N and similar for both



ALDRICH types. Despite similar melt viscosities of PPa and PPi, the electrical percolation was significantly lower in case of PPi (1 wt%) than for PPa (2 wt%) and HP500N (2 wt%). This indicates that a selective localization of CNTs in either the amorphous or the crystalline PP phase can be assumed. The electrical volume resistivity of PPa at 3 wt% loading is about 10E3 Ohm-cm which equals to 1.7 wt% CNT addition in PPi. Using the measured crystallinities, calculations on local CNT contents in the different phases support the assumption of selective localization within the amorphous PP phase.

S02-661

Palanisamy Vickraman

Electrochemical Studies on ceramic fillers X (X= Al2O3, TiO2, SiO2) dispersed LiPF6 based EC/DEC plasticized PVC/PVdF-co-HFP separator by Phase Inversion Technique

PVC/PVdF-co-HFP electrolyte membranes for fixed loading of Al2O3, TiO2 and SiO2 in three polymer blend ratios 1:1, 1:2, and 2:1 labeled respectively as ASA3, ASA4, and ASA5, TSA3, TSA4, and TSA5, and SSA3, SSA4, and SSA5 have been prepared by phase inversion with 0.5 M LiPF6 in EC/DEC (1:1) v/v electrolyte solution and the electrolyte uptakes (EUTs) of membranes are observed. All membranes are subjected to a.c. impedance measurements, and only membranes of higher ionic conductivity (not depending on electrolyte uptake as noted) in each filler ie., ASA4 (3.61 10-4 Scm-1), TSA3 (1.53 10-4 Scm-1), and SSA3 (4.81 10-4 Scm-1) are chosen as separator cum electrolyte for the preparation of 2032 lithium coin cell. The charge/discharge studies are carried out for these samples at C/10 rate in the voltage range 2.8 V – 4.2 V and it is noted that TSA3 sample showed better cycling performance with good capacity retention ie., 50 cycles with 66% capacity retention than ASA4 of 28 cycles with 65% and SSA3 of 5 cycles with 56%. The Coulombic efficiency (CE) calculated for respective cycles have been presented. While comparing the start up (first) cycles of samples, TiO2 based (TSA3) sample showed higher CE 71% than SiO2, (SSA3) 66% and Al2O3, (ASA4) 62%. Key words: PVC/PVdF-coHFP, Phase Inversion, impedance/Charge-Discharge, 2032 coin cell.

S02-662

Kim Minjung, Lee Jong-Hwan, Park Changsin, Park Sangwoo, Nah Changwoon

Preparation and characterization of a conductive and adhesive rubber ink for flexible electrodes

Recently, electronic devices have been focused on the development of functionalities pursuing flexibility and stretchability. The inkjet printing technology has been an attractive tools to fabricate flexible electronics devices. The flexible inks based on polymer liquid containing conductive filler for inkjet printing are appearing in recent literatures. The performance of the flexible electrode is found to be sensitive to the sintering temperature, the pattern design, the adhesive-substrates interaction, and process conditions employed. In this study, a conductive carbon black (Ketjen black) is mixed with liquid rubber by varying the content in the range of 5~25 phr to produce a conductive and adhesive rubber ink. Initially the influence of tensile deformation on the electrical resistance of the fabricated ink was investigated. An electron microscope (FE-SEM) was used to observe the dispersion of the Ketjen black within the rubber matrix. Also, the adhesion strength of the rubber ink was measured. The results indicated that the reduced electrical resistance gradually bv increasing the content of the Ketjen black. However, the adhesive strength of rubber ink was significantly not affected by the filler content. The electrical resistance was found to decrease with tensile deformation owing to the alignment of conductive filler networks.

S02-664

Huang Wen-bin, Zhang Ting-ting, Mao Han-jun, Zhang Nan, Huang Ting, Yang Jing-hui, Wang Yong

Largely improved toughness of immiscible blend achieved by adding chemically modified graphene oxide



Graphene oxides (GOs), which has been extensively investigated as promising precursors for the mass production of graphene, exhibits a unique type of building block with hydrophilic oxidative debris on the edge and hydrophobic domains on the basal plane. Based on this "amphiphilic" feature, GOs can be applied as surfactants and emulsifiers in polymer blends. With the improvement of GO decoration by various functional groups, it is proposed that the GOs could be chemically tailored to be have dual or "amphiphilic" interactions with polymer pairs in order to realize the effective interfacial adhesion of immiscible blends. In this work, polystyrene (PS) grafted graphene oxide (PS-GO) was chemically designed to strengthen interfacial adhesion of immiscible blends polyamide/acrylonitrile-butadiene-styrene

(PA6/ABS). It was found that in the blend composites, the PS–GO located at interface of immiscible blends PA6/ABS and enhanced the interfacial adhesion via the dual interactions with two components, in which one was the electronic stacking interaction between grafted PS on PS–GO and ABS while the other one was the interaction between polar groups on PS–GO and PA6. Finally the mechanical testing showed the elongation at break increased by nearly 400% and the impact strength increased by nearly 200% with only 0.5 wt% PS–GO, indicating the significant toughening effects of PS-GO. This work provides a new strategy to realize the interfacial enhance of immiscible blends.

S02-671

Jang JunYeol, Lee SangHwan, Kang SeokIn, Jeong Byeong-Heon, Hong BoKi, Nah Changwoon

Interfacial adhesion between rubber sheets under different crosslinking level

The interfacial adhesion between two rubber sheets depends not only on the surface energy but also the degree of physical or chemical crosslinking at interface. It is known that autohesion occurring between elastomer sheets of same type depends on interfacial diffusion and molecular interlocking by either physically or chemically. In case of adhesion of two different rubbers crosslinked at different degrees, it is not well known that what type of bonds and what mechanism of fracture are involved at the interfaces. This paper describes the adhesion behaviors of carbon black-filled elastomer sheets based on ethylene-propylene-dienetermonomer (EPDM) and fluoroelastomer (FKM), where the degree of crosslinking was controlled to figure out the type of interactions involved in the adhesion strength. The adhesion strength was measured by the 180,, a peel test. As expected, the adhesive strength Ga was found to increase as the degree of crosslinking of one rubber sheet was controlled to be lower (the degree of crosslinking at the interface will be higher). When the degree of crosslinking of one layer was kept to be minimum (two uncrosslinked rubber sheets), the Ga was approaching to the level of their tearing strength Gc of fully-crosslinked rubber sheet. One interesting observation was that a considerable value of Ga was found even for the fully-crosslinked FKM sheets, which was not observed in the fullycrosslinked EPDM sheets. The abnormal behaviour of FKM sheets seems to responsible for the strong electrostatic attractions between hydrogen and fluorine of the FKM elastomer.

S02-706

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Solid Polymer Electrolyte: Thermal Characteristics, Ion-Conductivity And Permittivity Of Epoxy Oligomer And Lithium Perchlorate Salt

It is a common knowledge that the polyethylene oxide (PEO) has a significant ability to solvate the alkali metal salts, low lattice energy and, as a consequence, the presence of high ionic conductivity (above the melting temperature, when it is not in the crystalline state) in materials on its basis. The choice of the epoxy oligomer of diglycide aliphatic ester of polyethylene glycol (DEG) was caused by its chain structure that is similar to the PEO, but it is amorphous. In the present study the epoxy oligomer DEG, an epoxy-dian resin (ED-20) and the salt of lithium perchlorate LiClO4 were



used for synthesis of ion-conductive epoxy polymer composites. DEG-ED-20-LiClO4 solutions were respectively prepared with content from 0 to 30 phr of lithium perchlorate on 70/50/30 phr of DEG and 30/50/70 phr of ED-20. Polyethylene polyamine hardener (PEPA) was used as a curing agent (10 phr for all cases). Thermal characteristics were studied by DSC. The increase of the content of LiClO4 from 0 to 30 phr leads to the rise of glass transition temperature of the obtained polymers from +7 to +65 °C (1), from +40 to +103 °C (2) and from +89 to +149 °C (3). Composites DEG(70 phr)-ED-20(30 phr) (1), DEG(50 phr)- ED-20(50 phr) (2), DEG(30 phr)- ED-20(70 phr) (3) with LiClO4 contents.Dielectric studies have been carried out using broadband dielectric spectroscopy. It was found that the ionic conductivity increased with the addition of lithium perchlorate salt due to the increase of the charge carrier amount up to an optimum value. The highest ionic conductivity σ' and the permittivity ε' were 5•10-5 S/cm and 2,9 104 (at 103 Hz), respectively, for the composite with 30 phr of LiClO4 in DEG(30 phr) -ED-20(70 phr) system at 200 °C. The perspective of such composites is in the field of electrical and energy devices.

S02-710

Müller Michael Thomas, Krause Beate, Kretzschmar Bernd, Pötschke Petra

Influence of a supplemental filler in twin-screw extruded PP/CNT composites using masterbatch dilution

To increase the electrical conductivity of polymer composites by a minimum filler amount, carbon nanotubes (CNTs) are a good choice as due to their high aspect ratio relative low percolation thresholds can be achieved. An excellent state of CNT dispersion is an important prerequisite to enhance the composite properties. However the distribution and dispersion of the as-produced agglomerated and entangled CNT powders during the melt processing is challenging. If the state of CNT dispersion is insufficient, the full potential, like the electrical conductivity and mechanical properties, of the CNT material is not fully accessible. During the well-known masterbatch dilution process, the CNT agglomerates are subjected to shearing twice, whereby not in all cases a better dispersion is observed as compared to direct CNT incorporation. To increase the probability to obtain polymer composites free of agglomerates we used a second filler to apply further rupture and erosion interactions onto the primary CNT agglomerates. In this investigation electrically conductive composites containing commercially available multiwalled carbon nanotubes (MWCNT) with electrical nonconductive talc or conductive carbon black were prepared using a twin-screw extruder ZE25 (Berstorff). The resulting electrical and mechanical properties were measured on injection molded parts. The evaluation indicates that the presence of both secondary nanofillers, talc or carbon black, affected the formation of the percolating MWCNT network and resulted in better nanotube macro dispersion. As a result the electrical percolation threshold is decreased to lower MWCNT contents using secondary fillers. In comparison to the direct CNT feeding method the masterbatch dilution showed а higher threshold. percolation Additionally, the improvement in dispersion was not reflected in the mechanical properties. Modulus and stress values increase with MWCNT, carbon black and talc addition, but not in a synergistic manner.

S02-74

Becker Daniela, Bohn Samara, Balzer Palova Santos

Influence Of Plasticizer And Dispersion Methods On The Properties Of Poly(Vinyl Chloride) And Clay Nanocomposites

Poly (vinyl chloride) (PVC) is one of the most employed polymers in the world and it is interesting to change some of its properties to broaden its usage. In this paper we aim to evaluate the effect of the plasticizer type and the mixture method of clay dispersion in the PVC matrix. It was employed three plasticizers: dyoctil adipate (DOA), dioctyl phthalate (DOP) and a green plasticizer (poly- ε -caprolactone – PCL). Besides, it was also evaluated the effect of clay pre-dispersion in plasticizer using two mixture methods: sonication

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and mechanical mixture. It was characterized the morphology by transmition electronic microscopy and mechanical properties by stress-strain test. It was observed a heterogenic dispersion of the clay in PVC matrix and different plasticization regions. However, the pre-dispersion decreased clay agglomerates size and intercalated/expholiated regions were also observed. The clay addition increased 5% and 10% on Young's modulus for PVC/DOP with clay dispersion using sonication methods and PVC/PCL with clay dispersion using mechanic mixture, respectively. The DOA addition leads to a decrease in Young's modulus. According to these results, it can be reasoned that clay predispersion in plasticizer may facilitate intercalation but does not eliminate all of clay agglomerates, and the type of plasticizer influences on mechanical properties of plasticized PVC/clay.

S02-741

Mohammadi Seyedeh Raziyeh, Tabatabaei Seyed H, Ajji Abdellah

Polymer nanocomposite sealants for easy to open packaging: effect of surface chemistry of nanoclay

Today in food packaging industry, polymer composites are extensively exploited to produce cohesive peelable sealants for easy to open packages. Using nanoparticles for easy opening packaging is a quite new topic and very few studies have been conducted on this issue. Due to the layered structure and high aspect ratio, nanoclays show considerable effects on the rheological, thermal, mechanical and barrier properties of homopolymers. In this study, nanocomposites of low density polyethylene (LDPE) and different kinds of nanoclay in term of surface modification with 6 weight % of nanoclay were produced with twin screw extruder and then were filmed. The films were sealed using a heat sealer machine and then the peel behavior of the heat sealed samples were analysed using a tensile tester machine. X-Ray diffraction (XRD) was run on the films to study the level of dispersion of the nanoclay in the nanocomposites. Differential scanning calorimetry (DSC) was used to study the effect of nanoparticles on the melt temperature and crystallinity of the

films and consequently on their seal and peel behavior. According to the results, heat seal initiation temperature of all the nanocomposite sealants reduced by incorporation of nanoclay in seal area compared to pure LDPE sealant. The nanocomposite made of non-modified nanoclay Na+ showed tactoid dispersion and its peel behaviour is similar to the sealant made with pure LDPE. Surface modified nanoclay with higher initial d-spacing resulted in better dispersion and consequently lower peel force as well as broader peelable heat seal temperature window. It is concluded that the seal and peel behavior of the nanocomposite sealants significantly are affected by dispersion and distribution of the nanoparticles in polymer matrix.

S02-748

SERGHEI Anatoli, BOITEUX Gisèle, SAMET Mariem, Kallel Ali

Electrical and dielectric properties of composite materials: the role of morphology, volume fraction, form factor, orientation, presence of interphases and gradients of local properties.

A general route to adjust the electrical performance of polymeric materials represents the composite approach, when fillers of different morphologies, sizes and electrical properties are embedded into a The resulting macroscopic polymer matrix. properties of the composite material depend on the volume fraction and the spatial distribution of the fillers as well as on their interaction with the polymeric material. The current contribution aims to develop a complete theoretical description of the electrical and dielectric properties of multiphase composite materials in systematic dependence on volume fraction, morphology, form factor, orientation, presence interphases and gradients of local properties. Three scientific challenges are addressed: (a) Understanding the impact of internal interfaces and interphases on the dielectric response of composite materials; (b) Detailed quantitative analysis of the impact of heterogeneity on the dependence of existing spectral molecular relaxation processes; (c) To develop and propose a criterion which enables one to distinguish, in the



case heterogeneous materials, true relaxation processes from dielectric dispersions caused by the phenomenon of interfacial polarization.

S02-760

Bajjou O., MONGWAKETS N., KHENFOUCH M. , BAÏTOUL M. , Mothudi B., Dhlamini M. , LEKALA M. , MAAZA M.

PH and concentration effect on the optical absorption properties of porphyrin nanorods functionalized graphene oxide

Graphene oxide (FGO) decorated with nanostructured porphyrin (PN) was synthesized and the interfacial interaction between these two components were investigated by using Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Raman scattering, Fourier transform infrared (FT-IR), X-ray, and Uv-visible. SEM and TEM showed good dispersion of GO and PN. FT- IR and Raman results revealed a π - π intermolecular confirming interaction the energy/charge transfer. Moreover, X-ray diffraction study confirmed the intercalation of PN in GO and their disaggregation. The Uv-visible results showed an important interaction between GO and porphyrin nanorods under pH values and different concentrations resulting an effect on the optical absorption of GO-PN. The findings presented here are important to achieve the functionalization of graphene oxide with PN for various optoelectronic applications

S02-781

L. MRAH , R. Meghabar , M. Belbachir

Poly styrene Nanocomposites: Characterization , Investigation of Mechanical Properties

A reactive cationic surfactant cetyltrimethylammonium bromide (CTAB) was synthesized for intercalation of montmorillonite Mmt. a Maghnite type of clay. The pristine montmorillonite (Mmt) was obtained from Algerian plant with a cation exchange Organophilic Mmt was prepared by ion exchange between Na+ ions in the clay. CTAB-intercalated Mmt particles were

easily dispersed and swollen in styrene monomer, poly(styrene) / Mmt-CTAB nanocomposites were synthesized via in situ polymerization, in-situ polymerization, this method is based on the swelling of the silicate layers with the liquid polymer. The polymer composites were characterized using different techniques such as Xray diffraction (XRD), The results were showed that, the basal space of the silicate layer increased, as determined by XRD, from 12.79 to 32.603 Å and transmission electron microscopy TEM revealed that the modified montmorillonite layers were uniformly dispersed and exfoliated in the styrene matrix for low levels of clay. In our current research, we continue this research and study infrared spectrophotometery (IR), differentialscanning calorimetery (DSC), and electron microscope (MEB) balayage thermal (TGA), gravimetric analysis force atomic and tensile measurements microscopy (AFM) Keywords: cetyltrimethylammonium bromide, nanocomposite, force atomic microscopy, Organophilic

S02-786

Jeong Eun Jea , Dao Trung Dung , Mo Jeong Han

Graphene prepared by thermal reductionexfoliation of graphite oxide: Effect of raw graphite particle size on the properties of graphite oxide and grapheme

We report the effect of raw graphite size on the properties of graphite oxide and graphene prepared by thermal reduction-exfoliation of graphite oxide. Transmission electron microscope analysis shows that the lateral size of graphene becomes smaller when smaller size graphite is used. X-ray diffraction analysis confirms that graphite with smaller size is more effectively oxidized, resulting in a more effective subsequent exfoliation of the obtained graphite oxide toward graphene. X-ray photoelectron spectroscopy demonstrates that reduction of the graphite oxide derived from smaller size graphite into graphene is more efficient. However, Raman analysis suggests that the average size of the in-plane sp2-carbon domains on graphene is smaller when smaller size graphite



is used. The enhanced reduction degree and the reduced size of sp2-carbon domains contribute contradictively to the electrical conductivity of graphene when the particle size of raw graphite reduces. Keywords: A. Nanostructures A. Surfaces D. Defects D. Electrical properties D. Electronic structure

S02-795

Bouacherine B. , Iddou A. , Benhammadi S. , de Ménorval L. C.

Adsorption Of Lead (Ii) In Liquid-Solid Interfaces Of Natural Hydroxiapatite. A Batch Study

The removal of lead from aqueous solutions was studied using the liquid-solid extraction method. The solid used is the crude phosphocalcichydroxapatite [Ca10(PO4)6(OH)2] noted (HAPc), and the treated with a solution of lactic acid (HAPal). The extraction results showed the influence of parameters: the initial concentration of Pb(II) and the temperature of the suspensions. The application of Langmuir adsorption model showed maximum adsorption capacities of each material (HAPc and HAPal). The One specific to hydroxiapatite treated with a solution of lactic acid, was the most important (41.84mg/g). Isotherms established at different temperatures showed that this parameter affects adsorption. The best results were obtained for a temperature of 25°C compared with those recorded at 50°C. Finally, the results of this study allow us to note that the hydroxiapatite material can be a good extractant solid, for heavy metals, especially when it is modified with lactic acid. Key words: Pb(II), hydroxiapatite, chemical modification, lactic acid, adsorption. References: "K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Separation and Purification Technology.44 (2005) 53." "C. Bleuel, D. Wesenberg, K. Sutter, J. Miersch, B. Braha, F. Bärlocher, G.J. Krauss, Science of the Total Environment. 345 (2005) 13." "K. Kalbitz, R. Wennrich, The Science of the Total Environment. 27." 209 (1998) "S. Saxena, S.F. D'Souza, Environment International. 32 (2006) 199"



S03- Extrusion and Extrusion Processes

Keynotes

S03-39

Carrot Christian, Raveyre Claude, Monchatre Benjamin

Experimental measurements of pressure, temperature and residence time in a co-kneader: effect of melt viscosity.

The effect of the melt viscosity on the residence time distribution (RTD), pressures and temperatures in a modular co-kneader was investigated during the extrusion polypropylene samples, by varying the regulation temperature of the kneader or the molecular weight of the polymer. The co-kneader is a special modular single-screw extruder with simultaneous rotating and axial movements of the screw, with pins on the barrel fitting threads of the screw, commonly named reciprocating single-screw extruder. The RTD was obtained using a colored tracer. Material temperature was measured by sensors integrated in the pins of the barrel. Pressure was measured at the die. Experiments with four PP samples were carried out at various feed rates. One PP was selected for experiments varying feed rates and screw speeds. Both series of experimental results consistently show an increase of the temperature of the melt and of the pressure at the die when the viscosity of the melt increases. Increasing the feed rate increases the die pressure but reduces the temperature, while increasing screw speed produces self-heating. The experimental RTD remains the same at a given feed rate and screw speed, regardless of the viscosity of the material induced either by changing the barrel temperature or the molecular weight distribution of the polymer.

S03-98

IBAR Jean Pierre

40 Years Of Vibration Assisted Polymer Processing: Understanding Polymer Physics As A Source Of Innovations

In 1973, in the basement of an MIT laboratory started a journey which led to many innovations in the field of processing of plastics, using vibration to modify and enhance the properties of the molded products. First there was vibrated compression molding, which was described as Rheo-cooling, a method to simulate the effect of fast cooling rates across thick samples. Then came Rheomolding, pulsating melts as they were injected into molds, which was initially conceived to decrease melt viscosity and modify the filling flow pattern to obtain orientation or eliminate birefringence (in compact disks). Finally, the vibration was added to an extruder, cross-laterally to the flow direction, more like an added oscillation combined with pressure flow and extensional flow. This was called Rheo-Fluidification, an add-on to extruders capable of extruding melts at 50 to 100 oC below the normal processing temperature, a feature which appeared to be related to a decrease of viscosity due to "disentanglement". In this review, we also discuss the underlying source of inspiration to these innovations, the quest for understanding the physics of interactions between the polymer chains under conditions of non-linear flow deformation. This quest led to question our understanding of entanglements and may lead to new innovations in the way plastics can be recycled and used as mechanical batteries, storing energy for future use.

Oral

S03-131

Wilczyński Krzysztof J., Nastaj Andrzej, Lewandowski Adrian , Wilczyński Krzysztof

Experimental and Theoretical Study on Starve Fed Single Screw Extrusion of Polymer Blends

An extensive experimental study has been performed for starve fed single screw extrusion of polymer blends. Several materials have been used in the study: PP/PS, PP/PMMA, and HDPE/PS blends of composition of 85%/15%. "Screw Pulling-



out Technique" has been used to study the melting mechanism and flow in the machine. CSM melting mechanism (contiguous solids melting) has been observed for flood fed extrusion with an obvious presence of minor component inclusions. This mechanism has not been observed for starve fed extrusion. A new melting mechanism for starve fed extrusion of polymer blends has been proposed. This includes conductive melting in a starve fed region, and dispersed melting in a fully filled region, and takes into account the solid and molten phases of major and minor components. A new computation approach has been proposed for modeling of the polyblend melting process. Moreover, forward/backward scheme а of computation has been applied for global modeling of the extrusion process of polymer blends. A new global SSEM_SF computer model has been applied for simulation of experimental runs.

S03-162

Zitzenbacher Gernot, Längauer Manuel, Huang Zefeng

Influence of Temperature on the Contact Angle of Polymer Melts on Tool Surfaces

The wettability of tool materials used for polymer processing is often determined at room temperature. However, it has to be considered that polymeric materials are processed at higher temperatures. Contact angle measurements of polymer melts on tool materials at different temperatures were performed in this work using a KRUESS Drop Shape Analyzer DSA30S with a high temperature chamber. The contact angle of a polypropylene (PP), a high density polyethylene (HDPE), a polymethylmethacrylate (PMMA) and a polyamide 6.6 (PA 6.6) melt was determined on different solid samples at varied close-to-process temperatures. The solid samples were polished and ground steel as well as TiAlN-, TiN-, DLC-, CrNand PTFE-coated steel. The polymer sample was placed on the hot tool material sample in the high temperature chamber under a nitrogen gas atmosphere. After melting of the polymer, the drop shape was recorded dependent on time using a camera system. PP, HDPE and PMMA show a decrease in the contact angle with time. PA 6

exhibits a static contact angle. The results show a linear decrease in the contact angle of the polymer melts with higher temperature on the different tool materials. The surface tension of a liquid decreases linearly with higher temperature according to the equation of Eötvös. Young's equation describes the contact angle dependent on the surface energy of the solid, the surface energy between the liquid and the solid and the surface tension of the liquid. The decrease in the contact angle of the polymer melts can be explained by combining both equations. Dependent on the polymeric material and the tool surface, the intensity of the temperature influence on the contact angle is different. There is a steeper decrease in the contact angle of the polymer melts on steel and TiN compared to PTFE. This can be related to the lower surface energy of PTFE compared to the other tool materials.

S06-179

Eggenreich Karin, Schrank Simone, Koscher Gerold, Roblegg Eva, Laske Stephan, Khinast Johannes

Influence of Process Route on the Property Profile of Polymer Based Intravaginal Drug Delivery Systems

Intravaginal drug delivery systems (intravaginal rings; IVRs) are designed to release one or more active pharmaceutical ingredients (APIs) to the vaginal tract and finally into the systemic circulation over extended time periods. From the technological point of view, IVRs are classified into matrix and reservoir type IVRs whereat the majority of marketed IVRs is matrix systems based on silicone, one IVR, a reservoir based system, comprises two types of EVA co-polymer. In matrix systems, the API is homogeneously dispersed throughout the polymer. A route to produce matrix IVRs is hot melt extrusion to obtain drug-loaded polymer intermediates, which are then injection molded to yield the ring shape. The drug release rate is governed by drug diffusion through the polymer. The release rate, following Higuchi's law, is proportional to the square root of time and is altered by modifications in the surface area, the drug loading and/or the API chemistry. In reservoir system, the polymer contains core the



homogeneously dispersed API and is surrounded by drug-free skin. The production route of reservoir systems includes co-extrusion of the layered structure followed by a joining process to obtain the ring. The drug release rate is determined by diffusion through the skin and remains constant (= zero order release). It can be altered by modifications of the skin thickness and/or the API chemistry. Regarding the mechanical properties, the ring is required to be flexible. Prior/during insertion, the IVR has to be easily compressed, followed by fast recovery to remain in the vaginal cavity without causing damage. Yet, the junction deriving from ring closure needs to be strong enough to prevent ring opening. IVR's mechanical properties can be affected via its formulation. In this study, the impact of process parameters, used polymer (polymer crystallinity) and formulation on mechanical properties of EVA based rings was investigated.

S03-226

Bironeau Adrien, Guinault Alain, Regnier Gilles, Miquelard-Garnier Guillaume, Sollogoub Cyrille

Existence of a critical thickness in coextruded multilayer films

Coextrusion through a series of multiplying die elements enables the production of polymeric films containing thousands of layers of alternating polymers with individual layer thicknesses below 100 nm [1]. Previous studies have shown improved macroscopic properties (especially permeability) related to the nanoconfinement of the polymers within the layers [2], [3]. However, when a lower limit in thickness is reached, breaks and instabilities during process may occur and thus affect integrity and homogeneity of layers. In this study, films with 1025 to more than 8000 alternating layers of PMMA and PS, mass ratio of 50/50, 90/10 and 95/5 wt% and different draw ratios were fabricated in order to identify the materials and processing parameters responsible for these instabilities. Films were characterized by atomic force microscopy (AFM) and a statistical analysis was used to determine the distribution in layer thicknesses and the stability of layers. Results demonstrate the existence of a

critical thickness around 20 nm for the PS/PMMA multilayer system, below which the layers break up. This critical thickness is reached whatever the processing parameters studied, suggesting it might be a physical limit due to macromolecular parameters. This work, through ISOCEL project, is supported by the French government agency ADEME and Région Aquitaine. [1] W. J. Schrenk, 3,884,606, 20-May-1975 [2] M. Ponting, A. Hiltner, E. Baer, Macromol. Symp. 2010, 294, 19-32 [3] H. Wang, J. K. Keum, A. Hiltner, E. Baer, Macromolecules 2009, 42, 7055-7066

S03-284

Ndao Makha, Domejean Hugo , Valtier Michel, Allal Ahmed

How to postpone the Gross Melt Fracture in linear Polymer melt extrusion

Extrusion is one of the main processes in the thermoplastic and rubber industry. However, various defects and flow instabilities occur not only to limit the production rates but also to influence the appearance and the quality of polymer extrudate products. A melt instability called gross melt fracture is often observed when the extrusion rate is increased beyond a critical value. This instability is characterized by a helical or periodic distortion evolving toward chaotic distortion. Because gross melt fracture limits the production rate, much attention has been devoted to predicting when it will occur. However, there is still no general understanding of the origin of this phenomenon. In this work, we focused on two series of polystyrene (monodisperse IP<1.5 and polydisperse IP > 2) to understand the physical mechanisms at the origin of this phenomenon. The studies of the critical shear rate for the onset of gross melt fracture show that this defect appears when the residence time of the melt in the die is lower than its reptation time for the monodisperse polymers or the relaxation time of the tube caused by constraint release for the polydisperse ones. This result shows the importance of the shape of the molecular weight distribution and more precisely its low molecular weight tail on the onset of the



gross melt fracture defect. That gives a tool to postpone or to eliminate this defect.

S03-422

Luger Hans-Jürgen, Marschik Christian, Gillhofer René , Grubauer Markus, Miethlinger Jürgen

Experimental Investigation of the Mixing Quality of High-Performance Screws

Besides achieving high outputs, the melt quality is a crucial factor of efficient polymer processing using screw extruders. On the one hand, it is desired to achieve a homogenous melt, when it comes to the incorporation of fillers as carbon-black. On the other hand, melt temperature non-uniformities should be minimized, since melt temperature variation results in problems like non-uniform wall thickness and warpage. Over the decades several high-performance single screw designs, as double or triple flighted screws, various barrier screws, multi-stage screws and screws with mixing elements have been developed with the goal of improving mixing and melting capabilities. The aim of the present study is to assess and compare the mixing performance of different barrier and energy-transfer screws with respect to their throughput/pressure-behavior. The used extruder had a 34 length-to-diameter (L/D) ratio and a 35 mm barrel with a grooved inlet section. For the assessment of the temperature homogeneity a measurement cross was used. Furthermore, the study involved the gray-value analysis of extruded polymers mixed with carbon-black masterbatch for the evaluation of the transversal mixing behavior. longitudinal mixing performance The was investigated via fluorescence spectroscopy.

S03-431

Miethlinger Jürgen, Pachner Sophie, Marschik Christian, Luger Hans-Jürgen, Löw-Baselli Bernhard

Current Achievements in Experimental and Computational Modeling of Screw Extrusion

For decades screw extrusion is the most important continuous process step of polymer processing. Single and multi-screw extruders are the heart of many extrusion plants. Due to the economic importance and the complex transport phenomena in plasticating extruders screw extrusion is subject of current research. This paper deals with current achievements in experimental and computational modeling of single and twin screw plasticating extrusion. COMPUTATIONAL MODELING For computational modeling following advanced methods were used: DEM (discrete element modeling) LIGGGHTS® for solid conveying, network theory for phase transition resp. melting for barrier screw types and a generalized analytic equation for the pressure-throughput behaviour, developed by using an evolutionary heuristic optimization algorithm, for melt conveying. Additionally a parameterized creation of twin screw geometry for counter as well as co-rotating extruders by using analytic equations and triangulation is used for CFD simulation in order to reduce the most time consuming step of CFD simulation (compared with the simulation and pre-processing. post-processing step), the EXPERIMENTAL MODELING Not only for validation, but also to deepen the knowledge regarding the transport phenomena in plasticating extruders and to study the performance in terms of productivity and quality computational modeling was supplemented with procedural instructions for experimental modeling including the determination of pressure-throughput behaviour, energy and thermal monitoring by using temperature gradient sensors, axial pressure profile inside the barrel, radial temperature distribution inside the melt tube after the extruder screw, residence time distribution and self-cleaning time by using fluorescence spectroscopy, mixing performance by applying grey value analysis and change of molar mass distribution.

S03-452

Kneidinger Christian, Schuschnigg Stefan, Längauer Manuel, Zitzenbacher Gernot, Miethlinger Jürgen

Solids Conveying in Lab Scale Smooth Barrel Single Screw Extruders Regarding the Material Parameters` Dependence on Pressure, Temperature and Velocity

This work deals with the modeling of the solids conveying zone of a smooth barrel single screw Extruder (SSE) regarding two different shaped polypropylene homopolymer bulk solids (spheroidal and cylindrical) and compares the results to experiments performed at a lab scale SSE. The bulk density and the pressure anisotropy coefficient were measured in dependence on pressure and temperature utilizing a special measuring device. The external coefficient of friction was measured in dependence on pressure, temperature and the sliding velocity using a unique tribometer. In this work a segmented model of the solids conveying zone of a smooth barrel SSE is utilized in combination with a damped Newtonian solver to calculate the pressure rise of the single elements at a given solids conveying rate which is known from practical extrusion experiments. Furthermore the interface- temperature between the polymeric bulk and the barrel of the extruder is calculated. The bulk density and the pressure anisotropy coefficient are applied as functions of temperature and pressure, the coefficient of friction additionally depends on the frictional velocity. Numerous iterations are needed to gain a convergent result for every single segment. The results obtained by the different approaches of Darnell and Mol, Schneider, Schöppner or Hyun et al. [1] are compared to values measured at a lab scale single screw extruder. In the extrusion experiments the cylindrical shaped bulk solids showed a higher throughput and a faster pressure build-up development than the spherical shaped bulk solids. The determination of the bulk solid properties showed rather low differences of the bulk density, the external coefficient of friction and the pressure anisotropy coefficient. This work shows the results of a segmented calculation of the solids conveying zone regarding the material parameters' dependence on pressure, temperature and velocity and the differences to a simplified calculation considering averaged values. [1] J. L. White, H. Potente: SCREW EXTRUSION SCIENCE AND TECHNIOLOGY, Hanser Publishers, Munich, 2002

S03-488

PPS[®]32

Carneiro O. S., Rajkumar A., Ferrás L. L., Fernandes C., Becker M., Nóbrega J. M.

Flow balancing in profile extrusion dies: a novel simplified methodology

One of the major challenges of the profile extrusion process is to obtain a homogeneous melt flow distribution at the die outlet, i.e., a balanced flow. The geometric complexity of the profiles to be extruded, along with the rheological properties of the polymer melt and their dependence on shear rate and temperature, complicates the die design process. In order to obtain an adequate flow distribution at the die exit, the flow channel geometry must have a specific design. In most cases this encompasses an experimental trial-and-error procedure, which consumes a huge amount of time and resources, and relies utterly on the designer's experience. The large number of works on computer aided die design clearly indicates the ability to accurately predict and adjust the fluid flow distribution using numerical tools. These tools are a better alternative for the usual experimental trial-and-error approach, with the advantage of reducing the cost and resources involved during the required trials. However, there is a limited number of industrial die designers that can have access to numerical tools. Considering these facts, it is of significant importance to provide those with simplified die design guidelines. In this work, numerical modelling tools were employed to devise analytical equations to balance the flow in T and L shaped extrusion dies. The two modular geometries, T and L, where chosen since the majority of the complex profiles can be built through their combination. The above referred equations establish relationships between the parallel zone lengths and the thicknesses of the different sections composing these dies, with a view to obtain a balanced flow distribution. A design methodology was proposed for complex geometry dies (composed by several L and T modules) to guide the die designer through a series of steps/calculations needed to define all the parallel zones lengths. The usefulness of the proposed methodology is illustrated in a number of case studies.

S03-527

Sanchez-Olivares Guadalupe, Sanchez-Solis Antonio, Calderas Fausto, Medina-Torres Luis, Manero Octavio

A novel extrusion process using a special static mixer die and on-line ultrasound simultaneously

A novel extrusion process was used in order to obtain flame retardant polymer nanocomposites. Ultrasonic waves were applied on-line during single screw extrusion process coupled to a special static mixer die, which promotes extensional flow. The effect of on-line ultrasound application on two polymer matrices (high density polyethylene, HDPE and polypropylene PP), halogen free flame retardant additives and an organo-clay was thoroughly studied. For each polymer matrix, different halogen free flame retardant additives were employed. The morphology, thermal stability, fire behavior by UL94, as well as mechanical and rheological properties were investigated. Morphological studies demonstrated that the novel extrusion process is able to reduce the size of nonhalogen flame retardant additive particles and improves their dispersion and distribution in both polymer matrices, with respect to traditional extrusion processes (twin screw). This effect had a great impact on the flame retardant and mechanical properties of the materials. According to UL94 results the materials obtained with ultrasound system reached V2 classification. The addition of an organo-clay at specific content and the use of ultrasound system demonstrated that it is possible to reach an optimal V0 classification and to reduce the flame retardant additive content greatly, -40% in the case of HDPE and -30% in PP, with respect to twin screw extrusion process. Mechanical properties, Izod impact resistance, tensile strength, strain at break and tenacity were greatly increased. Rheology test performed in simple shear and linear oscillatory shear flow modes evidenced the enhanced particle dispersion and finer particle morphology which produced larger values of the moduli and deviations from the semicircular shape observed in the Cole-Cole diagram as compared to the system with no ultrasound application. Keywords: Ultrasound system, static mixer die, flame retardant

S03-543

Miethlinger Jürgen, Marschik Christian

A Novel Grooved Single Screw Extruder Design

Grooved barrel single screw extruders have been known for many years and are widely used in industry especially for high molecular weight thermoplastics respectively for the production of pipes, blown films or blow-molded parts. The grooves are classical designed with a tapered profile with a length of three to five times the screw diameter. In case of the so called HELIBAR® system, invented by Grünschloß, the inner wall of the feeding and the melting section are provided with tapered grooves. In case of the invented single screw extruder the grooves are not designed with a tapered profile. The diameter of the barrel at the end of the grooves corresponds to the diameter before the end of the grooves plus approx. twice times the groove depth. At the same time the outside screw diameter after the grooves equals the barrel inside diameter taking a necessary clearance into account. A larger volume at the end of the grooves is a result of this construction, and thus the risk of a pressure peak is reduced and the conveying capacity is increased. Due to the extended grooves without compression the mass throughput fraction of the grooves as well as the total mass throughput can be increased. Melt pumping of the melt conveying zone is more efficient due to the increased screw diameter after the grooves. This enables also the usage of sophisticated and frequently pressure consuming geometries like wave or energy transfer concepts. Low melt temperatures and high mass throughputs can be achieved with barrier screw concepts as a consequence of an observed melt cooling effect based on a solid conveying mechanism from the extended grooves into the melt channel. In summary the new grooved single screw extruder concept offers significant benefits not only compared to smoothed barrel extruders, but also towards classical grooved feed single screw extruders in terms of mass throughput, pressure build up capacity and melt temperature.

S03-549



Bobzin Kirsten, Brögelmann Tobias, Kruppe Nathan C., Naderi Mona

Synthesis and Tribological Investigation of PVD Hard Coatings deposited via Hybrid dcMS/HPPMS for Application in Plastics Processing

In the plastics processing industry extrusion process is a widely used manufacturing process. One of the most important requirements for an extruder is the highest possible mass flow rate, low wear on the extruder screw, a corrosion resistance towards plastics and the provision of a high melt quality throughout the lifetime of an extruder. In order to influence the interactions between the plastic melt and extruder surface, the extrusion tools can be modified using innovative coating technology such as physical vapor deposition (PVD). In this regard, direct current magnetron (dcMS) and power sputtering high pulse magnetron sputtering (HPPMS) hybrid technology offers many advantages, e.g. high ion flux, dense coating morphology, smooth surfaces and uniform coating thickness distribution on complex geometry components. Within the scope of this paper, ternary and quaternary chromium based nitride (Cr,Al)N and oxynitride (Cr,Al)ON PVD hard coatings, were used as protective coatings due to their mechanical, chemical and tribological properties to reduce wear and adhesion forces between extrusion tools and plastic. These hard coatings were deposited by means of hybrid dcMS/HPPMS technology in an industrial scale coating unit under oxygen gas flow variation (F(O2) = 25 sccm and F(O2) = 50 sccm) on plasma nitrided steel 34CrAlNi7-10 (1.8550). The influence of the oxygen content on the coatings morphology and its chemical composition as well as the tribological and the mechanical properties characterized. An industrial were plastic Makrolon® ET3113, PC, was considered for tribological investigations. Adhesion behavior of molten PC (corresponding the processing temperature) on PVD hard coatings was analyzed by high temperature contact angle measurements. Wear tests were performed by using pin-on-disctribometer measurements at room temperature T = 23 °C and higher temperature T = 150 °C against solid PC. A reduction in the adhesion tendency and

friction coefficients through the coating in comparison to the uncoated substrate was observed. Keywords: Extrusion, extruder screw, plastics industry, polycarbonate, PVD, hybrid dcMS/HPPMS, Wear, Tribology.

S03-55

Meilwes Peter, Schöppner Volker

Development of a method for a realistically and reproducible contamination of polymer melt filters

In the field of polymer processing, the extrusion is one of the most common processing methods. Not only in the processing of recycled materials, also when using virgin polymers there can be contaminations during the storage or processing of the material. This may adversely affect the melt quality and by this also the quality of the final product. Examples for extrusion possible contaminations are metal particles which are caused by wear and tear of the extruder, or degradation products of the processed material itself. As a result of increasing demands on the quality of extrusion products, especially in the field of fiber and film extrusion, filtration of polymer melts is widely used and state of the art today. To remove unwanted debris out of the melt, different metal filter media is used. Some examples for typical filter media are different kinds of wire mesh, filters out of nonwoven metal fibers or sintered metal powder discs. Using this filter media, it is possible to remove foreign particles like solid particles, as well as soft components, the so called "gels" from the melt. This ensures a high quality extrusion result. In order to compare the filtering effect of different filter media and to assess the contamination and selective filtration it is necessary to develop a possibility for reproducibly rapid contamination of filter materials. In this work this should be elaborated as part of the PET processing. For this, a real filter contamination is analyzed. After this a definition of an adequate substitute dirt is effected. The focus is both on solid particles, as well as on gel contamination. With this it is possible to generate realistic and reproducible filter soiling so that pressure rise curves can be



generated in order to compare the behavior of different filter media in the extrusion process.

S03-668

Guo Shaoyun, Shen Jiabin

Facile route to fabricate polymeric materials with alternating multilayer structure: toward high performances

Multilayer assembly is regarded as one of preferred structures in the nature and has been widely mimicked in the past decades. As a kind of efficient processing technology, layer-multiplying coextrusion has been applied to fabricate polymeric materials with alternating multilayer structure. By combining an assembly of layer-multiplying elements with a conventional coextrusion block, the number of layers can be multiplied conveniently followed by the enrichment of layer interfaces. Studies have found that the distinct structure endowed the final products with unique performances. Taking the carbon black (CB)-filled system for instance, the confined layer space allowed for a more compact connection between CB particles. Thus, the multilayer composites were substantiated to have higher electrical conductivity and microwave absorbing efficiency than the conventional ones where the conducting particles were randomly distributed in the polymeric matrix. Moreover, the layer interfaces in the multilayer system were also effective to inhibit the propagation of cracks in the stretching process, so that a larger elongation was achieved before fracturing, which provided a potential route to fabricate electrical materials with optimal mechanical properties

S03-685

Kretz Richard, Thummert Michael

Turnkey Extrusion Lines for Highly-Filled Compounds: Compounding of CaCo3 Formulations Setting up extrusion lines for highly-filly compounds is a very challenging task since the raw materials - and in particular CaCo3 - oftentimes have differing quality aspects and material characteristics. The various raw materials, setup of the line components and parameters of the extrusion process itself open up a wide field of options - not just in terms of improving the final product, but in the worst case also in terms of making things worse. Thus the extrusion process is affected by many factors that need to be taken into account for achieving optimum product quality and a stable process of the extrusion line. With many years of experience in compounding highly-filled compounds, the paper offers a wide repository of good clues and ideas how to optimize extrusion lines and what aspects have to be taken into consideration to achieve an optimum layout of the extrusion line for such demanding compounding tasks.

S03-702

Neubert Benedikt Paul August, Wortberg Johannes Karl

Numerical Investigation of Geometrical Changes in the Cooling Configuration for Improving the Output of High Capacity Blown Film Extrusion Lines

One of the most important production processes for manufacturing plastic films is the blown film extrusion. The conventional way to improve the output of a production line can be achieved by a substitution or a modification of the limiting air respectively cooling ring, of the cooling configuration. In order to verify an output intensification, typically the trial and error method is being used. For reducing the experimental costs, a numerical procedure called Process Model has been developed for simulating the formation of the bubble with regard to changing process conditions and rheological behavior. The applicability of the Process Model has been proven for small production lines with a maximum output of approximately 100 kg/h (LDPE). According to industrial concerns the focus lies on improving the output rate of high capacity blown film extrusion lines. For accomplishing this strategical and



economic goal, it is fundamental to take a closer look at the thermal and fluid mechanical phenomena that occur. By adapting the numerical simulation procedure as well as the material model, the Process Model is now capable in simulating the blown film process for industrial extrusion lines. In this paper, the simulation results of the application of the Process Model for an industrial blown film extrusion line including an internal bubble cooling system will be presented. Furthermore, the influences of small modifications and optimizations of the cooling configuration and the implementation of flow guiding elements are numerically analyzed in detail. The resulting thermal and fluid mechanical phenomena will be discussed.

S03-707

Kajiwara Toshihisa, Nakayama Yasuya, Takemitsu Hiroki, Esaki Satoshi, Takeuchi Takahide, KImura Koichi, Tomiyama Hideki

Melt-Mixing by Pitched-Tip Kneading Disks in a Twin-Screw Extruder- Experimental Verification

Twin screw extruders are widely used as a continuous manufactureing machine of polymeric such as polymer alloys, blends, materials composites and other materials. Our research group has been studied on the development of computer simulation technique to predict the materials behavior in a twin-screw extruder and the evaluation method of mixing performance based on the simulation results. The simulation has applied to evaluate the mixing by pitched-tip kneading discs whose tips are pitched to the screw axis. We have studied the performance of mixing elements with different combinations of stagger and tip directions for pitched-tip kneading discs. In this study, we carry out the twin-screw extrusion expariment for a blend of ABS (acrylonitrilebutadiene-styrene copolymer) and AS (acrylonitrile-styrene copolymer). We performed the morphology observation via scanning electron microscope and evaluated the diameter distribution of despersed rubber particles. We also measured the rheological properties. We compared these results with the mixing performance obtained by

the previous simulation, and discussed the melt mixing mechanism by pitched-tip kneading discs and reliability of the numerical simulation. Keywords: Twin Screw Extruder, Polymer Blend, Numerical Simulation, Rheological Property, Morphology

S03-730

ABGRALL Florent, DEVISME Samuel, BEAUME François

Die build-up issues in extrusion - Tailor made fuoropolymers as useful and efficient processing aids

High filled polyolefin with mineral fillers (talc, TiO2, CaCO3...) are currently used in industrial and food packaging. These additives bring some specific properties like UV protection or thermomechanical properties, but are sometimes associated to specific extrusion troubleshooting like die build up or die drool. These refer to the continuous or intermittent accumulation of materials around the die exit, due to chemical factors linked to the polymer composition itself, physical factors related to the process setting and environmental factors like moisture. This phenomenon is widely known in production as it can affect dramatically the productivity due to off spec products and periodic shut down for cleaning. For a practical standpoint, applying extrusion coating to polypropylene (PP) allows designing a wide range of multilayered structures with an improved thermal resistance. This environmentally friendly process is also particularly attractive thanks to his high productivity but these products are sensitive to die build up due to the high extrusion temperature, moisture and the presence of mineral fillers. This presentation will try to give an up to date overview of the state of the art and give a practical fluoropolymer use as processing aid to reduce die build issue in PP extrusion coating.

S03-81

Hopmann Christian, Yesildag Nafi, Windeck Christian, Bremen Sebastian, Wissenbach Konrad, Merkt Simon



Opportunities and challenges of profile extrusion dies produced by additive manufacturing processes

The design and manufacture of profile extrusion dies is characterised by costly running-in-trials. Significant cost and time savings can be achieved by replacing the experimental running-in-trials with virtual ones. A simulative optimisation, however, often leads to complex, free-formed flow channels. A feasible manufacture of such dies is possible additive manufacturing only with processes such as the Selective Laser Melting (SLM). Against this background, the manufacture of profile extrusion dies by SLM is investigated. A major challenge is to ensure a sufficient surface quality of the extruded profiles. The roughness of SLM surfaces does not meet the high demands that are placed on the surface quality of extrusion dies. Therefore, in case of the SLM die a concept for the surface finishing of the flow channel is required, which can be applied to arbitrarily shaped geometries. For this purpose, plastics profiles are extruded both with a conventionally and additively manufactured die. In case of the SLM die only the die land of the flow channel was reworked by polishing. The comparison of PP profile surfaces shows that the SLM die with polished die land delivers the same surface quality as the conventional die (Ra $\approx 1 \ \mu m$). Another important task in the manufacture of profile dies by SLM is the optimisation of the die topology. The efficiency of the SLM process largely depends on the volume of the part being produced. To ensure the highest possible efficiency, it is necessary to adapt the die geometry to its mechanical loads and minimize its mass. For this purpose, the internal pressure in the die was numerically calculated and used for a first optimisation of the die topology. The optimisation, however, leads to a free-formed outer die wall so that the die cannot be tempered with heating tapes anymore. This problem is solved by using the high potential of SLM for functional integration and integrating contour adapted tempering channels into the extrusion die.

S03-83

Düngen Matthias, Müller Michael, Koch Michael

Groove Geometry and Bulk Material Properties Impacting on Pressure Build-up in Single Screw Extruders

Single screw extruders with a grooved feeding section can show a forced conveying of solid particles leading to high specific throughputs. The requirements for such a forced conveying were discussed in literature, and models to describe them were presented. Actual visual ob-servations of the processes inside the feeding zone are difficult due to high pressures and thus are scarce to find. Therefore this study deals with a simplified experimental setup based on an unwound flat screw channel implementing a kinematic reversal. It allows the visual observation of the solid movements and the measurement of the force to move the movable wall of the setup. It features variable screw channel heights, groove geometries and different bulk materials (PE, PP, PS). This setup allows insight into the actual formation of the particles in the groove and the interaction of the particles in the channel with those in the groove. The experiments show particles agglomerating into wedges above the groove for certain configurations. These wedges support the movement of the particles towards the end of the channel. The experimental setup allows the material to be compressed towards the end of the channel which leads to a pressure build up in the channel. For each combination of channel height, groove geometry and material type a maximum pressure level exists which can be achieved until the wedge collapses. Relative to material kind, dimensions and shape, varying conditions are observed. Accordingly, particular material characteristics are identified to reflect the difference in solid conveying. In this study a modeling approach based on the Hertzian theory for contact stresses is pre-sented to calculate maximum pressure level for different this configurations of bulk materials, channel height and groove geometry.

S03-96

Pohl Max, Schöppner Volker

First insight into the High Speed Extrusion of Polycarbonate



Increasing the economical efficiency of single screw extrusion is an important factor in the area of research and development in extrusion technology. Enlarging processing machines is an approach which raises the mass flow rate but at the same time increases costs for maintenance or batch changes. This is why the focus of this essay shall lay on increasing speed at a constant diameter in order to improve the output. Investigations with polyolefins show, that in terms of high-speed extrusion (from 2m/s on) special attention has to be paid on the partially poor feed behavior and the high processing temperatures. Building on the results based on previous studies, the investigation of amorphous thermoplastics (polycarbonate) in combination with high-speed extruders is being pushed on at the KTP institute. Because of the other molecular structure amorphous to partially crystalline (polyolefin) it can be assumed that already gathered knowledge in areas of feed behavior, temperature development or mixing homogeneity can be transferred only partly. This is due to the lack of melting enthalpy of amorphous polymers. This essay introduces the first observations of temperature homogeneity and pressure development partially at high-speed extrusion with polycarbonate. These observations are based on the evaluation of various speed ranges on an extruder (D=30) with vacuum degassing and torque direct drive. The measurements occur with a temperature sensor in the area of the screw tip and with several pressure sensors along the axial screw length. This arrangement allows making statement about temperature homogeneity, pressure development and melting process. Based on these results, approaches to process optimization are introduced.

S13-100

Huang Yan-Fei, Xu Jia-Zhuang, Li Zhong-Ming

Melt Processed and Self-reinforced Ultrahigh Molecular Weight Polyethylene Used for Total Joint Replacement

The longevity of ultrahigh molecular weight polyethylene (UHMWPE) implant faces an ongoing challenge that the number of younger and more active patients needed total joint surgery is growing steadily. It is, therefore, of great importance to enhance the mechanical performance of UHMWPE without sacrificing its wear resistance and fatigue resistance so as to decrease the risk of revision. Besides, melt processing of UHMWPE is a bottleneck due to the extremely high melt viscosity. Currently, the processing of UHMWPE is mainly limited to ram extrusion and compression molding, which are of low efficiency and prone to generate structural defects. In this study, we demonstrated that, by addition of 9.8 wt% ultralow molecular weight polyethylene as a flow accelerator, UHMWPE could be easily melt injection molded. During the packing stage of injection molding, a controllable shear flow was exerted, which increased the overall crystallinity and efficiently self-reinforced superstructure, induced i.e., interlocked shish-kebabs and oriented lamellae. As an advantage, mechanical performance of meltprocessed UHMWPE (MP-UHMWPE) was significantly enhanced compared to compressionmolded UHMWPE (CM-UHMWPE). Especially, yield strength and ultimate tensile strength increased to 46.3 ± 4.4 and 65.5 ± 5.0 MPa, with increments of 128.0% and 57.4%, respectively. Impact toughness climbed from $68.7 \pm 1.3 \text{ kJ/m2}$ for CM-UHMWPE up to 90.6 ± 1.6 kJ/m2 for MP-UHMWPE. Simultaneously, wear rate dropped to 7.1 ± 0.3 mg/MC, which was 2.9 mg/MC lower than that of CM-UHMWPE. Our work provides a way to fabricate high-performance feasible UHMWPE by manipulating the crystal structure during melt processing.

S03-512

EL HAJJ SLEIMAN Ghinwa, BELHABIB Sofiane, PETIT Isabelle , ALLANIC Nadine, DETERRE Rémi

Study of the Rheological Behavior of Polypropylene/Polyethylene Extruded Mixture Using an Instrumented Die

Regardless the type of the recycled plastic, the final product will always contain impurities and pollutants that will affect the mechanical and physical properties of the processed pieces. Given that polypropylene (PP) and polyethylene (PE)

represent over 40% of the world consumption of plastic, the study of behavior of recycled matter derived from these two polymers is of a great interest (Colbeaux, 2001). PE is the majority pollutant in recycled PP, which tends to form a heterogeneous mixture with it due to the incompatible nature of those two polymers (Wignall, 1978) (Joseph, Renardy, & Renardy, 1984). For that, the determination of the composition of the plastic waste streams is therefore important, because it determines the appropriate management procedure for the end-of-life material. The aim of the current study is to develop an instrumented device that is able to detect the presence of the as well as their impurities concentration fluctuations in recycled thermoplastics during their processing. This device is equipped with pressure and temperature sensors allowing an online measurement of pressure drop variations as well as dissipation variations viscous through the temperature field within the flow. These detections might hopefully lead to a future control of the processing parameters thus controlling the final parts qualities. In the present study, PP and PE were extruded with different percentage in weight of PE. The pressure drops and the temperature within the flow in cylindrical die -using a measuring temperature cell (MTC) - were measured (LAUNAY, 2013). A mixing law was proposed to describe the rheological response on immiscible mixtures (HAN, 1981). A level set based finite element model is set up using Comsol Multiphysics software in order to predict the various rheological behaviors of different polymer mixtures flowing in the cylindrical die (VORONETSKA, 2012). The primary results of the model agree with the experimental results. The results obtained in this work show that the rheological response of a mixture is very sensitive to the viscosity of the minor polymer when the viscosity of the latter is lower than the major one.

Poster

S03-386

Yi Longfei, Shen Jiabin, Guo Shaoyun

Shell-mimicking structure of polylactide fabricated through layer-assembly extrusion: toward high strength and toughness

From the perspective of balancing performances, achieving high strength and toughness in a polymer material has caught great attention in past decades. In this work, shell-mimicking polylactide (PLA) was fabricated through a layer-assembly extrusion which combined an assembly of layermultiplying elements (LMEs) with an extruder. By applying nine LMEs, multilayer-assembled shishkebab morphology could be observed which was ascribed to iterative stretching and laminating effects occurring in the layer-multiplying process. When the number of LMEs was increased from zero to nine, substantial increments of 60% and 200% in tensile strength and elongation at break were achieved and a transition from brittle to ductile damage was observed. Besides, accompanied with the evolution of crystalline morphology, the surficial roughness became smaller when experiencing a scratch process. The critical normal load, a significant parameter for evaluating the scratch-resisting ability, was distinctly enlarged from 35.4 to 65.2N indicating that the scratch resistance of PLA got enhanced. High orientation of molecules was considered to be capable of resisting the mechanical deformation, while the interfacial shearing occurring between layers contributed to restraining crack propagation. Thus, it is believed that the shell-like multilayer structure developed in the layer-assembly extrusion shows a great potential in fabrication of superior PLA products with high mechanical strength and toughness.

S03-398

S03-773

Thongthanom Ratiporn, Manuspiya Hathaikarn

Perolo A., Castiglioni A., Ferri D.

Wasted Tire Ground Rubber/ Wood flour optimized ratio Toward the High Mechanical Properties in Polypropylene composite

Among the environmental concern, tire rubber has become a significant problems because its nonbiodegradable character due to crosslinked network and caused the waste rubber accumulation. Ground Tire Rubber (GTR) or crumb rubber is the recycled waste tire rubber in a small size that can be incorporated as raw materials with Wood flour (WF) and virgin or waste polyolefin such as PP and HDPE in order to obtain a new type of rubber wood plastic composite with improved the impact properties and toughness when compared with conventional. In this studied, Polypropylene (PP) was used as a polymer matrix filled with WF and GTR in different ratios by varied the composition of polymer matrix to fillers in 60:40 and 70:30 and then varied fillers for 1:3 1:1 and 3:1 of WF to GTR in all compositions. The specimens were prepared by extrusion and injection techniques. The results showed that the density of composite materials is reduced when compared with neat PP showed the lightweight materials were obtained. The morphology showed incompatible between polymer matrix and fillers due to the different hydrophobicity of polymer matrix and hydrophilicity of fillers and it can be effected to the overall mechanical properties that slightly dropped from those of neat PP but the impact properties were improved when increased GTR. Polypropylene-grafted-Maleic anhydride (PP-g-MA) was selected as the compatibilizer between fillers and polymer matrix. Esterification reaction and H-bond occurred at hydroxyl group (-OH) on the interface of the cellulosic wood flour and surface of GTR to improve the compatibility and higher miscibility between polymer and fillers. The composition of PP (70) to fillers (30) and WF to GTR (1:3) was chosen to improve the miscibility and compatibility by the PP-g-MA. From SEM result showed that the presence of PP-g-MA, the matrixfiller interface was improved and increased the strength of composite materials.



Electrification of polymers during capillary extrusion

In this work we investigated the phenomenon of electrification of polymer melts during extrusion. A dedicated measurement apparatus has been built in order to measure the electrostatic charge Q induced by a polymer melt similar to those used in literature. The system consists of a Faraday cup connected to an electrometer and a digital acquisition system for acquisition and analysis. The electrification was measured on commercial PS grades which have different molecular weigth (MW). Each one has been extruded at different temperatures (T), velocities (v) and capillary geometries (L/D). According to the literature on the topic, results have been expressed in terms of volume density of electric charge QL (nC/cm3) of the extrudate. We acknowledged a strong effect of both T and L/D over QL. Keywords. Polymer melt, Electrification, Electric double layer, Faraday cup, capillary rheometry.



S04- Polymer Blend and Alloys

melted. It means that the molecular chains were rearranged to form stereocomplex crystallite after the melted of the homocrystallite.

Keynotes

S04-307

Ko Huan-Chieh, Shyr Tien-Wei

Transformation of Homocrystallite/Stereocomplex Crystallite of PLLA/PDLA Blended Filament during the Heating Process

Tsuji et al. investigated the crystallization behavior of poly L-lactic/poly D-lactic (PLLA/PDLA) blends with different ratios. The stereocomplex crystallite was observed using Differential Scanning Calorimeter (DSC) and Wide Angle X-ray Diffraction (WAXD). The melting temperature of stereocomplex crystallite is higher than that of PLLA homocrystallite. The presence of stereocomplex crystallite increases the total crystallization rate of PLLA/PDLA blend. Fujita et al. reported the blends of PLLA and PDLA homocrystallite exhibits the transition to stereocomplex crystallite during their lamellar thickening process. This peculiar phenomenon is hardly explained. Therefore, this study focused on transformation the of homocrystallite/stereocomplex of crystallite PLLA/PDLA (LD) blended filament, which were blended with the weight ratios of PLLA and PDLA in 50:50. The transformation of homocrystallite and stereocomplex crystallite was studied using WAXD, DSC, and Hot Stage Polarizing Microscope (HSPM). WAXD analysis showed that there have no homocrystallite and stereocomplex crystallite can be observed in the L5D5 filament. DSC results showed that the endotherm of both of homocrystallite and stereocomplex crystallite can be observed in the filament. HSPM was therefore used to observe the transformation from homocrystallite to stereocomplex crystallite of the L5D5 filament during the heating process. The results showed that the stereocomplex crystallite was formed at 150 °C after the homocrystallite was



Oral

S04-13

Saito Tomotaka, Hao Yan, Sumiya Nobuhiro, Moriyama Tomokazu

Enhancement of Impact Strength at Ambient and Low Temperature for Polycarbonate-based Polymer Alloy without Reduction of Flexural Modulus

The impact strength and the flexural modulus are important properties for industrial use of polymer materials. However, because these two properties are usually considered as trade-off, enhancing one of the properties causes decreasing the other. The impact strength not only at ambient but also at low temperature is required for practical use. In general, the impact strength drastically decreases at low temperature. Here, we introduce a method for enhancing impact strength at room and low temperature without reduction of flexural modulus. Polycarbonate (PC)/low density polyethylene (LDPE) polymer alloys of 0.6, 1 and 10% in weight ratio of LDPE were prepared by melt compound. The impact strength is controlable by LDPE addition, and the values of PC and the alloys at 23oC and -45oC are 65.0 and 8.7 kJ/m2 (PC), 81.3 and 8.9 kJ/m2 (0.6 wt%), 78.3 and 12.3 kJ/m2 (1 wt%), 60.1 and 43.2 kJ/m2 (10 wt%). The impact strength of PC with 1% of LDPE alloy at room and low temperature are 20% and 40% higher than those of PC, respectively. The flexural modulus of PC/LDPE 1 wt% alloy is 2.4 Gpa, and the value is almost same as that of PC (2.2 GPa). The impact strength at room and low temperature are enhanced without reduction of the flexural modulus. Morphologies of PC/LDPE alloys show sea-island structure and gaps are formed at the interfaces of PC matrix and LDPE particles. In other words, cells were formed by non-contact interfaces of PC and LDPE. The cells and the particles diameters increase with increasing LDPE content. We will report the relation between the

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morphologies and impact strength in the presentation.

S04-181

Sahnoune Mohamed, Taguet Aurélie , Otazaghine Belkacem, Kaci Mustapha, Lopez-Cuesta José Marie

Influence of the selective functionalization of halloysite on the morphology and the rheology of co- continuous polystyrene/polyamide 11 blends

Halloysite (HNT) is a natural mineral which exhibits a characteristic tubular structure at the nanometric scale. Its surface chemistry presents aluminol groups at the inner surface and silanol ones at the outer surface. This asymmetry of surface composition leads to differences of reactivity which allows selective modification of the halloysite particles to be performed 1,2. In this work, internal surface of halloysite was selectively modified using styrene/(methacryloyloxy)methyl phosphonic acid copolymer (P(S-co-MAPC1(OH)2)) , which was previously synthesized in our laboratory. FTIR, TGA, Py-GC/MS and solvents dispersion tests were used to evidence this surface modification of halloysite. Then, the hybrid nanoparticles were incorporated at various percentages (3 and 10 wt%) in co-continuous polystyrene/polyamide 11 (60/40) blends, using a twin-screw mini-extruder. SEM micrographs showed the preferential localization of halloysite nanotubes at the interface after functionalization, with some nanotubes also in the polystyrene phase. This presence of modified HNT in the PS phase was also evidenced by TGA, where improvements in terms of thermal stability were observed. Rheological measurements were carried out to study the influence of the surface modification of HNT on the morphology of the systems. A gel-like behavior was observed for all HNT reinforced compositions that was enhanced in the case of 10% of functionalized halloysite. References (1) Yah, W. O.; Takahara, A.; Lvov, Y. M. J. Am. Chem. Soc. 2012, 134 (111), 1853. (2) Yah, W. O.; Xu, H.; Soejima, H.; Ma, W.; Lvov, Y.; Takahara, A. J. Am. Chem. Soc. 2012, 134, 12134.

S04-197

Nishino Kohhei, Shindo Yuichi, Takayama Tetsuo, Ito Hiroshi

Effects of Reactive Polymer as Modifier on Impact Strength and Hydrolytic Stability of PC/ABS Blend

PC/ABS blends have been widely used for specific applications such as in automotive interior & exterior parts and office automation equipment parts. In this study, the effects of a reactive polymer as a modifier on the properties of PC/ABS blends were investigated. The reaction between PC and maleic anhydride group cannot be expected usually because the end hydroxyl group of PC is capped with end-capping agents such as t-butyl phenol to improve the properties of PC. However, we have found that a reactive polymer which has maleic anhydride group reacted with the end hydroxyl group of PC which was hydrolyzed with metal salts. From the results, the impact strength of PC/ABS was improved with the reactive polymer.

S04-232

Salehiyan Reza, Lee Sumkun, Kim Minguen, Hyun Kyu

Evaluation of influence of nano particles on morphology of PP/PS blends by FT-rheology from LAOS test

Effects of various types of nanoparticles on PP/PS (80/20) blends were investigated using rheological properties. Large Amplitude Oscillatory Shear (LAOS) tests were carried out at frequency of 1 rad/s to probe nonlinear rheological properties and linear rheological properties were measured using Small Amplitude Oscillatory Shear (SAOS) tests. Large Amplitude Oscillatory Shear (LAOS) is a test method for the characterization of complex fluids. Among several LAOS analysis methods, the Fourier Transform (FT)-Rheology is sensitive method. I proposed a new nonlinear coefficient Q established from FT-Rheolgy under LAOS. The parameter Q is defined as Q=(I3/1)/(gamma^2) where I3/1 is the normalized 3rd harmonic contribution. Asymptotic value zero-strain nonlinearity, Q0, the inherent non-linearity for vanishing strains can be defined. Using this concept entangled linear monodisperse polymer and comb polymer melts were

investigated towards these nonlinear parameters (Q and Q0). A strong influence of the molecular topology on these nonlinear parameters (Q and Q0) was found. In this study, we also applied Q and Q0 to study polymer blends. For better comparison of polymer composite system, we propose new parameter as the Nonlinear-Linear viscoelastic Ratio (NLR). The NLR was used to quantify the degree of dispersion and distinguish the different response of nanoparticles. SEM and TEM images were taken to investigate morphology and internal structure.

S04-334

Abbasi Atiyeh , Sheikh Nejad Moghadam Abdollah , Amir Aslani Saba Reza , Keshavarzian Ali

Synthesis of Poly(ethylene terephthalate-conaphthalene) to Achievement the Hot Fill Properties

Polyethylene terephthalate (PET) is one of the most important thermoplastic materials with wide field of applications. The production of PET items such as fibers, films and bottles for food and household packaging involves many processing steps. These steps result in changes of morphological and structural characteristics. Increase or decrease in the crystallinity caused changes in the physical properties of the end product. Shrinkage, dimension stability, stiffness, dye-ability, mechanical behaviour and gas barrier properties of the final products are related to the degree of crystallinity and the glass transition temperature of PET. Chemical modification via copolymerization is one of the most attractive techniques in order to differentiate the properties of PET. Hot filling procedure used for the production of shelf-stable juice involve pouring the heat-treated juice, without significant cooling, directly into the package. Usually, the temperature for hot filling of juice in PET is 80 to 88°C. In this research, synthesis of poly(ethylene terephthalate-co-naphthalene) (PETN) copolymer was studied in presence of different amounts of 2,6- naphthalene dicarboxylic acid (NDA) to Achievement the Hot Fill Properties. The microstructure of the synthesized polymer was studied with Fourier Transform Infrared (FTIR) and

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Nuclear Magnetic Resonance (NMR). Differential scanning calorimetry (DSC) was used to study the thermal properties. The DSC results have shown that the modification of PET with low levels of naphthalene comonomer (5-8 mol%) increases the Tg. This property has a significant effect on the thermal stability potential of many hot applications to resist higher temperatures without shrinkage. Based on the FTIR and NMR results, the synthesized copolymer was Poly(ethylene terephthalate-co-2,6naphthalene dicarboxylic acid). Results showed that PETN was suitable for use in the manufacture of hot fill containers.

S04-470

Esmaeili Mohsen, Pircheraghi Gholamreza, Bagheri Reza

Morphology-rheology relationship in thermoplastic starch/ polylactic acid blends

In this work, we have prepared thermoplastic starch (TPS) / polylactic acid (PLA) blends, and investigated the rheological properties as well as morphology of the blends. Thermoplastic starch, prepared using a combination of sorbitol and glycerol plasticizers, was melt blended with PLA in the concentration range of 20 to 80 wt.% in a laboratory twin screw extruder. Compatibilized blends were also obtained with substitution of 20 wt.% of PLA by maleic anhydride grafted PLA (PLA-g-MA). Scanning electron microscopy (SEM) images revealed co-continuous morphology in blends containing 40 and 60 wt.% PLA, while in blends with 20 and 80 wt.% of PLA, matrixdispersed morphology was observed. Incorporation of compatibilizer resulted in formation of finer morphology in the entire blends. Moreover, in the presence of the compatibilizer, morphology of the blend containing 60 wt.% turned to matrixdispersed. Rheological evaluations illustrated reduction of complex viscosity by introduction of compatibilizer. It was observed that the rheological properties of compatibilized blends were lower than those of their non-compatibilized counterparts. This observation was attributed to the chain session of PLA during maleic anhydride grafting reaction as evidenced by lower complex viscosity of PLA-g-MA compared to the neat PLA.

In addition, it was found that in the samples with co-continues morphology, rheological properties are strongly dominated by the TPS phase. Moreover, in the blend samples containing 80 wt.% PLA, the rheological properties are negatively deviated from mixing rule; probably due to migration of glycerol and sorbitol plasticizers into the PLA matrix.

S04-5

Dutta Joyeeta, Chatterjee Tuhin, Naskar Kinsuk

Blends Based on Ethylene Vinyl Acetate (EVA) and Thermoplastic Polyurethane (TPU): Exploring the Influence of Electron Beam Irradiation on Performance Properties

Novel blends based on Ethylene vinyl acetate/Thermoplastic Polyurethane (EVA/TPU) at different ratios were prepared via melt blending technique. EVA/TPU 80/20 blend was observed to exhibit optimum tensile strength and elongation at break. Various models have been applied to predict the change in modulus with blend composition and Veenstra B model was found the best to correlate the experimental modulus values. All the blends show a single Tg and a shift in Tg with change in blend composition was observed through Differential scanning calorimetry (DSC) and Dynamic mechanical analysis (DMA), indicating technological compatibility. The effects of electron beam radiation (EBR) on the blends of Ethylene vinyl acetate/Thermoplastic Polyurethane (EVA/TPU) were investigated in details. The samples were irradiated by using a 2.5 MeV electron beam accelerating energy over a dose range from 25 to 200 kGy. The blends exhibit drastic improvement in mechanical properties with increasing radiation dose upto an optimum dose. Modification of the blends via EBR enhances the elastic recovery of the blends resulting significant improvement in tension set behaviour. Scanning electron microscopy (SEM) study was performed to explore the changes in morphology before and after irradiation. All the irradiated blends have higher electrical resistivity than the blends without irradiation and the volume resistivity increases upto 150 kGy. The samples were found to exhibit



remarkable improvement in oil resistance property after irradiation which is more prominent in EVA/TPU 70/30 blends.

S04-519

Bharati Avanish, Hejmady Prakhyat , Cardinaels Ruth, Won Seo Jin , Moldenaers Paula

Inducing conductivity in immiscible PP/PS blends by a percolated polyaniline/PA filler selectively localised by interactions with the SEBS-g-MA compatibilizer

We have investigated the effect of master batch preparation techniques such as by extrusion and solution casting to develop a double-percolated network of conducting Polyaniline (PANI) in immiscible PP/PS blends. The strategy adopted to develop conducting blends was to concomitantly drive the morphology of the immiscible blend to a cocontinuous structure and control the localization of the PANI using specific interactions with an interfacially segregated SEBS-g-MA compatibilizer. A percolated composite of PANI in Polyamide (PA) is used as the conducting filler, and we envisage that the hydrogen bonding of PA with MA of the copolymer drives the localization of the PANI to the copolymer. Hence, master batches of the conducting PANI and copolymer with increasing PANI concentration were prepared by extrusion and solution casting. The master batches were subsequently added to the polymer constituents (PS or PP/PS) using different sequences of solution and melt mixing to localize the PANI either in the polar PS phase or partially at the interphase. The thus prepared blends led to a synergistic increase in the conductivity (6 decades) and dynamic moduli with increasing PANI and copolymer concentrations, whose effect was investigated for various blend compositions. Our findings were warranted by STEM micrographs, in which for blends with master solution casted batches, PANI-PA selectively localized at the interphase or in the minority matrix phase of the PP/PS blend. The latter was attained due to phase inversion with increased copolymer concentration. In addition, we established the essential role of interactions between the conductive PANI-PA composite and

the MA functionality of the SEBS-g-MA in the localization process. In summary, various master batch techniques were employed to optimize the percolation of the conductive polymer PANI in PP/PS blends, allowing to generate easily processable conductive PP-PS blends.

S04-580

Schmidt Jochen, Romeis Stefan, Wirth Karl-Ernst, Peukert Wolfgang

Production of PBT/PC particle systems by wet grinding

Comminution of plastic or visco-elastic materials is known to be energy-intensive and costly. Typically impact mills, cutting mills and jet mills are applied for comminution and the feed material frequently is pre-cooled using liquid nitrogen or solid carbon dioxide. Therefore, especially the production of fine polymer particles by the aforementioned dry grinding methods is challenging. We demonstrate that wet grinding of polymers [1] is a feasible approach for production of fine polymer particles that e.g. may be used as a starting material in a process chain for production of spherical polymer particles that can be used in in additive manufacturing [2]. Wet comminution of polymers will be discussed amongst others for polybutylene terephthalate (PBT), polycarbonate (PC). Moreover the possibility to produce mechanically alloyed PBT-PC blends will be addressed. The products are thoroughly characterized by means of vibrational spectroscopy (IR, Raman), X-ray diffraction and dynamic scanning calorimetry. The dependency of the grinding result on fundamental process parameters, such as e.g. stirrer tip speed or grinding media size as well as on the process time, process temperature and the system composition will be discussed. In any case high load conditions, i.e. high stress energies are needed to initiate breakage of polymer materials. Optimization of the process with respect to process time and energy consumption by appropriate selection of process temperature and solvent will be demonstrated. Especially the selection of appropriate solvents allows for remarkable reduction of mass-specific comminution energy needed. [1] J. Schmidt, M.



Sachs, C. Blümel, B. Winzer, F. Toni, K.-E. Wirth, W. Peukert, Powder Technol 261 (2014) 78-86. [2] J. Schmidt, M. Plata, S. Tröger, W. Peukert, Powder Technol 228 (2012) 84-90.

S04-621

Kevin Verilhac, Desse Melinda, Fenouillot Françoise, Carrot Christian

Mixing of Polar and Non-Polar Molten Olefinic Co-polymer with Polar Liquids in Conditions of Very Low Viscosity Ratio: Shear Dominated Flows

The work focuses on understanding the mixing of low viscosity fluids in molten polymers, i.e. with components with a large difference in viscosity. The idea is to complete de Grace curve for low viscosity ratios and to understand the effect of polarity on the dispersion. Mixing of fluids is not well understood but is largely used in industrial processes such as a monomer in a high viscosity polymer or yet the use of water as a carrier for blending small-sized carriers. To this end, two olefinic copolymers with low crystallinity rates were chosen as matrixes and a range of PEG with various molar masses were used at first as polar dispersed phase. Finally, ethylene glycol, glycerol and water were also dispersed in the matrixes. Droplet sizes were calculated in equilibrium conditions. Special care was taken to work at dispersed phase concentrations sufficiently low to prevent coalescence. Interfacial tension was a crucial parameter in determining the critical capillary number and was therefore carefully determined through theoretical, semi experimental and experimental methods. Critical capillary numbers for each blend were calculated and compared to the Grace Curve.

S04-636

Razavi Aghjeh Masoud , Jafari Seyed Hassan, Yousefi SeyedMojtaba , Khonakdar Hossein Ali

A rheological and morphological study on flame retarded PP/EVA blends and its nanocomposites For the first time attempts were made to study the rheological and morphological properties of polypropylene/ ethylene vinyl acetate copolymer blends and its nanocomposites containing a new generation of halogen-free flame retardants commercially known as "NOR116". Scanning electron microscope (SEM), transmission electron microscope (TEM) and wide angle X-ray scattering (WAXS) analysis were implemented in order to study of morphological properties. Effect of presence of two different types of compatibilizer, flame retardant and organoclay on morphology of samples was investigated. By considering chemical nature of compatibilizers and SEM images, TEM micrographs and organoclay localization were predicted. accurately Using rheological measurements in three different modes of frequency, temperature and time sweeps, linear properties, alterations viscoelastic in these by properties increasing temperature and morphological evolution at higher temperatures investigated. Using frequency were sweep experiment miscibility level of blends and their interfacial properties were studied. A good between correlation these properties and morphological observations was established. Also, It was found that variation in linear viscoelastic properties of samples by temperature strictly depends on blend morphology and chemical structure of components. In the case of pure blend a single phase morphology which was indication of increasing miscibility was detected at higher temperatures.

S04-779

Wang Dong

Novel Strategy for Compatibilization of Immiscible Ternary Polymer Blends and Its Morphology Development

Development of high performance multicomponent immiscible polymer blends and recycling and reusing scrap or waste plastics have been difficult because of the difficulty of compatibilization, especially the preparation of an effective compatibilizer for such blends. Here we present a novel and effective strategy to



compatibilize three immiscible polymers, polyolefins, styrene polymers, and engineering plastics, achieved by using a polyolefin based multi-phase compatibilizer. Compatibilizing effect and morphology development were investigated in a model ternary immiscible polymer blends consisting of polypropylene (PP)/polystyrene(PS)/polyamide(PA6) and a multiphase compatibilizer. The results show that, as a multi-phase compatibilizer, (PP-g-(MAH-co-St) exhibits strong compatibilization in the above immiscible blends, as demonstrated by the improved tensile and impact properties, finer dispersion of the PS and PA6 phase, and increased interfacial adhesion. This work provides a novel strategy not only for developing ternary or multicomponents polymer blends with unique performance, but also useful for recycling and reusing three immiscible polymers, polyolefins, styrene polymers, and engineering plastics from the waste stream.

S04-93

Krooß Tim, Gurka Martin, Breuer Ulf

Development of high-performance thermoplastic PPS/PESU blends as matrices in fiber reinforced composites

The share of high performance thermoplastic composites within airframe structures is relatively small, although these materials offer the potential of very short cycle time processing. Only PEEK and PPS are used for primary structure applications, however PEEK has a high price and PPS cannot deliver the whole range of properties. This investigation focuses on the development of thermoplastic polymer blends on the basis of polyphenylene suflide (PPS) and polyether sulfone (PESU) as substitutes for high-cost polyether ether ketone (PEEK) and neat PPS in fiber reinforced composites. It is targeted to deepen the understanding of PPS/PESU blends processing and resulting properties. First studies, utilizing injection molding processing, revealed a strong dependency of the resulting property profile on processing conditions and the relative polymer portions [1]. In this study we focus on the relationship between the

rheological behavior and resulting morphology of PPS/PESU blend films, made via а film casting/extrusion process. Properties especially affected by the blends morphologies are the mechanical and thermo-mechanical behavior as well as the resistance towards liquid media. Analytical effort is primary focused on characterization of the crystallization kinetics, morphology changes in single films and solid plates and the influences on the mechanical (strength and toughness) and thermo-mechanical (storage modulus at high temperature) properties. Additional attention is paid to thermal annealing of PPS/PESU samples, to significantly increase the blends performance. A primary finding was that the degree of crystallization increases with higher PPS fractions, strongly affecting the overall performance and thus depends on extrusion parameters, consolidation conditions and thermal treatment of tested samples. Conclusions of this work evidence the high potential of tailored PPS/PESU blends for film extrusion and stacking processes, partly outperforming PEEK and neat PPS.

Poster

S04-149

Sako Takumi, Yamaguchi Masayuki

Surface localization behavior in injection-molded plate of polycarbonate/poly(methyl methacrylate) blend

The blend composition at the surface of an injection-molded product for binary blends of polycarbonate (PC) and poly(methyl methacrylate) (PMMA) is studied. As well known, low molecular weight fraction is segregated on the surface of an injection-molded plate with broad molecular weight distribution to minimize applied shear stress, which was confirmed also in our experiments using pure PC. In the case of the blend of PC and PMMA, having a relatively low viscosity, the PMMA content at the surface of the injection-molded plate is found to be dependent upon the temperature in the barrel. At the low barrel

temperature, PMMA localizes at the surface, which is detected by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) measurements at the surface and cross-section of the plate. The difference in the viscosity could be the origin of this phenomenon. Since the surface localization behavior significantly affects surface properties of molded products, this phenomenon is important to control the surface composition for this blend system.

S04-170

Moriyama Tomokazu, Sumiya Nobuhiro, Saito Tomotaka, Hao Yan

Enhancement of impact strength of PA11 by dispersing PBS particles without reduction of flexural modulus

Bio-plastics are widely used in dishes, packaging and electronic automotive parts, containers, products. То expand bio-plastic usage, improvements in impact strength, heat resistance, and flame resistance are required. As a method of improving the impact strength of plastics, alloying a matrix polymer with a compatibilizer and soft materials such as rubber has been studied. In contrast, elastic modulus reduction due to the rubber component is pointed out. Here, we introduce the impact strength improvement of bioplastic without reduction of the flexural modulus. The impact strength of polyamide 11 (PA11) is 2.5 times (32.8 kJ/m2) that of neat PA11 (12.9 kJ/m2) by dispersing 10-30 wt% poly(butylene succinate) (PBS) without adding a compatibilizer and soft materials. The PA11/PBS alloy has a sea-island structure with a PA11 sea and PBS islands. Gaps of several tens of nanometers are observed at the PA11-PBS interfaces, and the sea and islands are connected by string-shaped bridge phases of 10 nm in diameter. The formation of dilational stress fields in the PA11 are suggested because tensile stress due to shrinkage of PBS particle is transmitted to matrix PA11 through these bridge phases during the cooling of the melt compounded PA11/PBS alloy.

S04-183

LI Kanshe, Zhou Yuan , Niu Honfmei, Yan Lanying, Chen Chuangqian, Kang Jie

The Synthesis of Polyester Thermoplastic Polyurethane Elastomer and Effects on Toughening Modification of PVC

With advantages of flame retardant, insulation, corrosion resistance, wear resistance and low cost, wide raw material source, Polyvinyl chloride (PVC) has excellent comprehensive performance. However, in the application of PVC, the impact strength is low and the thermal stability in processing is poor, which limits its application in the field of functional materials. In order to further improve its comprehensive performance, the study choose polyurethane elastomeric (TPU) to toughening modification. The main research purpose of this experiment is design formula to compound polyester TPU. Using diphenyl methane diisocyanate (MDI), poly-caprolaclone glycol (PCL), and 1,4-butanediol (1,4-BDO) as raw materials.Under the condition of isocyanate index temperature(T=60~70 (R=0.98), reaction •Ž), reaction time(t=1 h) design formula. Through infrared spectroscopy (FTIR), NMR, elemental analysis, nuclear magnetic resonance, differential scanning calorimetry (DSC) and gel chromatograph surveying its molecular weight, determine the hard segment content of TPU and chemical structure. By blending with PVC, we evaluate the toughening effect of synthetic TPU to PVC. Through the mechanics performance test, DSC and SEM to characterize the structure properties of the blending material, reveal the toughening mechanism. Results show that there is a good compatibility between the synthesized TPU and PVC. Compared with the commercially TPU brand screening by blending experiments, which has a good effect on PVC toughening modification. When PVC:TPU = 170:30, mechanical performance reached the best level, and toughening effect exceed commercially available brand TPU; When PVC:TPU:CPE=170:15:15, the mechanical properties is optimal; Respectively adding light CaCO3 and heavy CaCO3, reached the goal that toughening and strengthening PVC.

S04-216



Huang Yan-Fei, Xu Jia-Zhuang, Xu Ling, Li Zhong-Ming

Cross-linking and Structural Manipulating of Ultrahigh Molecular Weight Polyethylene with Simultaneously Improved Wear Resistance and Mechanical Performance

The pivotal concern in limiting the longevity of total joints is particulate debris-induced implant loosening mainly generated by the wear of ultrahigh molecular weight polyethylene (UHMWPE). Radiation crosslinking shows great promise for minimizing the wear of UHMWPE, but undesirably deteriorates the mechanical properties. This study aimed at simultaneously enhancing wear resistance and mechanical performance of UHMWPE by cross-linking of the UHMPWE before melt processing followed by structural manipulation. Wear rate decreased substantially from 12.1 ± 1.1 mg/MC for compression molded UHMWPE (CM-UHMWPE) to 1.5 ± 0.7 mg/MC for melt injection molded cross-linked UHMWPE (MPxUHMWPE). Owing to imposing a shear flow, large amounts of self-reinforced oriented lamellae were formed. Mechanical properties were thus remarkably improved, which compensated for the loss of mechanical performance caused by crosslinking. Especially, the yield strength and ultimate tensile strength increased significantly by 98.3% and 51.0%, climbing to 41.6 \pm 1.4 and 62.8 \pm 1.3 MPa, respectively. Interestingly, melt processing recombined the residual free radicals in MPxUHMWPE induced by radiation cross-linking, generating a notably lower oxidation level (0.7 ± 0.1) of MP-xUHMWPE compared to xUHMWPE without any thermal treatment (4.7 ± 0.4) after accelerated aging. Our work opens a radical avenue to fabricate high-performance UHMWPE bearings, enabling its use under high stress, particularly for younger and more active patients.

S04-247

Pawar Shital Patangrao

High performance millimeter wave absorbers derived from uneven distribution of conducting

and magnetic engineered nanoparticles in biphasic polymeric blends

High performance millimeter wave absorbers were developed by the uneven distribution of lossy particles like conducting multiwall carbon nanotubes (MWNTs) and magnetic ultra-small ferrite (Fe3O4) particles (of 2-3 nm) nucleated on reduced graphene oxide sheets (rGO-Fe3O4) in biphasic polymeric blends of polycarbonate (PC) and poly(styrene -co-acrylonitrile (SAN). This acted micro-absorbers manifesting outstanding as millimeter wave absorption (85.5%). The strategy of nucleating magnetic ferrites of 2-3 nm size on rGO high coercive sheets resulted in field; а characteristic of hard magnets. The detailed millimeter attenuation mechanism was wave investigated electromagnetic various using parameters in biphasic blends containing various microwave active nanoparticles like (i) MWNTs, (ii) rGO-Fe3O4 and a combination of (iii) MWNTs and Fe3O4 as well as (iv) MWNTs and rGO-Fe3O4. The primary mechanism of millimeter wave attenuation in PC composites was reflection whereas in case of blends the attenuation was mostly through absorption mechanism. This is corresponding to the selective localization of nanoparticles in PC phase manifesting heterogeneous dielectric media with multiple interfaces. In order to enhance absorption, the surface reflection of millimeter wave was minimized by high surface resistivity whereas the absorption was facilitated by high bulk electrical conductivity (5 S/cm) in combination with the lossy inclusions through multiple scattering. Herein, the blends consisting of both MWNTs and rGO-Fe3O4 depicted a total shielding effectiveness of -34.1 dB (at 18 GHz) manifesting 99.96% attenuation of the incoming millimeter wave radiation. Taken together all the microwave attenuation parameters, it is revealed that the unique structure of blends localization and selective of nanoparticles associated with engineered nanoparticle results in extraordinary synergy in millimeter wave absorption.

S04-298

Luo Wei, Chen Yang, Zou Huawei, Liang Mei



Research on tribological behavior of PPS/PTFE/CF composites

In this paper, polyphenylene sulfide/ polytetrafluoroethylene (PPS/PTFE) composites reinforced with short carbon fibers (CF) were prepared by extrusion and subsequently injectionmolding. The mechanical and tribological properties of PPS/PTFE were improved by the incorporation of CF. At the CF loading of 15vol%, the average frictional coefficient and specific wear rate of PPS/PTFE/CF composite under loading of 500N reached to 0.09 and 5.52•10-6 mm3/N•M respectively. The SEM photographs of worn surface confirmed that the direct contacted area between steel ring and the matrix PPS was decreased due to the existence of CF. Meanwhile, CF might be helpful to the formation of strong transfer film under high loading, thus improved the wear resistance of PPS/PTFE.

S04-321

Zhu Yanling, Fu Qiang

Combined effects of ultrafine full-vulcanized powdered rubber and β nucleating agent on mechanical properties and heat distortion temperature of isotactic polypropylene

In this work, ultrafine full-vulcanized powdered rubber (EA-UFPR) and β nucleating agent were incorporated into isotactic polypropylene (iPP) in order to investigate the combined effects on its mechanical properties and its heat distortion temperature (HDT). A large improvement of Izod impact strength verified as a synergistic effect had been obtained by introducing small amounts of EA-UFPR ($\leq 2 \text{ wt } \%$) into β -nucleated iPP. Decreased crystallization kinetics was found with increasing the content of EA-UFPR. More interestingly, the transformations of crystalline morphologies from β spherulites to bundle-like β-crystals were detected due to a possible suppressed self-assembly of nucleating agent after adding small amounts of EA-UFPR. On one hand, the largely improved Izod impact strength can be attributed to the synergistic effects between EA-UFPR particles and βcrystalline morphology on promoting the plastic

deformation of matrix. On the other hand, the unique interconnected structures formed by the bundle-like crystals and dispersed EA-UFPR particles were proposed for the enhancement in toughness and HDT. Our work provides an effective way to improve the toughness and heat distortion temperature of iPP by adding small amounts of EA-UFPR (≤ 2 wt %), which are crucial for the industrial application of iPP. Keywords: mechanical properties, heat distortion temperature, crystallization behaviour, crystalline morphology

S04-390

Kong Miqiu, Huang Yajiang, Zhao Xueyan, Li Guangxian

Assessment of preparation route-dependent compatibilization efficiency of triblock copolymer in immiscible polymer blends by morphology, rheology and fractionated crystallization behavior

Blending immiscible polymers provides an efficient way to obtain new materials with balanced properties. In order to optimize the final properties of immiscible blends, block or graft copolymers whose segments have diverse affinities with the components of blends are often utilized as compatibilizers to develop compatibility between phases. In this study, the dependence of compatibilization efficiency of styrene-(SEBS) ethylene/butylene-styrene triblock copolymer in immiscible polypropylene (PP)/polystyrene (PS) (20/80) blends on the preparation route was evaluated in terms of morphology, rheology and fractionated crystallization behavior. Combined experimental results with theoretical quantification, it was found that the morphology refining efficiency of SEBS showed a strong dependence on their dispersion in the blend, which could be varied by changing the mixing sequence. SEBS exhibited relatively higher compatibilization efficiency in the blends prepared by mixing SEBS and unfavorable PP in priority and the blends prepared by mixing SEBS, PP and PS simultaneously. The results were interpreted by the migration of compatibilizer during blending in which the affinity of compatibilizer with the two components and the mixing time played crucial



roles. The rheology and crystallization behavior of compatibilized blends also demonstrated the similar results. It was noteworthy that the fractionated crystallization behavior of PP/PS (20/80) blends was suppressed at relatively high SEBS loadings, which could be explained by the migration of impurities from the PS phase to the PP phase promoted by the interface-located SEBS.

S04-624

Javadi Azizeh, Karimi Samira, Nazockdast Hossein

The study of Rheology and Morphology of High Density Poly Ethylene (HDPE) / Ethylene Octane Copolymer (EOC) / Nano Silica / Nanocomposites

In this research, HDPE/EOC blends containing 10, 20, 40 and 80 Wt. % of EOC, also their Nanocompositses with 5 Wt. % Nano Silica were prepared via melt mixing using a brabender. The Rheology and Morphology of samples were studied using Rheomechanical analysis and Atomic Force Microscopy (AFM). The results showed that HDPE/EOC blends are incompatible and show two phases Morphology in all studied compositions. AFM micrographs showed that in blends containing less amount of EOC (10 and 20 Wt. %), the morphology is matrix dispersed and this result confirmed by palierne model too. In was HDPE/EOC/Nanosilica samples, it was found that the Nanosilica particles are located in EOC phase. The location of nano particles in EOC, leads to increasing the viscosity of this phase, so it will be closer to HDPE viscosity. By approaching the viscosity ratio of HDPE and EOC to 1, the smaller size of EOC phase in PE matrix was obtained. So it is concluded that nanosilica particles can have a compatibilising effect in HDPE/EOC blends. HDPE, Keywords: Polymer blends, EOC, Nanosilica, Nanocomposites

Xue Bai, Zhang Junhua

Highly Electrically Conducting Poly (L-lactic acid)/Graphite Composites Prepared Via in Situ Expansion and Subsequent Reduction of Graphite

In this paper, highly electrically conductive polymeric composites were obtained by lowtemperature expandable graphite (LTEG) filling poly(L-lactic acid) in the presence of ascorbic acid via an in situ exfoliation and subsequent reduction process during the melt blending. The electrical conductivity of the poly(L-lactic acid)/reduced and expanded graphite (PLLA/R-EG) composites was determined by a two-point probe resistivity determiner and compared with that of the poly(Lacid)/expanded lactic graphite (PLLA/EG) composites. The percolation threshold of PLLA/R-EG blends decreased from 11.2 wt% to 7.1 wt%, which illustrated the superiority of R-EG to the electrically conducting ability of PLLA composites. At the graphite concentration near the percolation threshold, the electrical conductivity of PLLA/R-EG composites was much higher than that of PLLA/EG composites. The effective in situ expansion and reduction of LTEG was crucial to the overall electrical conductivity of the blends, which was confirmed by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analysis. Dynamic rheology analysis confirmed that the connected networks that were the major cause of the rapid increase in electrical conductivity were much more easily formed for PLLA/R-EG blends than those of PLLA/EG blends. Thermogravimetric analysis (TGA) was applied to determine the decomposition and thermal stability of the PLLA/R-EG composites.

S04-679

Lee Sumkun, Kim Mingeun, Hyun Kyu

Effect of Organoclay on Poly(lactic acid)/Biodegradable Polymer Blends

Due to environmental disposal and increasing cost of polyolefin and petroleum-based product, biodegradable polymers have recently been studied. Among various biodegradable polymers, poly(lactic acid) (PLA) has received attention because of its outstanding mechanical properties, but PLA has drawback of its brittleness. To



S04-663

overcome this mechanical drawback, making blend with other polymer has studied as the easiest method. In this study, we blended PLA with poly(å-caprolactone) (PCL), poly(butylene adipateco-terephthalate) (PBAT) and poly(butylene succinate-co-adipate) (PBSA) to overcome its brittleness. We also added organoclay (Cloisite 30B, Southern Clay Products) to improve miscibility of PLA blends. We investigated this PLA/biodegradable polymer nanocomposites including rheological, mechanical properties and biodegradability.

S15-766

Liau Wen-Bin , Huang Tun-Hao , Chang Shuang-Yuan

The effect of PDLA on the crystallization and morphology of PLLA

The crystallization behaviors and morphology of PLLA with a few amount of PDLA (<10%) were studied. Besides the homo-crystallization of PLLA, PDLA and PLLA polymer chains can co-crystalliz together with 1:1 ratio to form a stereocomplex crystal (SC). The effect of SC on the crystallization behaviors and morphology of PLLA were investigated utilizing DSC, POM, and XRD . Interesting, the melting point of SC is about 50 oC higher than that of PLLA homo-crystal. Therefore, the SC was formed before the crystallization of PLLA. From the results of POM and XRD, it was found that the PLLA homo-crystals were able to be formed in three different sides: "inside of SC spherulite", "front edge of SC spherulite", and "between SC spherultes". The crystallization behaviors in these sides were different. The induction time for the nucleation of PLLA in the side, "between SC spehrulites", was the longest among three sides. They were about the same in other sides, "inside of SC spherulite" and "front edge of SC spherulite". Obviously, SC acted as a nucleating agent and accelerated the nucleating of PLLA crystals. However, the growth rates of spherulite for three sides were about the same and slower than that of neat PLLA. Obviously, the amorphous of PLDA acted as impurity and reduced the growth rate of PLLA spherulites. Growth rate was not influenced by SC

S04-791

Rigoussen Alan , Verge Pierre, Dubois Philippe , Raquez Jean-Marie, Habibi Yous

Reactive compatibilization of immiscible polymers blend using a natural compatibilizer

Polymer blending is one of the most straightforwardly implementable strategies to enhance the properties of Polylactide (PLA) such as mechanical performances aiming at extending its applications. PLA is generally blended with acrylonitrile-butadiene-styrene (ABS), a polymer with interesting thermal and mechanical properties. However, the incompatibility between PLA and ABS remains challenge requiring а compatibilization to obtain a good combination of both polymers. Cardanol, a naturally occurring phenolic compound, has been used to compatibilize PLA and ABS by reactive extrusion. In this presentation, we will detail the compatibilization mechanisms based on the reaction of cardanol with the polymers. The impact of this bio-compatibilizer onto the final materials properties will be given to evidence its efficiency.



S05- Polymer Foams and Lightweight Structures

Keynotes

S05-333

Wang Long , Ohshima Masahiro, Asaoka Fumiya, Yamamoto Satoshi , Goto Hideto, Yusa Atsushi

A New Foam Injection Molding Technology - Use Non-Supercritical Fluids as Physical Blowing Agents

A new foam injection molding technology was developed for producing microcellular foams with non-supercritical fluid. The developed technique does not need any pressure pumps for bringing nitrogen (N2) and carbon dioxide (CO2) to their supercritical state. The screw and its operation scheme were specially designed so that physical blowing agent, such as N2 and CO2, can be delivered directly from a gas cylinder into the molten polymer through an injector valve and mixed with molten polymer in barrel of the molding machine. A venting vessel is equipped in a downstream of the barrel to stabilize the concentration of the physical blowing agent in molten polymer. In the case gas might not be completely dissolved into molten polymer in gaspolymer mixing zone, the excess gas can be discharged from the molten polymer through the vessel. In the case that the concentration does not reach the solubility limit at metering zone, additional gas can be dissolved into molten polymer through venting vessel. Thus, the amount of dissolving gas was controlled and stabilized by not only a gas dosing time of the injector valve and a secondary pressure of reducing value of the gas cylinder but also the pressure of venting valve. Experiments were conducted with both short-shot and core-back operations using either N2 (12MPa) CO2 (6MPa) or Air (12MPa) as a physical foaming agent. Experiments clearly showed that the

developed technology could prepare the foams with 6MPa CO2, N2 and Air. The maximum expansion ratios of the foam that we could achieve with CO2 and N2 were five. Based on the experiments, the developed foam injection molding technology could give an clear answer to the present ill-grounded arguments on the necessity of pressurizing CO2 to the supercritical state for preparing microcellular foams.

S05-48

Shaayegan Vahid, Wang Guilong, Park Chul B.

The Effect of Melt/Gas Mixture Compressibility on the Cell-Nucleation Behaviors in High-Pressure Foam Injection Molding

We investigated the formation of gas bubbles in foam injection molding (FIM) using an in-situ visualization technique. In this regard, an innovative visualization mold, equipped with cavity pressure transducers, was designed and manufactured. We used a polystyrene/CO2 system to carry out experiments with (i) high-pressure FIM, and (ii) full-shot FIM using gas-counter pressure (GCP). To perform high-pressure FIM experiments, we removed all the gate-nucleated bubbles using a melt-packing pressure. A higher gate-nucleated cell density increased the meltpacking pressure required to remove all the gatenucleated cells. Therefore, the required meltpacking pressure increased as the injection speed, the gate resistance, and/or the blowing-agent content increased. The shrinkage-induced bubbles governed the final cellular structure in highpressure FIM after complete dissolution of the gatenucleated cells, whereas the gate-nucleated cells would govern the cell structure in case of dissolution during packing. incomplete In experiments with GCP, a higher cell density was obtained upon the release of the GCP. The twophase polymer/gas mixtures with undissolved gatenucleated cells could not result in a higher cell density because of their higher compressibility. In contrast, the one-phase polymer/gas mixtures, formed either by removing the gate-nucleated cells, or by full-shot FIM with GCP, could obtain a higher pressure drop rate because of their lower



compressibility (equivalently higher bulk modulus), and thereby a higher cell density.

S05-528

Gu Senlong, Jana Sadhan C.

Open Cell Aerogel Foams

This paper presents technologies for manufacturing of open cell aerogel foams. An aerogel foam is a macroscopic material with two functional elements. First, as in open cell foams, the large body of the materials are air-filled open cells. Second, the solid polymer network of open cell foams is replaced by polymer strands organized in the form of mesoporous aerogel films. It is imperative that fabrication of aerogel foam materials is not a straightforward task. This paper evaluates several strategies based on the use of porogens and selective dissolution of immiscible polymer components and reaction-induced phase separation process. The resultant aerogel foams exhibit bulk density lower than 0.05 g/cm3, BET surface area ~ 100 m2/g, mesoporous solid networks, close to 2000% weight gain in a few seconds when brought in contact with liquid, and high air permeability.
Oral

S05-187

Keller Jan-Hendrik, Altstaedt Volker

Hysteresis Measurements as a tool to monitor the non-linear mechanical deformation behavior of bead foams during fatigue loading

Technical components, such as crash absorbers in automotive industry or running shoues in sports produtcs, made by bead foams are today exposed very often to complex large scale cyclic loading conditions in combination with different environmental loadings. In order to characterize the time and temperature dependant mechanical behavior during fatigue loading, the principles of in-situ mid-curve and subsequent hysteresis evaluation are best suited. These recently furtherdeveloped tools can provide instantaneous feedbacks about the state of fatigue in the specimen or the component. In addition, using these methods, complementary information about the prevailing deformation mechanisms of the sample can be derived (e.g. linear, non-linear, failure) at any time during the test. Within this paper, the results of low density EPS and EPP bead foams (30 g / l) under several fatigue loading conditions are discussed, where non-linear mechanical behavior could be seen even at low stress amplitudes. Also the long term mechanical behavior is correlated to the actual bead deformation state via optical analysis methods.

S05-242

Walluch Matthias, Uray Anna, Holzer Clemens, Langecker Günter Rüdiger

Physical foam extrusion of polyolefin/cycloolefin copolymer blends

In foam extrusion there are a lot of possibilities, like the processing conditions, the amount and type of the used nucleating or foaming agent, to take influence on the achievable foam properties. Another approach is to change or blend the used matrix polymer. To improve the foamability of polypropylene (PP) it is often blended with LDPE, because of its higher melt strength. In this study an additional strategy to improve the foam morphology was followed. Several studies show that the combination of polyolefins and cycloolefin copolymers (COC) leads to blends with an unusual phase morphology and special properties, which may be useful for the foaming behavior for example as an improvement of the cell nucleation. In a first study it already could be shown that the foam morphology of polypropylene may be improved by blending it with COC. The aim of this study is a further improvement of the achievable foam morphology by a variation of the used polymers and the processing parameters. All samples were foamed using a grooved single screw extruder. Nitrogen was used as physical blowing agent and talcum as nucleation agent. A positive influence of COC on the foam morphology could be shown again and the reached mean cell diameter was reduced compared to the first study.

S05-244

Gensel Julia, Pawelski Christin, Altstädt Volker

Welding quality in polymer bead foams: in situ SEM study

Polymer bead foams are lightweight materials consisting of fused microcellular beads. Their multiscale structure makes bead foams, on the one hand, unique in terms of a free choice of shape combined with extreme low density, excellent thermal insulating properties, and good energy absorption properties.[1] On the other hand, fusion of the beads plays a crucial role in determining the performance and thus the application range of bead foams. Still, the question how processing affects the structure and the mechanical strength of the fused regions lacks a clear answer today. Conventional tensile tests and fracture surface analysis give some general information on the fusion strength. However, the proper understanding of the bead fusion requires local weld structure analysis and the fracture path monitoring on the nano- and microscales. In this contribution, we present an in



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situ study of the interbead failure behavior by means of tensile experiments in the Scanning Electron Microscope. This experimental study allows for direct observation of both, the cell and bead deformation, and more importantly the evolution of the fracture in space and time. Combined with Atomic Force Microscopy measurements on the weld-zone, we discuss the influence of moulding conditions on the interfacial structure and bonding quality in polypropylene bead foams. It was found that low moulding temperatures and short steaming time leads to a pull-out of polymer chains at the beads interface during the tensile test. In contrast, with increasing time and temperature, polymer chains at the interface were solidly anchored resulting in higher mechanical strength of the weld and thus, elastic stretching of the foam cells and beads and finally cohesive matrix break down. [1] D. Raps, N. Hossieny, C.B. Park, and V. Altstädt, Past and present developments in polymer bead foams and bead foaming technology, Polymer, 2015, 56, 5-19.

S05-264

Tateishi Junichiro, Taniguchi Norihiko, Nishiwaki Tsuyoshi, Sukumaran Sathish K., Sugimoto Masataka

Visual Observation of One-shot Chemical Foaming Process by X-ray Transmission Imaging

In chemical foaming process, forming mechanism of cell structure has not been revealed yet. Although visualization of foaming process is useful technique for understanding the cell structure formation mechanism, it has not been applied to chemical foaming process. In this study, visual observation of one-shot chemical foaming process was carried out by x-ray transmission imaging method at SPring-8 BL24XU. Specimen compound was composed by linear-low density polyethylene (LLDPE) containing chemical foaming agent (CFA) particle, CFA kicker and cross-linker. Foaming process progressed at sealed cavity with pressure sensor. As the experimental result, visualized image changed from homogeneous to inhomogeneous granular one. It was shown that low electron density structure was formed by gas resulting from CFA decomposition. In other words,

it was found that the cell growth occurred in the sealed cavity. Furthermore, bubble size and number increased with internal mold pressure increase. It was indicated that the generated gas by CFA decomposition was not fully dissolved to specimen compounds, and as the result, initial cell structure was constructed in cavity during chemical foaming process. Keywords: Chemical foaming process, xray imaging, cell structure, polymer foam

S05-28

TRAN Minh-Phuong, PARK Chul, Detrembleur Christophe, THOMASSIN Jean-Michel, Gong Pengjian, Buahom Piyapong, Saniei Mehdi, Kenig Samuel, Lee Seung-Eon

Reducing Thermal Radiative Conductivity of Polymeric Foams using Expanded Graphite

Thermal radiation is electromagnetic radiation generated by the thermal motion of charged particles in matter when the temperature is greater than zero. Thermal Radiative conductivity has long been recognized as an important heat transfer mechanism. In the literature, a heat transfer of 20% to40% through low density foams has been reported. Carbonaceous materials are known to be efficient infrared absorbers in order to reduce the radiative contribution in insulating materials by absorption, reflection and/or scattering. Among allotropes of carbon aforementioned, graphite has great potential in using as efficient infrared attenuation agents. In addition to its cost effectiveness and easy processability, the expanded graphite was expected to absorb thermal radiation more efficiently than carbon nanotubes with the same volume content. Using the Rosseland model, we quantitatively undertook a first-time study of how expanded graphite significantly reduces thermal radiative conductivity. We found that particle-added polystyrene foams with a 0.018%vol of expanded graphite nanoplatelets and a 25-fold volume expansion ratio could block 92% of the overall thermal radiative thermal conductivity. The short wavelength i

S05-413



Foaming behavior of Novatein and blends with polyethylene compatibilised by maleic anhydride

Novatein® Thermoplastic Protein (NTP) is a biodegradable and compostable bloodmeal-based thermoplastic which can be extruded and injection moulded. This research explores the suitability of NTP for extrusion foaming, which would help supplement demand for biodegradable packaging materials. The foaming ability of NTP was expected to be limited by the material which has a high extensional viscosity, so it was blended with up to 40 wt% low density (LDPE) or linear low density polyethylene (LLDPE) with 10 wt% polyethylene grafted maleic anhydride (PE-g-MAH) compatibiliser. Foaming was investigated using two twin screw extruders (L/D 25 and 40) and a BOY 35A single screw injection moulder with an L/D of 44. Extrusion foaming using the twin screw extruders produced foams with irregular cells from 0.5 to 4 mm in diameter with low expansion ratios <1.8. Increasing NTP content further lowered the expansion ratio of the blends. Foaming with sodium bicarbonate as a blowing agent produced a consistent cellular morphology of cells <0.2 mm in diameter, but similar expansion to blends without blowing agent. Both extruders were unable to produce a desirable foam which was attributed to insufficient pressure drops across the dies and the loss of evolved gases through the feed hoppers. Foaming using the BOY 35A was successful. Free expansion of the material was enabled by withholding the screw from the mould. A preliminary foaming window for NTP was developed such that NTP alone was able to foam with an expansion ratio of around 4 (density of 0.3 g/cm3). The foam exhibited a fibrous open-celled network, similar to those reported in literature for extrusion foamed Thermoplastic Soy. Blends of NTP with any of the previously mentioned additives resulted in a lower degree of foaming than straight NTP. Most importantly it has been shown that NTP can be foamed without requiring additional blowing agents, blending or rheological modification. Keywords: Free Expansion Foaming, Single Screw, Protein Bio-polymer, Polyethylene, Compatibilised Blend, Thermoplastic.

S05-427

Jariyakun Kotchaporn, Pomrawan Thongchai, Aussawasathien Darunee, Hrimchum Kittipong, Yeetsorn Rungsima, Prissanaroon-Ouajai Walaiporn

Preparation and Properties of Low Density Polyethylene-Activated Carbon Composite foams

The aim of the present work is to develop composite foams based on low density polyethylene (LDPE) and activated carbon (AC) for ethylene gas adsorption. Ethylene gas is the main cause, accelerating the ripening of ago-products. Therefore, LDPE-AC composite foams may have a potential to be used as packagings to deaccelerate the ripeness and protect ago-products from impact damages during packaging and transportation. containing AC was LDPE foamed with azodicarbonamide (ADC), an exothermic chemical foaming agent, through an extrusion process. The effect of ADC contents (1, 3, 5, and 7% by weight) with 5% by weight of AC on the cellular structure, void fraction, cell density, thermal and mechanical properties, and crystallinity of LDPE-AC composite foams were investigated. The cellular structure, cell density, and the void fraction were strongly dependent on the ADC contents. The average cell size and density of the LDPE-AC composite foams were reduced as the content of ADC increased. Maximum reduction of density by 28% was achieved when ADC was applied at 7% by weight with the average cell size of $< 500 \mu m$ and at a void fraction of 28%. However, larger content of ADC led to LDPE-AC composite foams with lower tensile strength as well as impact strength, as a result of the formation of thinner cell walls. The % crystallinity and thermal properties such as crystalline temperature (Tc), melting temperature (Tm), and decomposition temperature (Td) insignificantly changed as the ADC content increased. The influence of AC dosages (5, 10, 15, and 20% by weight) with 7% by weight of ADC on the properties of LDPE-AC composite foams will be further investigated. The ethylene gas adsorption capacity will be determined as well.

S05-445



Mitrias Christos, Hulsen Martien A., Anderson Patrick D.

Simulation of interacting bubbles with multilevel adaptive local refinement

The interaction of bubbles during manufacturing process can greatly affect the final properties of a product. That can be done in many different ways, an essential one is the changes in bubble shape that can affect the flow. The distance between interfaces of the bubbles can get up to five decades smaller than the original radius and thus making simulations very challenging. To achieve this, a locally refined mesh which can adapt with deformation and movement of the bubbles is required. To describe the flow dynamics we assume that inertia can be neglected and that the volume of the fluid remains constant. For now, we study the case of Newtonian fluid. The interface between the bubble and the fluid is modeled as a sharp interface and we apply appropriate boundary conditions. The resulting equations are discretized in space using the finite element method employing a mesh of quadratic triangles for the bulk, whereas the interface mesh consist of quadratic lines while maintaining conforming geometry. For the time discretization second order backwards differencing is used. Remeshing is performed when the mesh becomes too distorted. The interface mesh is refined by splitting elements into two new while the rest of the volume is refined by locally defining the element size in Gmsh. For each element level the parent and the sibling element is stored. This way it is possible to move back and forth through element levels easily. To be able to study the bulk rheology of a suspension of bubbles we apply a periodic meshing method where a small number of bubbles could represent the whole system that contains a of bubbles. After the field huge number computation, the integration of stresses is performed over the fluid domain in order obtain the apparent viscosity. Studying the rheology can help us control the material properties and the final product properties by affecting the behaviour of the material during the manufacturing process.

Hopmann Christian, Kreimeier Suveni, Schoengart Maximilian

Laser Transmission Welding of Foamed Thermoplastic Injection Moulded Parts

The laser transmission welding is a suitable way to join parts which have been produced in structural foam injection moulding. Besides a reduced weight and density such parts show a reduced cycle time as well as improved size accuracy. Until now there are no empirical values regarding the laser transmission welding of foamed injection moulded parts. For the use of the laser transmission welding process on a larger scale it is important to acquire knowledge in how far the structure of the foam influences the welding process, the bond strength and the structure of the joint. This knowledge allows an application-specific adjustment of the injection moulding process and the joining process. As part of a research project the dependence of the foam structure to the injection moulding parameters have been determined using a breathing cavity. In this way it is possible to produce parts which have a defined thickness of the surface layer as well as specified average cell size. The integral foam parts are analysed via light microscope, where it can be shown that the injection flow rate has a major influence on the cell structure and the injection time has a significant influence on the thickness of the surface layer. Furthermore the opening speed while mould breathing has an influence on the cell size as well. In addition to these results the transparent parts have been investigated regarding their transmission properties to show that the cell structure influences the optical path of the laser beam and therefore the intensity distribution. In further research the welding suitability of foamed parts is investigated. For this purpose the energy input into the material is varied to create process windows and to determine suitable process parameters for the welding process. In addition it is necessary to research the welding pressure since a high pressure can expel the melt from the joining area and destroy the cell structure.

S05-461

S05-467



Ouali Ahmed-Amine, Rinberg Roman, Nendel Wolfgang , Kroll Lothar, Siegel Carolin , Buchelt Beate , Wagenführ Andre, John Rico , Trommler Katja, Schreiter Katja, Spange Stefan

Natural Unidirectional Sheet Processes for Fibre Reinforced Bioplastics

Technical Natural Fibre semi-finished products are mainly used in lightweight automotive components as random fiber mats which are often combined with petrochemical matrix resins for large series production process. However, random fiber arrangement and limited fiber length restrain the complete utilization of the material-inherent strength reserves of natural fibers. With high-levels of petroleum-based plastics (about 20-50 wt -%) in the structure, these applications have a clear potential in terms of eco-friendliness and sustainability. The development of new fully biobased composites and efficient manufacturing methods suitable for series processing is the purpose of the current sub-project C4 "Flexible textile / plastics processes with renewable raw materials" in the framework of the Excellence Cluster MERGE EXC 1075, funded by DFG Forschungsgemeinschaft). A (Deutsche highefficiency of mass-production, in terms reproducibility and flexibility requires the performance of successive steps in the manufacture semi-finished and final products. The of appropriate process line comprises the steps of the preparation of the thermoplastic matrix sheets (such as from Bio-polyethylene or Bio-polyamide) and a specific chemical modification of the reinforcing materials (wood veneer and unidirectional flax fibers) on the concept of a continuous production of discontinuous or unidirectional reinforced Natural Fibre Composites (NFC) prepregs. Moreover, the shaping of hybrid lightweight structures from NFC prepregs makes possible the incorporation of these innovative technologies into new concepts and potential applications in several fields such as automotive industry or sport equipment. The mechanical properties profile of the flax - natural unidirectional sheet for fibre reinforced bioplastics has been here studied in detail with press-engineered samples and has confirmed their high application potential

as an alternative to glass fiber-reinforced composite sheets.

S05-486

Cafiero Livia, Oliviero Marica, Landi Giovanni, Sorrentino Luigi, Sorrentino Andrea

Preparation and characterization of conductive foams based on PBS/carbon nanofibers composites

Conductive polymers combine the attractive properties associated with conventional polymers and unique electronic properties of metals or semiconductors. Recently, conductive polymeric foams have aroused considerable research interest owing to their unique properties over their bulk counterparts. Large surface area, lower density and higher specific properties make them promising candidates for broad applications in energy conversion and storage, sensors, actuators, and biomedical devices. This work reports on the preparation and characterization of novel conductive polymeric foams based on а biodegradable polymer (Polybutylene succinate, PBS) and carbon nanofibers (CNF). Foaming has been performed on PBS/CNF composites using a batch process by using supercritical CO2 as blowing agent. The control of foaming parameters prepare foams with allowed to tailored morphologies, and cellular structures with macro to micro sized cells were obtained. An in deep discussion about the general design rules, advantages, and also the actual limitations of such novel conductive polymeric foams are provided. Results demonstrate their potential applications as active electrode materials for next-generation biodegradable energy storage.

S05-489

Abbasi Mahdi, Faust Lorenz, Riazi Kamran, Wilhelm Manfred

Foaming of model linear and branched polystyrenes

The presence of long chain branching (LCB) topologies in polymer molecules improves the

112



processing properties of polymer melts particularly in extensional flows. Bubble grows phenomenon in foaming process imposes a biaxial stretching on the surrounding molecules. deformation Therefore extensional properties of polymer melt have distinct effect on the bubble growth rate and final size of the bubble. Many studies have been conducted on the effect of LCB on the foam characteristics, however well-characterized long chain branched model structures have not been used in these studies. We synthesized monodispersed comb polystyrene (PS) using the anionic polymerization method to control the molecular weight of the back bone, Mw,bb, and branches, Mw,br, as well as number of branches per molecule, Nbr. Two groups of long chain branched PS were synthesized. One set with constant molar ratio of back bone to side arms about 1/3 to 2/3, respectively, where Mw,bb = 95 kg/mol was fixed in all samples. In the other sets of branched PS, Nbr was changed between 0 to 63, while Mw,bb = 275kg/mol and Mw,br = 42 kg/mol kept constant in all samples. Foaming experiments were performed in an autoclave system under CO2 as foaming agent at a constant pressure of 180 bar and pressure release rate about 40 bar/s. The temperature varied from 100 – 145 °C. Foaming analysis showed that presence of sparsely branched structure (Nbr = 3) increases the nucleation density (1E9 - 1E10 cell/cm3) by a factor 100 compare to the linear monodisperse PS (1E7 - 1E8 cell/cm3), where polydisperse PS (PDI > 1.3) reached only a nucleation density 1E6 - 1E7 cell/cm3. Increasing the branching to 63 branches per molecule has not distinct effect on the nucleation density, however the stability of the foam was improved and the volume expansion ratio enhanced to 35 at 145 °C. Cell sizes decreased from 300 micro meter for polydisperse PS to 30 and 15 micro meter for monodisperse and long chain branched PS respectively.

S05-504

Song Seung A, Kim Seong Su

Double percolation effect on electric and thermal conductivity of the carbon foams derived from phenolic resin and mesophase pitch particle. The phenolic foams formed with pitch path were fabricated by using microwave and were carbonized using a furnace in the nitrogen condition. Thermal and electric conductivity were measured by hot wire method and four point probe, respectively. The physical property of carbon foam were characterized by measuring compressive strength. The cyclization index and crystal phase of carbon foam were observed with Xray diffraction (XRD) and Field emission scanning electron microscope (FE-SEM) images. The morphological observation of the double percolation effect was confirmed by transmission electron microscopy (TEM) analysis.

S05-514

Puentes Parodi Jaime Alejandro, Kuehnert Ines, Leuteritz Andreas

Artificial Aging and Failure Modes of TPU-Metal Hybrid Composites

Thermoplastic elastomers are being continuously used in industrial and commercial applications due to its versatility in terms of a wide range of mechanical properties and also because they can be easily processed. One of the main uses of these materials, are as bumping elements in polymermetal composites in the automotive or aeronautical industries. The soft-elastic polymer can also improve impact resistance and balance thermal deformation of two components with dissimilar thermal expansion coefficients. However, adhesion of polymers onto metal substrates is a task which has not been completely solved, especially in terms of long term applications and/or in humid or corrosive environments. The idea behind this research is to investigate the aging and failure modes of polymer-metal composites. Samples were prepared by applying an adhesive coating to a metal substrate with three different surface treatments which were subsequently cured in an oven for 150°C. Then, the coated plate is overmolded with a TPE, composites are afterwards subjected in a climate chamber to different



32nd PPS International Conference 2016, Lyon, France temperature and humidity conditions and evaluation of the progressive aging and final rupture of the component is done mainly by microscopy, FTIR and mechanical tests.

S05-552

Li Cong, Feng Lianfang, Gu Xueping, Zhang Cailiang, Hu Guohua

A new understand on the formation mechanism of bimodal polymer foams by a two-step depressurization process

Polymer foams containing a relatively larger cell size and a relatively smaller cell size, called as bimodal foam, have attracted much attention in industry and academia because they can combine the advantages of smaller cells which have better mechanical performance and thermal good insulation with larger cells that maintain a low bulk density. In this work, polystyrene (PS) was adopted as a model polymer to probe the formation mechanism of bimodal cell morphology by a twostep depressurization process using carbon dioxide (CO2) as a blowing agent. A static foaming visualization system with a high-speed camera and active heating controls was used to in situ observe the morphology development in the two-step depressurization process. Results show that at the holding stage between the two depressurization steps, cells formed in the first depressurization step continue to decrease in size instead of coalescing into larger cells as suggested by a previous work. Moreover, a new mechanism for the formation of bimodal foams by two-step depressurization is put forward. Based on this new mechanism, it is easy to control the amounts and sizes of big cells and small ones.

S05-557

Volpe Valentina, De Filitto Martina, Klofacova Vera , De Santis Felice, Pantani Roberto

Effect of processing conditions on the cell morphology distribution in foamed injection molded PLA samples

Foam injection molding uses physical blowing agents under high pressure and temperature to produce structural foams having a cellular core and a compact solid skin. This technology is particularly interesting for biodegradable polymers, which often present a very narrow processing window, with the suitable processing temperatures close to the degradation conditions. The addition of a supercritical gas can lead to the reduction of both the viscosity and the glass transition temperature of the polymer melt, which therefore can be injection molded adopting lower temperatures and pressures. In this work, the effect of different processing parameters on foam morphology of Poly(lactic) Acid, PLA, was studied. In particular, two commercial grades of PLA having different rheological properties were adopted to obtain foamed parts by injection molding process with nitrogen as physical blowing agent. For both PLA grades, the effect of mold temperature on the resulting cell morphology was assessed. Furthermore, the mold was opened soon after filling in order to let the foam expand in the thickness direction. The effect of the opening speed and of the cavity thickness after mold opening on the morphology and mechanical properties of foamed parts were analyzed.

S05-635

Long Kevin N, Roberts Christine Cardinal, Mondy Lisa A, Rao Rekha R

Depressurization and Warpage in Polyurethane Foams

We are investigating and endeavoring to simulate how manufacturing conditions result in the of moderate high warpage and density polyurethane foam components (10-40 pounds per cubic foot). Our previous year effort focused on high density chemically blown PMDI foams, which were below their glass transition at room temperature, in which we hypothesized that the manufacturing stresses and viscoelasticity of the matrix were the main drivers of dimensional change in foamed components. In this work, however, we now examine the effects of excess CO2 depressurization that originates from the foaming

and curing process, the role of density variation, and associated model characterization efforts. We also present improved experimental measurements of specific component manufacturing conditions and associated long-term warpage behavior. For moderate density foams, gas depressurization appears to be the dominant mode of deformation and give the correct time scale of warpage with compared our experimental data. Depressurization can be straightforwardly incorporated into our finite element cradle-to-grave framework for chemically blow foam component simulation, and we discuss varying levels of model predicted complexity and their associated responses. *Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

S05-761

Guo Peng , Xu Yaohui , Lu Mingfu , Zhang Shijun

Effects of saturation temperature/pressure on melting behavior and cell structure of expanded polyethylene bead

The expanded polyethylene (EPE) beads with microcellular structure were prepared by an autoclave-based batch foaming process using nonsupercritical CO2 as the foaming agent. Herein, smaller PP micropellets (~1mm) were obtained from ethylene-1-hexene and ethylene-1-butene copolymer resin by underwater micro-pelletizer system. The results from differential scanning calorimetry indicated that the double melting peaks of beads moved to higher temperature with increasing saturation temperature and pressure. The kind of comonomer did not exert noticeable influence on the double melting behaviors. The relationship between cell morphology and saturation temperature/pressure of EPE beads are discussed preliminarily by scanning electron microscope.



Poster

S05-132

Shaayegan Vahid , Park Chul B.

Cell Nucleation and Growth Mechanisms in Foam Injection Molding

We investigated the cell nucleation and growth mechanisms in various foam injection molding processes using an in-situ visualization technique. We designed and manufactured a visualization mold, equipped with cavity pressure transducers, which enabled us to observe the foaming phenomena throughout the entire process. Polystyrene and polypropylene were used as the resins, and carbon dioxide was used as the blowing agent. Talc was used as the nucleating agent. To demonstrate the effects of the processing conditions and materials on cell nucleation in the mold, three sets of experiments were carried out: (i) short-shot (low-pressure) foam injection molding without gascounter pressure, (ii) full-shot (high-pressure) foam injection molding without gas-counter pressure, (iii) full-shot foam injection molding using gascounter pressure. We identified the major cell nucleation mechanisms in low-pressure and highpressure foam injection molding processes, with and without gas-counter pressure. We visually demonstrated the effect of talc on cell nucleation in polystyrene, as well as the effect of the formed crystals on cell nucleation in polypropylene.

S05-199

Liao Xia, Xu Hao, Bai Jianwei, Yang Qi, Li Guangxian, Park Chul B

Effects of Viscoelastic Properties on the Foam Morphology of Silicone Rubber Using Supercritical Carbon Dioxide

Silicone rubbers are a special kind of elastomers, which are based on polyorganosiloxanes with a high molecular weight. The backbone is siliconoxygen (Si-O) bond and organic groups, which is directly attached to the silicon atom via siliconcarbon (Si-C) bonds. This unique structure results in silicone rubbers with superior performance properties, including superb chemical resistance, good electrical insulation capacity, and excellent ultraviolet and ozone resistance. Silicone rubber foams combine the characteristics of silicone rubber and foam materials, such as good resilience, high thermal stability, shape conformity, low density, and light weight. Hence, silicone rubber foams have been widely used in many fields such as thermal shielding, vibration mounts, and press pads. Solvent and chemical foaming methods are mostly used in foaming silicone rubbers. In recent years, supercritical carbon dioxide (scCO2), as a new kind blowing agent, has been broadly investigated in the microcellular foam production because of its unique properties. The viscoelastic properties of silicone rubber play a vital role in the supercritical carbon dioxide (scCO2) foaming process. This paper firstly investigated the effect of silica content, saturation temperature and pressure on viscoelastic properties of silicone rubber compounds. Further, the cellular morphology of silicone rubber foams generated by scCO2 was investigated with the rheological analysis, which will be helpful on uncovering the connection between the cellular structure and the viscoelastic properties. This study could provide an environmentally-friendly and convenient way to better control cellular morphology of rubber by adjusting experimental conditions.

S05-210

Tor-Świątek Aneta

Properties and structure analysis of polymer compositions obtained in cellular injection moulding process

Currently produced polymer products, because of physical, mechanical and functional properties are made from solid thermoplastic materials by conventional injection moulding. In order to make shapes diphase structure i.e. plastic-pores conventional injection moulding must be replaced with the cellular injection moulding. This occur through the change of process conditions as



temperature of particular plasticizing system zones and temperature of the mold and owing to inserting into plastic blowing agent (porophor). Porophor increase its volume repeatedly and then ensue change of the product structure from solid into cellular along the whole or partial (solid topcoat and a cellular core) section. Cellular injection moulding rest on inserting into the input plastic the blowing agent, i.e. a substance which in the transformation process boils or decomposes under increased temperature, emitting gas products which cause changes in the structure of the plastic. As far as blowing agents are concerned, the type and quantity of inserted porophors play significant role, inasmuch as they exert influence on the final density of cellular plastic and determine the choice of cellular method. The change of the polymer structure effects in obtaining new physical and functional properties of the product i.e. reduced and wear of the product, improved mass dampening properties and reduced processing contraction and low water and oil absorptivity. Lower density of the product caused decreasing of polymer material consumption with simultaneous reduction in their production costs. The article presents research of selected thermoplastic materials modified with both microspheres and blowing agent in injection moulding. During the process the amount of modifiers was changed. Studies involve measurements of physical and mechanical properties and structure analysis.

S05-393

Liu Pengju, Bai Shibing, Wang Qi

Preparation of Halogen-free Flame Retardant Poly (vinyl alcohol) Foam through Thermal Processing

This paper reports a novel halogen-free flame retardant poly (vinyl alcohol) (PVA)/aluminum hydroxide (ATH) composite foam prepared through thermal processing, using water as the blowing agent. PVA has good comprehensive properties such as good mechanical properties, biocompatibility and solvent resistance, but its melting point is close to the decomposition temperature, leading to the difficulty in thermal processing. Based on intermolecular complexation water as the blowing agent. However, the high flammability of PVA foam, owing to its chemical composition and porous structure, is its shortcoming. It is a big challenge to prepare the halogen-free flame retardant PVA-based foams. In this study, the environmental friendly ATH was selected as the main flame retardant for PVA, combining the heat-absorbing action of bound water formed in PVA and the synergistic effect of aluminum phosphinate (AP), a novel halogen-free flame retardant PVA foam was successfully prepared. The PVA/ATH/AP composite foam with addition of 53.3% ATH and 2.2% AP reached LOI value of 41% and UL94 V-0 rate, due to a more compact and continuous char layer generated by AP in the char-forming reaction. The apparent density, expansion ratio and cell size of prepared foam were 0.18 g/cm3, 14.1 and 70 µm, respectively. The influence of water content on melt viscosity, foam structure and mechanical strength was also studied, indicating that relatively high melt viscosity benefited a good quality foam structure. This work is supported by Specialized Research Fund for the Doctoral Program of Higher Education of China (20120181130010).

and plasticization, we have realized the thermal

processing of PVA and prepared PVA foam using

S05-442

Leuteritz Andreas, Below Heiko

Cyclic stress resistance of polyurethane from plastic jacket pipes

District heat pipes are prepared from steel pipes, which are surrounded by rigid polyurethane foam and covered with a polyethylene casing. Although such kind of plastic jacket pipes are in service for more than 50 years, there is less known concerning the aging behavior of such parts under use. Due to thermal expansion of the steel pipe cyclic stresses have to be transferred to the soil additionally to thermal and oxidative degradation of the material. The aim of this project is to describe generally the behavior of plastic jacket pipes during the time of use in order to allow secure investment planning. First results on degradation due to an additional effect caused by cyclic stresses will be presented. 117



S05-513

S05-604

Shigeta Tomohiro, Ohshima Masahiro

Mathematical Modeling and Visual Observation of a Chemical Batch Foaming and Crosslinking of Polymer System

Department of Chemical Engineering, Kyoto University 615-8510 This study focuses on an understanding the mechanism of chemical foaming process of polymer, where the crosslinking reaction simultaneously occurs in course of heating. Mathematical modeling of the chemical foaming behavior of crosslinking polymer was developed and numerical simulation was conducted for compare with the visual observation experiment. Using a temperature controlled view-cell with an optical microscope, the visual observation experiments of the chemical foaming process were conducted for observing and analyzing the bubble nucleation and growth behavior in crosslinking polymer. The experiments showed that the effects of processing temperature (heating rate), the reaction kinetics of CBA decomposition, and the viscosity change in polymer on the nucleation time and the growth rate of CBA-blown bubbles were significant, the bubble nucleation occurs at the site of CBA in course of heating. According to the experimental results, the gas generated from CBA decomposition directly produces the bubbles. Based on the observations data, a set of mathematical models of bubble nucleation and growth of chemical foaming process was developed. The cell model with influence volume region was employed as a basic of the foaming model. To determine the parameter values of the developed model, the reaction kinetics were measured by using thermogravimetric analysis (TGA) and the change in viscosity of polymer due to the crosslinking reaction was also measured. The kinetic reaction model and temperature dependent viscosity models were developed to accommodate the foaming gas generation rate and viscositycause-bubble suppression. The developed models are not perfect, however, some aspects of chemical foaming in course of cross--linking the polymer could be simulated.

Javadi Azizeh, Vaziri Nasab Elham, Garmabi Hamid

Effect of Foaming Conditions on PLA/Starch/Nano calcium carbonate nanocomposite foams structure

In his research, the influence of foaming conditions on PLA/Starch/NCC nanocomposite containing epoxidized soybean oil (ESO) foams is investigated. Hybrid samples were mixed in an internal mixer at 180 °C for min. of 12 Nanocomposite PLA/starch/ESO/NCC (75/12.5/12.5/4) were saturated in an autoclave at room temperature using a pressure of 100 bar for 8 hour. Then the samples were transferred to silicone oil bath and they were foamed at 75, 90 and 105 °C for 10, 20 and 40 s respectively. The result showed that the increasing in time and temperature of foaming process, leads to void fraction enhancement. Moreover, it was found that the cell sizes increase with increasing the time and temperature too. SEM micrographs showed that in samples which were foamed at 75 °C for 10 and 20 s, the small cell size foams were formed mostly on the surface of the samples. It could be because of the low temperature and insufficient time for heat transfer from surface to the bulk of the nanocomposites. So the complete foam structure was not formed in the bulk of the sample. The maximum void fraction occurred at 105 °C, but in this condition, because of decreasing the melt strength of the samples, the cells began to collapse, and the average cell sizes increased. It seems that the best foaming condition is 90 °C for 40 s, on the basis of maximum cell densities and minimum cell sizes. The presence of nano calcium carbonate led to increase the cell nucleation and forming the uniform cell size distribution. Keywords: Nanocomposite, Poly (lactic acid), Nano calcium carbonate, Foam

S05-654

Suld Tiia-Maaja

Some Influence Factors on the Rigid PVC Foam Formation

PPS[®]32

The aim of this study is to increase the knowlege and the understanding of the influence of different additives : heat stabilizers; Oil Shale Fly Ash; CaCO3, wood flour fillers, (on their concentrations 5% 10% and 20% by weight) on the cell size, the cell density and the achievable density reduction of extruded rigid PVC foams by chemical blowing agents (CBA). Just the mention some of the most important properties of CBA the carrier polymer, the particle size and the dosage of the used reactive substance should be named. Our study showed that the relationships between the processing variables and the properties of the PVC foam are complex and should be taken into consideration on optimizing extrusion conditions for the best results. The smaller cells and a higher cell density can be reach by using lower amount (2wt.-%) of CBA. The best quality foam appeared at 1850 to 1900C melt temperature and thermostability of compound was 180 min (pH 3-5 Kongo-red scale) at 2000C.

S05-692

Chen Xingyou , Chen Yinghong, Hua Zhengkun

Preparation, Structure and Property of Halogen-Free Flame Retardant Polyethylene Foam Material

Polyethylene (PE) foam, as a flexible polymer cellular material, is widely applied in antistatic packaging, cushion and shock absorption, heat insulation, etc. However, the fatal drawback is in its high flammability. How to impart good flame retardancy to the PE foam in an environmental friendly way is an extremely big challenge. In this paper, a technology combing nucleation and carbonization flame retardancy was used in preparation of the high-performance halogen-free flame retardant (FR) PE foam. Accordingly, a novel intumescent FR system was established by using a nitrogen-phosphorus compound (NP-IFR) as the main flame retardant and a nitrogen contained compound (NCR) with double functions of nucleation and carbonization as the synergistic char-forming agent. In order to verify the nucleation role of NCR played in the foaming of PE, the effect of NCR on foaming behavior of pure PE and FR PE system was firstly investigated. The results show that the NCR shows excellent

nucleation effect on PE foaming. Compared with PE foam without NCR, the one contained NCR has much lower density, less big cells formed and more uniform cell size distribution. Meanwhile, in the presence of NCR, the foaming performance of the FR PE material with high NP-IFR loading was substantially improved. Then, the effect of the NCR on flame retardancy of the NP-IFR incorporated PE foam was also investigated. The results show that the addition of NCR significantly improves the flame retardancy of FR PE foam material. Obviously, the introduced NCR shows both excellent nucleation and synergistic char-forming effects. The prepared halogen-free FR PE foam possesses excellent comprehensive performance with apparent density of 0.07 g/cm3, compressive strength of 0.35 MPa, expansion ratio of 14 and flame retardancy of HF-1 level (ASTM D4986-03), respectively. This work is supported by Specialized Research Fund for the Doctoral Program of Higher Education of China (20120181130010).

S05-697

Liao Shen-Kung, Lee Bing-Jhe, Wu Chung-Tes, Lai Yan-Rong, Tseng Huang-Kai

Factors Affecting the Morphology of Forming Polymers using Supercritical CO2 as a Forming Agent

In this study, we choose the five-kind of materials including linear low-density polyethylene (LLDPE), low-density polyethylene(LDPE), poly(ethylene-covinyl acetate) (EVA), polystyrene(PS) and polyvinyl chloride (PVC) to using Supercritical carbon dioxide (scCO2) as a Forming Agent. And the forming polymers were observed by macroscopic view and micrographic analysis. The effects of saturation time, foaming temperature, pressure and depressurization rate on the foam structure and volume expansion ratio were investigated. LDPE contains long chain branches, which give the melt a high elasticity, hence a high tensile strength. LLDPE can be produced by using Ziegler-Natta catalyst systems at low pressures; it has a narrower molecular weight distribution than LDPE. For experiments, polyolefin with expansion rate about 5-68% was manufactured. A rapid cooling just



downstream the die is important to solidify the structure. The die temperature allowed the control of the porosity structure. The properties of EVA copolymers are strongly dependent on the ratio of vinyl acetate to ethylene in weight, the amount of VA added to the ethylene are EVA-9%, 18% and 39% in the experiments. The results showed that EVA with the VA content increases foaming temperature will increase.VA content increases as the density is reduced. Pressure limit will decrease with increasing VA content. When the VA content is higher, its reach the minimum density need more time. When the VA content is lower, its reach the minimum density has less time. When the VA content increased, amount of carbon dioxide is increased and the expansion is larger. The forming Polymers were characterized by fourier transform infrared spectroscopy(FTIR), differential scanning calorimetry(DSC) thermogravimetric and analyzer(TGA), too. Keywords: polyolefin, poly(ethylene-co-vinyl acetate), supercritical carbon dioxide, foaming, morphology.

S05-784

Xu Yaohui , Guo Peng , Zhang Shijun , Lu Mingfu

The Study of Halogen Free Fire Retardant High Melt Strength Polypropylene: Preparation, Foaming Behaviors and Characteristics of the Foam

With the wide application of compression molded polypropylene foam (CMPPF) in many fields such as electric, construction and automotive, flame retardant will be an essential ingredient in CMPPF. Good burn characteristic are very important for CMPPF that require a fire rating such as foam used for building wall insulation or vehicle frame less weight. Intumescent Fire Retardants (IFR) are often used to meet fire ratings in resins. They work in such a way to create the porous carbon formed layer and inactive gas that will protect the resin from fire and oxygen. However, it rarely applied in molded polyolefin foams, especially CMPPF. In this paper, the flame retardant modification of high melt strength polypropylene(HMSPP)supplied by Sinopec(E02ES) was made by filling with 30% (wt) halogen free IFR. The effect of IFR on burn

characteristics and foamability of the flame retardant E02ES(FRE02ES) were studied by using limiting oxygen index (LOI), Rheoten, and cone calorimeter (CONE). Then, diverse expansion ratio flame retardant compression molded polypropylene foam(FRCMPPF)foams are prepared using FRE02ES as basic resin, using CO2 as blowing agent and using compression molding method. The effects of IFR and expansion radio on burn characteristics and cellular structure of FRCMPPF were studied by using LOI, CONE and scanning electronic micrograph (SEM). The results indicated that though the melt strength of FRE02ES reduced to 70% of the pure E02ES, FRE02ES still has good foam ability and excellent appearance foam board could be prepared in different expansion ratios (from 10.0 to 25.0). The results of LOI and CONE showed the rising expansion ratio of the FRCMPPF reduced the FRCMPPF's LOI and influence the burn characteristic. The SEM imagines of the section of samples show that the cellular structures of FRCMPPF are affected by not well dispersed IFR particle. Keywords: polypropylene foam, flame retardant, compression molded, high melt strength, intumescent fire retardant



S06- Biopolymers and Polymer from Renewable Resources

Keynotes

S06-130

Garrido Tania, Leceta Itsaso, Guerrero Pedro, de la Caba Koro

Potential of protein based-biocomposites prepared with lignin-free cellulose

Nowadays, plastic materials play an important role in almost every aspect of our daily life. However, they are not biodegradable and cause serious problems. environmental For this reason, biopolymers, such as proteins and polysaccharides, are becoming suitable alternatives. Soy protein is a potential option to reduce or even replace petroleum-based materials due to its abundance and availability. It is extracted as a by-product from the production of soy oil. Therefore, its use to manufacture added value-products can also contribute to the valorization of agro-industrial byproducts. Additionally, lignin-free cellulose can be obtained from algae waste when agar is extracted from red marine seaweeds and can be used as a filler to manufacture protein-based biocomposites. Regarding manufacture methods, the conventional techniques employed for conventional plastics, such as extrusion and injection, were used in this work to process the biocomposites in order to develop competitive materials for commercial applications. The changes observed by FTIR analysis indicated that there was a good interaction between the protein and the filler; this fact was supported by the morphology of the biocomposites, which showed no agglomeration. Furthermore, protein-based biocomposites exhibited excellent barrier properties against lipids and oxygen, highlighting the potential use of these biocomposites as food packaging.

S06-288

Tiwary Praphulla, Dawidziuk Karolina, Najafi Naqi, Kontopoulou Marianna

Reactive extrusion of poly (lactic acid): Effect of coagent type on the rheological and thermal properties

Poly (lactic acid) (PLA) suffers from poor melt strength and slow crystallization kinetics, hindering its application in various polymer processing processes like injection molding, blow molding etc. Chain extension and addition of nucleating agents are commonly used to overcome these problems. Recently it has been shown that reactive modification of PLA in the presence of a free radical initiator and a multifunctional coagent results in significantly improved melt strength, while at the same time inducing a nucleating effect. In this work melt state peroxide mediated reactive extrusion of PLA is implemented in the presence of different coagents: triallyl trimesate (TAM), trimethylol propanetrimethacrylate (TMPTMA), trimethylol propanetriacrylate (TMPTA), and pentaerythritol triacrylate (PETA). Oscillatory, extensional, thermal, and molecular weight characterizations were performed to investigate the effect of reactive extrusion on PLA. The types and amount of coagents and peroxide dosed was optimized to prepare formulations with increased melt strength and improved thermal properties. The chain branching and thermal properties of the reactively modified formulations were found be dependent on the type and amount of coagent dosed, with TAM being the most efficient in incorporating both chain branching and improving the thermal properties of PLA.

S06-331

Averous Luc

Innovative renewable systems based on aliphaticaromatic polyurethanes from different biomass.

Nowadays, the use of renewable biobased carbon feedstock is highly taken into consideration because it offers the intrinsic value of a reduced carbon footprint and an improved life cycle analysis



(LCA), in agreement with а sustainable development. Polyurethanes are more and more often biobased, since polyols and polyisocyanates biobased. Various researches can be were particularly focused on biobased polyols (i) from fermentation of biomass (white biotechnologies) or (ii) directly extracted from biomass and then chemically modified, such as the oleochemical resources. Most of the biobased PU are thermosets, however biobased TPUs (thermoplastics) have been also developed. In this presentation, we report an overview of 10 years of research @University of Strasbourg (France), on the elaboration and characterization of several innovative and biobased polyurethanes systems (PUs, TPUs and NIPUs), with controlled and organized macromolecular architectures. They are synthesized from different biobased building blocks: (i) aliphatic structures from modified glycerides, dimer fatty acids, sugarbased molecules (isosorbide,) ... (ii) and aromatic structures from lignins, tannins and furans. A large range of multiphase systems with nice properties and durable applications can be developed from these different macromolecular architectures, for a greener and durable future

S06-50

Ching Yern Chee

Kenaf Fiber Reinforced Biocomposites with Control Release Properties for Mulch Film Application

This research described the preparation of polyvinyl alcohol/kenaf fiber composites with entrapped urea. At the first stage of study, the solubility, release behavior, chemical water properties, and thermal stability of the composites were evaluated. In a wet environment, urea was released from the composites through its dissolution in water. The evidence of degradation of polyvinyl alcohol could be monitored by using FTIR spectroscopy. In addition, cracks and fungal growth on the surface of the materials could be clearly observed under the microscope. The rate of degradation could be monitored from the weight loss of the sample, which increased significantly when submerged in water. To slow down the

disintegration under conditions of excess moisture, the composite was slightly cross-linked with methylene diphenyl diisocyanate (MDI) at the second stage of the study. From the field test study, it was observed that the use of this kenaf reinforced biocomposite has successfully protected the seedlings of long bean from moisture loss. At the end of their life, the release of the the kenaf fibers from the degradation of polyvinyl alcohol matrix enable the kenaf fiber to serve as soil fertilizer to the plant. There was no any undegradable polymer waste was leave for disposal. This study showed that crosslinked kenaf reinforced biopolymer composite could serve as promising mulches to replace existing petroleum base polyethylene mulch film in the market.

S06-627

Manuspiya Hathaikarn, Thiangtham Satita

Modification of Isolated Microcrystalline Cellulose from Sugarcane Bagasse to Water-Soluble Sulfonated Cellulose

Microcrystalline cellulose (MCC) was extracted from agriculture residue of sugarcane bagasses by pretreatment under alkaline peroxide and acid hydrolysis treatment, successively, and it was further modified into sulfonated cellulose (SC). The SC was synthesized by oxidizing MCC with sodium periodate (NaIO4) in the dark condition to create dialdehyde cellulose (DAC), followed by sulfonation reaction with potassium bisulfite (KH2SO3). The ratio of MCC:NaIO4 was investigated in the first step of modification. The oxidative product was received from the ratio of MCC:NaIO4 1:1. Its FT-IR spectrum of oxidized cellulose clearly indicated the formation of dialdehyde cellulose after oxidation reaction which appeared at 890 cm-1. After that, the sulfonic acid content in subsequent sulfonation step was applied to dialdehyde cellulose in six levels. sulfonic acid contents, surface morphology, and water solubility of these treated celluloses property were characterized.Scanning electron microscopy showed a significant change from smooth surface of MCC to rough surface of SCs. The number-average molecular weight (Mn), the weight-average



molecular weight (Mw) and the polydispersity index (PDI) of these SCs were determined via gel permeation chromatography (GPC). Accordingly, the molecular weight of cellulose was remarkably increased during the sulfonation compared to that of the starting material indicated the addition of sulfonic acid group to the cellulose chain through oxidation/sulfonation reaction. The use of high amount of sulfonic acid agent led to strong increment of the Mn and Mw in comparison to low amount of sulfonic acid agent. Finally, the solubility of SC in water and structural characterization of the solubilized SCs will be carried out by means of 1H and 13C NMR spectroscopy, respectively

S06-646

Lafleur Pierre G, Karami Shervin

The impact of the development of mesomorohic phase on physical performance of PLA nanocomposites

A hot drawing process has been applied to improve the physical and the mechanical properties of polylactide nanocomposite films through the selfreinforcement of molecular structure. The structural evolution led to development of a mesomorphic molecular ordering during the stretching process. This was attributed to the predominant impact of the chain extension rate compared to relaxation rate, along with the influence of thermodynamic structural parameters. The mesophase is reflected in WAXS pattern by a diffraction peak associated with a repeated arrangement of segments, normal to the chain axis, with an intermediate lateral chain packing between the crystalline structure and the amorphous phase. The fraction of mesophase decreases with the nanoparticle content. This was interpreted by the enhanced contribution of matrix relaxation compared to deformation rate, at the stretching rate and the temperature, upon the incorporation of the nanoparticles due to the the accelerated matrix degradation with nanoparticle loading. The yield stress is enhanced in subsequent stretching process of the hot-drawn films at room temperature owing to the oriented microstructure, lied in the mesomorphic domain. Furthermore, with the development of mesophase

in hot-drawn film, the strain hardening behavior was detected in the subsequent drawing at room temperature. Then, the strain hardening occurs at a critical mesophase content since the mesomorphic domain act as physical junction. In this study, permeability was divided into diffusivity and solubility coefficients. The diffusivity decreased with the mesophase content in the hot drawn films. This was concluded that the synergistic influences of the presence of mesomorphic domain and the incorporation of the nanoparticles, in the absence of network structure, cause a considerable decrease of the diffusivity and the permeability of the hotdrawn films. The solubility was increased with the increase of nanoparticles content.

S06-716

Zhang Liqun

Design, preparation and properties of bio-based elastomer composites

products Bio-based polymer derived from renewable agricultural and biomass feedstock have become increasingly important as these sustainable and eco-efficient products bring a significant reduction in greenhouse gas emissions and saving of fossil energy in comparison with conventional pertrochemical-based materials.A series of biobased elastomersfrom large-scale produced and petroleum independentmonomers such assuccinic acid, sebacic acid, itaconic acid,1,3-propanediol, 1,4butanediol, soybean oil, glycerol, citric acid, etc have been developed by authors1-3. Same as conventional elastomers, bio-based elastomers possess low glass transition temperature, high elasticity and low strength, and this implies that they must be reinforced by nano-filler. However, they alsopossess particular and novel properties due to their characteristic macromolecular structures and aggregation structure. For example, the existence of abundant ester groups, terminal carboxyl groups, and terminal hydroxyl groups in bio-based polyester elastomers endow polar fillers like silica disperse homogeneous in the elastomer matrix without surface modification. Even though, for incorporation of easily agglomerated fillers like graphene4 and layered silicates5, elaborately



dispersion and interfacial tailoring technique is necessary. Combined with specific structures and relevanteffective composite technology, bio-based elastomer composites exhibit versatile potential applications in tire tread, PLA toughener, thermoplastic vulcanizates, biodegradable and biocompatible materials, and smart materials (electricalactuator, shape memory materials, etc.). [1]Wang RG, Ma J, Zhou XX, Wang Z, Kang HL, Zhang LQ, Hua KC, Julig K. Macromolecules. 2012, 45, 6830-6839 [2]Wei T, Lei LJ, Kang HL, Qiao B, Wang Z, Zhang LQ, Coates P, Hua KC, Kulig J. Advanced Engineering Materials, 2012, 14, 112-118 [3]Wang Z, Zhang X, Wang RG, Kang HL, Qiao B, Ma J, Zhang LQ, Wang H. Macromolecules. 2012, 45,9010-9019

S06-744

Carvalho Antonio Jose Felix

New processing techniques to produce blends and composites of high polar biopolymers with hydrophobic polymers

The combination of high hydrophilic materials with hydrophobic or non polar materials such as cellulose nanofibers with polystyrene in composites and chitosan with poly(lactic acid) in polymer blends has been one of the most relevant challenges in materials processing because of its very different nature and due to the growing interest in blends involving biopolymers and composites with nanocellulose fibers, among other materials such as inorganic nanofillers. The problem is related to the fact that these materials are usually processed in water as solution (p.ex. chitosan) or suspension (p.ex. nanocellulose) and when dried for do not melt in the case of chitosan or form hard agglomerates in the case of nanocelluloses. To overcome these difficulties we develop a process where water is used as a processing agent and is eliminate only when the non polar component is combined with the filler or with the water soluble polymer. The processes make use of emulsions and suspensions in order to conduct most of the process in water environment. The process develop are green and lead to very good dispersion that are absent of agglomerates. Composites of polystyrene

and nanofibers of cellulose and polythiofenes and titanioum dioxide nanoparticles were also produced successfully. Blends or chitosan and thermoplastic starch which are high hydrophilic polymers where combined with polylactic acid and polycaprolactones with very good results in thermos of mechanical properties.



Oral

S06-106

Gallos Antoine, Beaugrand Johnny, Paës Gabriel, Allais Florent

Influence of the chemical structure of ferulic acid derivatives on the aspect ratio of hemp fibres and on the mechanical properties of biocomposites materials by Confocal Raman Imaging

According to the global trend in the world, many studies are conducted to valorize the plant biomass at its best potential. On one hand, a significant part of these works is focused on the enhancement of thermal and mechanical properties of composites reinforced with lignocellulosic fibres. On the other hand, a huge part of the lignin fraction produced by wood and paper industries should be valorized throughout chemistry for the synthesis of high value-added compound instead of being burnt for the production of energy. In this work, we use ferulic acid, which can be obtained from lignin, and its derivatives, to influence the aspect ratio of lignocellulosic fibres incorporated in biocomposites materials in order to impact the properties. The aspect ratio being one of the key parameters for mechanical thermoplastic's fibre reinforcement. Ferulic acid derivatives are synthesized by enzymatic chemistry following a green process and are afterward pulverized on hemp fibres. These pretreated fibres are incorporated in polycaprolactone matrix during a single screw extrusion process. Fibres are extracted from the polymer by Soxhlet and analyzed to measure the aspect ratio distribution after process. Tensile test specimens are injected and mechanical properties are measured. Characterizations are also conducted the thermal properties of the measure to composites. Crude products are analyzed by Raman spectroscopy to define their spectral profile. As a result, we have determined by Confocal Raman Imaging the influence of the chemical structure of the ferulic acid derivatives on the aspect ratio of the fibres and on the thermomechanical properties of the composites after the extrusion process. Although this imaging technique require an advanced expertise level in image processing and expensive device, the reported method based on confocal Raman allows quantitative analysis and permits high-throughput screening of each individual component within a blend.

S06-120

Ramezani Kakroodi Adel, Kazemi Yasamin, Ding Weidan, Ameli Aboutaleb, Park Chul

The effects of morphological manipulations on the characteristics of polylactic acid (PLA)/nanofibrillar nylon-6 blends

Polylactic acid is one of the most promising biobased candidates for the substitution of the traditional petroleum-based polymers. However, PLA has numerous drawbacks (e.g. brittleness and low melt strength) which limit its use in different applications such as packaging. In this work, we propose the concept of in situ microfibrillation as a means to improve the properties of PLA/nylon-6 blends. PLA/nylon-6 blends were produced by a simple melt extrusion process followed by a hot stretching step which transformed the nylon-6's spherical domains into microfibrils with diameters of nearly 200 nm. Morphological characterizations of the compression molded samples confirmed that the nylon-6 phase was in the form of fully-stretched and well-dispersed microfibrils. The inclusion of the nylon-6 phase, in both spherical and microfibrillar shapes, improved the crystallization behavior of the PLA while the improvement was more substantial in the case of blends with microfibrillar nylon-6 domains. This improvement in the crystallization behavior of PLA led to an increase in its tensile properties. Crucially, it was observed that both the stiffness and the deformability of the PLA were improved which led to a significant increase in its tensile strength. Studying the linear viscoelastic behaviors and the extensional viscosities of the compounds showed that the physical entanglement of the long nylon-6 microfibrils led to their rheological percolation (gelation), which substantially improved the PLA's



melt strength and elasticity. The gelation occurred at a nylon-6 concentration of nearly 2.5 wt.%. The facile and cost-effective process which was used for the production of the microfibrillar PLA/nylon-6 blends makes this approach ideal for the improvement of PLA as a competitive candidate in the packaging industry.

S06-123

Frache Alberto, Battegazzore Daniele, Peduto Nicolangelo, De Sio Anna

Development of bio-based polyamides: films extrusion and composites preparation with natural fillers

Bio-based Polyamides (PA6.10, PA10.10 and copolymer PA6.10/6.6) were synthesized by Radici Chimica using renewable resources. Films 50-100micron thick were extruded and mechanical and barrier properties were carried out in order to check the packaging performances. Silica extracted from rice husk and organically modified montmorillonite (Cloisite® 30B) were used in order to obtain biocomposites with improved mechanical performances. The composites were prepared using a twin-screw extruder. A detailed morphological study in terms of adhesion, distribution and dispersion of fillers into the polymeric matrices were carried out. In particular was found a good dispersion degree of fillers in the PA6.10/6.6 copolymer. Thermal, mechanical and thermomechanical properties were studied and the Young modulus was increased for the composites in particular with the synergistic effect of silica and Closite 30B used together. Finally in the case of PA6.10 a significant value of storage modulus was obtained also at high temperature (160°C).

S06-136

Walallavita Anuradha Sammanie, Verbeek Casparus Johannes Reinhard, Lay Mark Christopher

Compatibilizing Effects of Itaconic Anhydride on Blends between Poly(lactic acid) and Novatein Thermoplastic Protein Novatein®, a protein-based thermoplastic, was blended with poly(lactic acid) (PLA) using reactive extrusion to produce a cheap and degradable material with improved mechanical properties over neat Novatein. Various compositions of Novatein/PLA were prepared with and without a compatibilizer, PLA grafted with itaconic anhydride (PLA-g-IA). Novatein had a tensile strength of 17.4 MPa while a blend of Novatein with PLA-g-IA at 50 wt. % loading increased the tensile strength to 34.4 MPa. All Novatein and PLAg-IA blends showed an improvement in elongation at break (i.e. from 0.74 to 1.88 at 50-50 composition). Scanning electron microscopy revealed that adding compatibilizer reduced the presence of cracks and voids in fracture surfaces, resulting in a more homogenous microstructure. In the 50/50 blend, the Novatein phase became finer and more evenly dispersed within the PLA matrix. The broad tan δ peak for compatibilized blends decreased in dynamic mechanical analysis of the 50/50 and 30/70 blends due to higher interfacial interaction between Novatein and PLA. Novatein is a hydrophilic polymer and absorbs 50 wt. % of water in just 24 hours, but blending with PLA reduced water absorption to less than 20 wt. %. Blending Novatein with PLA can widen its use in many agricultural and packaging applications, but require itaconic anhydride as compatibilizer.

S06-144

Düngen Matthias, Keller Stefan, Koch Michael

Modeling approach for the degradation mechanisms of PLA resulting from processing

Polylactides (PLA) are processed in single or multiple screw extruders where thermal and mechanical stresses occur. These stresses can lead to melt degradation in terms of molecular weight loss. The susceptibility of PLA to degradation during processing is well known. Studying this degradation on extruders relative to varying key influencing factors such as temperature, shear rate or residence time is complicated due to the interdependency of these factors and varying screw geometry, melt temperature, pressure and melt velocity gradients along the screw channel(s).



Therefore experiments with a rotational rheometer were performed. They allow a differentiated examination of shear and thermally induced degradation. The experiments show a considerable effect of the shear rate, temperature and residence time on melt degradation. Mathematical models describe the non-linear degradation mechanisms found in the rheometer experiments. An approach to transfer the rheometer results to a single screw plasticizing extruder (SSE) is presented. It shows a good qualitative agreement. Screw design and oper-ation point of the extruder are found to have a significant influence on the degradation of the processed PLA. During processing in a SSE a wide distribution of processing histories for different particles in the screw channel will occur due to longitudinal and transversal mixing of the melt. Thus a distribution of residence times, thermal and shear stresses has to be taken into account when using the models derived from rheometer experiments. Results of this model are presented.

S06-151

Xie Xu-Long, Zhong Gan-Ji, Li Zhong-Ming

Relationship between Crystallization and Thermal Property of Injection-molded Poly(Llactic acid) under the Coexistence of Carbon Nanotubes and Shear Flow

Effect of the coexistence of carbon nanotubes (CNTs) and shear flow on the crystallization of injection-molded poly(L-lactic acid) (PLLA) was explored in the present work. The wide-angle X-ray diffraction (WAXD) results show that CNTs increases the crystallinity of injection-molded PLLA with the mold temperature set at 40 or 80°C, due to its nucleation effect. However, CNTs decreases the crystallinity of PLLA with the mold temperature 100°C. Meanwhile, shear flow promotes the crystallization of PLLA significantly. For the coexistence of CNTs and shear flow, shear flow promotes the crystallization so significantly that the nucleation effect of CNTs is negligible. On the contrary, CNTs decreases the crystallinity of PLLA with the application of shear flow field. The reason why CNTs plays different roles in the crystallization of injection-molded PLLA under

different processing condition was studied by differential scanning calorimeter (DSC). The DSC and WAXD results indicate that CNTs promotes the crystallization of PLLA under the processing condition unfavorable for the crystallization of neat PLLA, such as high supercooling or lacking of shear flow. However, under the proper mold temperature or/and shear flow favorable for the crystallization of PLLA, CNTs decreases the maximum achievable crystallinity resulting from the restriction of chain motion or crystal disruption. The thermal property of the samples was also studied by dynamic mechanical analysis (DMA) and vicat softening temperature (VST), indicating that CNTs or/and shear flow increase storage modulus especially above the glass transition temperature and increase greatly the VST of PLLA due to the promotion of crystallization with the mold temperature 40 and 80ºC, respectively. Keywords: poly(L-lactic acid), crystallization, carbon nanotubes, shear flow, injection-molding. Acknowledgments: This study is supported by the National Natural Science of China (Grant NO. 51120135002, 51473101).

S06-156

Tuccar Kilic Nilay , Can Buse Nur, Kodal Mehmet, Ozkoc Guralp

Effects of POSS nanoparticles on the properties of PLA/TPU Blends

The increasing use of petrochemical based nondegradable polymers negatively affects the ecology due to the huge accumulation of solid wastes disposed to environment. One of the sustainable solutions of this problem is the use of biodegradable polymers. Recently, poly(lactic acid) (PLA) has attracted attention because of its industrial scale production with a reasonably comparable price to other petroleum-based polymers. Although PLA is relatively high strength and high modulus analogous to polystyrene, its inherent brittleness and low toughness due to the low entanglement density and the high value of characteristic ratio representing the chain stiffness restrict its application. Elastomeric thermoplastic polyurethanes (TPUs) can be used to toughen PLA; since the soft segment of a TPU is mainly polyester



32nd PPS International Conference 2016, Lyon, France it is expected to have a good compatibility with PLA. Polyhedral oligomeric silsesquioxanes (POSS) are useful candidates for reinforcement of polymers. The incorporation of POSS containing reactive groups into a polymer matrix creates a possible nanoscale reinforcement, in which POSS molecules may link to polymer chains covalently. In this study, the influence of POSS loading level and type of its functional group on the mechanical, thermal, rheological properties of PLA-TPU blends were investigated. PLA-TPU-POSS blends were prepared by melt compounding process using an Xplore Instruments laboratory compounder. Thermal, mechanical, rheological and morphological properties were characterized. Keywords: polylactide, thermoplastic polyurethane, blends, POSS Acknowledgement: This study is financially supported by TUBITAK (Grant Number:115M576)

S06-161

Kopietz Mark, Grishchuk Sergiy, Wetzel Bernd

Innovative Phosphate-Free Alternatives for Silicate Resins Applied in Sewer Rehabilitation

Damages in sewage pipes require efficient methods for trenchless and partial rehabilitation. Short distances are usually repaired with impregnated glass fiber fabric mats via inflatable packers (shortliner), longer damages with impregnated and inverse implemented polyester needle felting tubes (in-liner). Both techniques have special processing requirements to the resin, e.g. initial viscosity, reaction speed, pot life and gelation time are important for sufficient impregnation of the reinforcing material, accurate application and cycle time. Beside epoxy and unsaturated polyester resins silicate resins are widely used in trenchless sewer rehabilitation. Such two-component waterin-oil emulsion resins are using waterglass as silicate source, whereas organic phosphate esters are used as emulsifiers, phase transfer agents and plasticizers at the same time. In a two-step indirect reaction a primary amine is built from isocyanate and water (from waterglass), which afterwards reacts with remaining isocyanate to build the polyurea thermoset. Emerged CO2 gets bonded

directly to build an alkali metal (bi)carbonate which in-situ is accompanied with formation of polysilicate caused by silification of waterglass[1]. Because of the unfavourable diffusion of chemically non-bonded phosphates and the substitution of dangerous chemicals through REACH requirements (EG 1907/2006) this work focusses to replace phosphates by vegetable oils and their functionalized derivatives. These fulfill the functions of emulsifiers, plasticizers and phase transfer agents, and also get chemically bonded to the matrix and raise the bio-content. This work demonstrates that innovative, phosphate-free, so called 2P resins (polyisocyanate, polysilicate) have comparable processing conditions and mechanical properties than market available reference resins. [1] Castellà, N., Grishchuk, S., Karger-Kocsis, J., Schehl, M., J. Appl. Polym. Sci. 2011, 119, 7-14.

S06-165

Sobkowicz Margaret, Emery Kyla, Tan Bin

Aqueous Latexes of Biobased Copolyesters for Paper Coating

Biobased and biodegradable polyesters have high potential in compostable paper coatings as replacements for non-degradable polymers. The metrics for a successful coating include sufficient oil and water resistance and good surface properties. By tuning the polymer architecture, a wide range of coating properties can be accessed. This research aims to eliminate toxic solvents in polymeric coatings for paper and single-use, compostable packaging. In pursuit of this goal, biodegradable poly(butylene succinate) (PBS) was synthesized from bio-based 1,4-butanediol and succinic acid. Branched poly(butylene succinate-co-citric acid), poly(butylene-co-hexamethylene flexible more succinate), and amorphous poly(butylenesuccinate-co-furandicarboxylic acid) were also synthesized by incorporating citric acid, 1,6and furandicarboxylic acid hexanediol, respectively. The chemical structure, thermal properties and crystallization behaviors of these using characterized polymers were nuclear magnetic resonance (NMR), thermogravimetric analysis differential (TGA), and scanning



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calorimetry (DSC), wide-angle X-ray diffraction (WAXD). The resulting polymers showed good thermal stability and tunable crystallinity by varying monomers and monomer amounts. Additionally, stable latexes from these polymers were prepared by mini-emulsion. Coatings were created from both polymeric latexes and bulk melts by a doctor blade coating. The morphologies of films were investigated using atomic force (AFM) and scanning microscopy electron microscopy (SEM). The results showed that good films were formed both from aqueous suspension and bulk melt, and film properties could be tuned by polymer structures. These results illustrate the potential of polymeric coatings to eliminate chlorinated solvents and volatile organic compounds (VOCs) typically used in the coatings industry.

S06-186

Sälzer Philipp, Feldmann Maik, Heim Hans-Peter

Effects of Particle Characteristics on Mechanical Properties of Wood Plastic Composites

Fillers and reinforcing materials from natural resources offer various opportunities for usage in plastics technology. However, unlike synthetic fillers, they have no constant properties, but rather differ from each other, depending on harvest year, growing area or type. Together with the different processing parameters this results in a significant influence on the mechanical properties of the final component. Finally, these studies will lead to a precise statement of the material behavior thus contributing to safe and reliable materials. In earlier studies it was shown, that there is a huge influence of particle size on the mechanical properties of WPC. Additionally there are other geometrical factors like aspect ratio, convexity and sphericity with influences on mechanical properties. With a fractionation by size of the fillers before the compounding process, blends with different particle geometries are created and investigated. The used fillers derive from different plant resources, growing areas and are processed with different parameters. Furthermore the usage of a coupling agent is highly important, as it can

significantly improve the mechanical properties of the composites. Mechanical properties are represented by tensile, flexural and impact properties gained from injection molded specimen. The particle size distribution and particle shape in raw material, compound and finished component is determined with the dynamic image analysis, µ-CT optical examination methods. and further Additionally a thermal analysis was carried out to characterize the effect of thermal degradation during the processing.

S06-209

Refaa Zakariaa, Boutaous Mhamed, Xin Shihe

Crystallization of PLA: overall kinetics and morphology development

The Polylactide is a biosourced and biodegradable from renewable polymer, issued resources. Understanding its crystallization kinetics is a key parameter in order to tailor the final part properties versus processing conditions. We propose in this work a qualitative and quantitative study about its overall crystallization kinetics and morphology development after a shearing step. For a given shear rates ($\gamma > 1/\tau_s$), the overall kinetic of crystallization versus shearing time exhibits two kinds of accelerations. The first one is related to an enhancement of the point-like nuclei and the second is related to the formation of oriented structures or Shish-Kebabs. The saturation plateau of point-like nuclei was observed by in-situ optical microscopy and the development of Row-nuclei was confirmed in this zone of shearing time. The conditions of the formation of oriented structures are discussed and the flow induced point-like nuclei was modeled. Finally, the evolution of the overall crystallization kinetics is predicted.

S06-231

Gaugler Marc, Vaidya Alankar A, Smith Dawn A

Functionalisation of wood particles, cellulose and hemicellulose using reactive extrusion

Extrusion is a versatile process that has developed beyond its original uses for metals and plastics.

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Today, twin-screw extrusion is also used in nonplastic applications, e.g. processing of food, animal feed or refining of biomaterials. Reactive extrusion is regarded as a green route to chemical modifications, as it enables solvent-free reactions. The aim of our work was to produce functionalised bio materials that enable more tailored or targeted preparation of new bio-composites or their use for subsequent derivatisations. We used twin-screw extrusion to functionalise wood particles (WP), cellulose and hemicellulose. These materials were processed without any polymeric carrier, unlike other published work in this area. Succinic, dodecenyl succinic and maleic anhydride were used as reactants and under optimum conditions, esters between these anhydride and hydroxyl groups of the biomaterials were formed. The influence of extrusion conditions and catalyst on the reaction yield was assessed by infrared and nuclear magnetic resonance spectroscopy, thermal analysis and acid titration. Based on the acid titration, the highest degree of esterification was obtained for the succinilation of cellulose (1.4 mmol/g dry wood). Mass balance results suggest an almost complete conversion of succinic anhydride, indicating the formation of di-esters. The order of reactivity for succinic anhydrides was cellulose > WP > hemicellulose, while for maleic anhydride the order was WP > hemicellulose > cellulose. In the absence of catalyst, higher temperatures increased the yield from 1.1 to 1.4 mmol/g wood between 150 and 220°C, respectively. The yield was independent the extrusion temperatures assessed in of formulations with catalyst. The shear energy during extrusion led to a reduction in particle size, defibrillation and compaction as confirmed of the fibres by microscopy.

S06-258

Bendaoud Amine, Maigret Jean-Eudes , Leroy Eric, Cathala Bernard , Lourdin Denis

Cellulose-xyloglucan composite film processing using ionic liquids as co-solvents

All-cellulose composites (ACCs) are a promising new class of bio-composites which emerged to overcome especially the critical problem of adhesion in composites and to substitute the conventional petroleum-based polymers. Different processing routes have been used to develop these bio-materials, based on partial or complete solubilisation using different solvent systems. However, the potential industrial applications remain limited due to the using of hazardous and expensive solvents and to difficulties in controlling the consolidation mechanism in cellulose during regeneration. The aim of the present work is to develop a high-performance composite using biomimetic approaches that will exploit the fundamental interactions between two biopolymers, cellulose and xyloglucan, and these interactions are typically present within the cell walls of plants, according to the "tethered network" model. In this study, the attractive solubilisation potential of ionic liquids is used to co-dissolve and to prepare cellulose-xyloglucan blends. Films of regenerated cellulose, xyloglucan and various cellulose/xylogucan blends were prepared using [EMIM] Acetate or Choline acetate-DMSO as a cosolvent. The raw materials and regenerated composite films were characterized by chemical analysis, X-ray diffraction, FTIR, solid NMR, morphology, hygro-mechanical analysis and tensile testing. In terms of mechanical properties, a synergy could be observed in the regenerated blends with an increase of both modulus and elongation at break compared to the regenerated pure biopolymers. Strategies for upscaling the production to thick composite laminates will also be discussed. Keywords: Cellulose, xyloglucan, ionic liquids, polymers blends, biomimetic approaches, hydro-mechanical properties.

S06-262

Allais Florent

Chemo-enzymatic synthesis and polymerizations of bio-based bisphenols derived from lignin: an access to novel 100% renewable antioxidants and alternating aromatic/aliphatic polymers

Novel renewable bisphenols were prepared through chemo-enzymatic processes under mild conditions. The enzyme-catalyzed condensation steps have been optimized and lead to high purity



grade bisphenols in high to excellent yields. The antiradical/antioxidant properties of these biobased bisphenols were investigated and revealed activities similar or higher than that of current available antiradical/antioxidant commercially additives such as Irganox 1010. The bisphenols were then used as monomers for the preparation of various types of alternating aliphatic/aromatic polymers such as copolyesters, polyurethanes, poly(ester-alkenamers). The newly obtained homoand copolymers were then characterized by NMR, GPC, DSC and TGA. These analyses revealed not only good thermal stabilities but also a broad range of accessible Tg. Linear phenolic homo-oligomers were also prepared through oxidase-mediated oligomerization; their thermal properties and antiradical activities were evaluated.

S06-267

Li Chunhai

Molecular insight on the interaction between PLLA and a self-assemble nucleating agent: the mechanism of the crystallization enhancement and the control of the crystalline morphology

In this work, octamethylenedicarboxylic dibenzoylhydrazide (OD) with intense hydrogen bonds in its molecules, was chosen as the nucleating agent of polylactide (PLLA). As the specificity and directionality of hydrogen bonds, OD can self-assemble into different superstructures like dendritic or fibrillar superstructures in the PLLA melt. Most interesting, we found that the selfassemble behaviors of OD depends on its concentration and external temperature, and the dendritic or fibrillar superstructures can serve as nucleation templates to induce the crystallization of PLLA on their surface, resulting in a large enhancement in crystallization rate. Moreover, we obtained PLLA successfully the crystalline morphology with dendritic, shish kebab and sunflower-like structure, respectively. The weak interaction between PLLA and OD molecules, which is proven by the two-dimension correlation spectra, can change the conformation distribution of PLLA molecules and play key role in the crystallization mechanism of the PLLA/OD system.

Keywords: Self-assemble, nucleating agent, weak interaction, PLLA, crystallization, Two-dimension correlation spectra

S06-292

HEUZEY Marie-Claude, HUNEAULT Michel, JAUZEIN Thibault Henri

Properties And Processing Of Pla/Ether-Amide Copolymer Blends

Biobased polymers have been widely studied as substitutes for petroleum-based materials. Among these polymers, polylactide (PLA) has gained commercial acceptance in thermoformed and blow molded packaging applications because of its transparency, high tensile modulus and strength and its cost competitiveness. However, the low impact strength of PLA and its poor temperature resistance have prevented its widespread use in many industrial applications. The present study focuses on the improvement of impact properties and particularly on the interaction between crystallinity development and mechanical properties of PLA-based blends. The PLA was toughened by the addition of a random linear ether-amide copolymer (Pebax 3533TM) that acted as an impact modifier. A random copolymer of methyl-methacrylate ethylene, and glycidylmethacrylate (Lotader AX8900TM) was also used to reactively compatibilize the ether-amide copolymer with the PLA matrix. The rheological, mechanical and thermal properties of quenched and annealed blends and their morphology were investigated. In terms of melt rheology, the blends were investigated in oscillatory shear to determine if the impact modifiers could increase the melt elasticity of the material. The Izod impact resistance and tensile properties were measured using standard testing protocols. The thermal resistance of the annealed blends was examined using dynamic mechanical analysis. A micron-size dispersion of the impact modifier was achieved in the presence of the reactive compatibilizer. Significantly improved impact strength was found with as low as 10% of additives. Annealed samples showed the highest impact strength with values attaining 80 kJ/m².



S06-293

Omonov Tolibjon S., Kharraz Ereddad , Grushcow Jack, Curtis Jonathan

A New Biobased Polyol That Can Be An Alternative To Castor Oil In Polymer Formulations

Castor oil is a natural polyol widely used in the manufacture of polyurethanes, lubricants, surfactants and many oleochemical products. Castor oil is a renewable biobased product, but its production is geographically limited resulting in fluctuations in supply and price. We have developed plant lipid-based polyols which have properties similar to those of castor oil and which could be drop-in replacements for it in various applications. These will be cost competitive to castor oil and made from seed oils that can be grown on the Canadian prairies. Camelina oil is used produce castor oil replacement polyols (COROL) and advantageously, it is has been developed as a non-edible vegetable oil for use in industrial applications. Camelina oil contains suitable amounts of unsaturated fatty acids for further chemical modifications. In this work, oil is subjected to a controlled derivitisation process, as described in a recent patent application, which both preserves the triacylglyceride structure and results in a similar amount of hydroxylation and viscosity to that found in castor oil. The reaction of castor oil and COROL polyols with p-MDI to produce polyurethanes was studied via their rheological behavior during curing, which established the relative reactivities of castor oil and COROL polyols. The thermo-mechanical properties of the PU produced using castor oil and COROL polyols were evaluated by DSC and DMA. Results indicate that in PU applications the reactivity of COROL polyols can be readily adjusted to match that of castor oil. However, the thermo-mechanical properties (e.g. Tg) of cured PU made using COROL significantly exceeds those made using castor oil. Overall, this study demonstrates that biobased polyols from plant oils can be produced with a range of viscosities, hydroxyl functionalities and overall reactivities that include those found in

castor oil. The ability to adjust these parameters offers a significant advantage over castor oil.

S06-351

Berzin Françoise, Beaugrand Johnny, Dobosz Simon, di Giuseppe Erika, Vergnes Bruno

Modelling Of The Fiber Morphology Changes During The Preparation Of Polypropylene-Lignocellulosic Fiber Composites By Twin Screw Extrusion

Thermoplastic-lignocellulosic fiber composites are usually prepared by compounding using a twin screw extruder. During the process, the local thermomechanical conditions lead to a severe decrease of fiber dimensions, with a global diminution of length and diameter, thus reducing the potential of mechanical reinforcement of the polymer matrix [1, 2]. In order to optimize the compounding process for maintaining satisfactory fiber dimensions, it is necessary to understand the leading to fiber mechanisms breakage (defibrization). Therefore, experimental data have been interpreted using flow modelling allowing to the local flow parameters, like calculate temperature, specific energy, stress, strain... In the present study, we have considered lignocellulosic fibers of various botanical origins. We have first characterized the changes in fiber dimensions along the screws, by performing dead-stop experiments, collecting samples and analysing length and diameter distributions. Then, we used the modelling software Ludovic© [3] to determine the values of the local flow parameters, all along the screw profile. From evolutions laws of fiber morphology obtained using internal mixer experiments [4], it is now possible to predict the change in fiber diameters and lengths along the extruder. These calculated results have been satisfactorily compared to experimental ones. After validation, the methodology can be used for optimizing either the screw profile (location, number and type of mixing elements) or the processing conditions (flow rate, screw speed, barrel temperature, fiber introduction...). [1] J. Beaugrand & F. Berzin. J. Appl. Polym. Sci., 128 (2013) 1227-1238. [2] F. Berzin, B. Vergnes, & J.



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S06-365

Rabiei Tabriz Kamand, Katbab Ali Asghar

Preparation and Characterization of PLA-grafted-TiO₂/PLA Nanocomposite Films with Enhanced Microstructure, Photodegradability and Antibacterial Properties, for Food Packaging Applications

Today, from the point of view of environmentally concerns, the nanocomposites of PLA are from great interest among the manufacturers of food packaging plastics. Among the all types of PLA nanocomposites, the ones including the oxide of semi-conductive materials such as TiO2, have attracted the attention of many research centers and industries. Although there seems to be a great interest about producting the nanocomposite of PLA and TiO₂ nanoparticles, but aggregation of TiO₂ nanoparticles in an organic matrix like PLA, makes it difficult to reach a homogenous film with good properties. In this study first, PLA chains were grafted onto TiO₂ nanoparticles surface via reactive melt mixing using a novel approach in presence of SnCl₂ as catalyst. PLA grafted chains were characterized on the TiO₂ nanoparticles using FTIR and TGA analysis, and the optimum ratio of TiO₂ nanoparticles to SnCl₂ in order to abtain the highest amount of grafting, was determined 7.5. Then, PLA-grafted-TiO₂/PLA nanocomposite films, were produced using a twin screw extruder. The microstructure of the nanocomposite films was characterized using SEM and EDAX techniques, and this way, it was observed that the dispersion state of TiO₂ nanoparticles has been greatly improved after modifying TiO₂ surface. Finally, the nanocomposite films were put under UV irradiation(360-420 nm), for 2 months and the weight loss of the films was followed during this period. The nanocomposite films containing modified TiO₂ nanoparticles, showed higher amount of weight loss in comparison with the film

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containing bare TiO₂ nanoparticles. The nanocomposite films were also used to investigate the antibacterial properties, under UV irradiation for 2 hours, using a combined method of JIS Z2801:2000 and ASTM E2180-07. The nanocomposite films showed high antibacterial properties against E-coli gram negative bacteria, although this amount was lower in case of St.aureous gram positive bacteria.

S06-368

Belkhir Kedafi, Jegat Corinne, Taha Mohamed

BlendsBasedonBranchedBiodegradableFunctionalPolymerswithControlledMacromolecularDesign and Functionality

Kedafi Belkhir*, Corinne Jegat, Mohamed Taha Ingénierie des Matériaux Polymères (IMP), UMR CNRS 5223, Université de Saint-Etienne, Jean Monnet, F-42023, Saint-Etienne, France Université de Lyon, F-42023, Saint-Etienne, France e-mail kedafi.belkhir@univ-st-etienne.fr address Macromolecular architectures are of great importance in contemporary polymer science, the polymer design, functionality, control over composition and topology allows the elaboration of with various properties, different polymers behaviors and a large field of applications. [1,2] In a recent work, [3] we have reported a facile new method to synthesize branched polymers with controlled macromolecular architectures; these materials have been endowed with high controlled thiol functionalities and based on biodegradable polymeric segments, their structures and functionalities were confirmed by spectroscopic analyses and a new chemical method was adapted. The effect of the macromolecular design on thermal properties of these materials was investigated. These materials with thiol functions offer opportunity to further modifications: a thiol-ene click chemistry approach has allowed to graft molecules with active sites on these functional materials thus giving them a biological activity. The kinetic of grafting was studied and the amount of active sites in the materials was controllable. The processability of the final products was investigated in melt state; they were also blended with matricial



polymers, such polylactic acid as and polycaprolactone for applications in packaging and coatings. Morphologies like droplets in matrix to co-continuous were obtained. Physico-chemical and rheological properties were investigated. Biodegradability and antibacterial activity were also controlled. References 1) Bernhard V.K.J.Schmidt, Martin Hetzer, Helmut Ritter, Christopher Barner-Kowollik, Progress in Polymer Science, 2014, 39, 235. 2) Andrew Gregory, Martina H. Stenzel, Progress in Polymer Science, 2012, 37, 38. 3) Kedafi Belkhir, Hang Shen, Jianding Chen, Corinne Jegat, Mohamed Taha, European Polymer Journal, 2015, 66, 290.

S06-384

Zheng Yu, Shen Jiabin, Guo Shaoyun

Shape memory performances of thermoplastic polyurethane/polycaprolactone multilayer materials

As one of typical stimulus-sensitive shape memory polymers (SMPs), thermal induced SMPs (TSMPs) have been found wide applications in smart fabrics, intelligent packaging, biomedical devices, sensors and actuators. In this work, a kind of TSMPs containing alternating layers of thermoplastic polyurethane (TPU) and polycaprolactone (PCL) were fabricated through layer-assembly extrusion technology. The multilayer structure with stable and well-defined continuous layer spaces was controlled by changing the number of layers. Compared with conventional TPU/PCL blends, the multilayer system with the same compositions demonstrated better shape memory performances. Each component in the multilayer structure was considered to be capable of endowing the maximum contribution to both of the shape fixing (Rf) and recovery ratios (Rr). With increasing the number of layers, higher Rf and Rr were achieved, which could be ascribed to the interfacial shearing effect occurring between TPU and PCL layers based on a viscoelastic model. Furthermore, when neat PCL layers were replaced by TPU/PCL blend with co-continuous morphology, the Rf only reduced from 97.2 to 96.0%, but Rr had a distinct increase from 87.9 to 92.9%. This revealed that the

combination of co-continuous morphology and multilayer-assembly structure would be benefit for achieving outstanding shape memory performances.

S06-54

Kao Nhol, Islam Sakinul Md., Bhattacharya Sati N., Gupta Rahul K

An Investigation between High and Low Pressure Processes for Nanocrystalline Cellulose Production from Agro-waste Biomass

Nanocrystalline cellulose (NCC) has widely been used for miscellaneous applications due to its superior proprieties over other nanomaterials. The major problems associated with the production of NCC are long reaction time, low production rate and inefficient process. The mass production of NCC within short time remains a great challenge currently. The main objective of this study is to overcome the present problems by investigating the performance of a high pressure process (HPP) and a low pressure process (LPP) for NCC production from raw rice husk biomass (R-RHB) by chemical extraction. The general steps of chemical extraction are delignification, bleaching and hydrolysis. Delignification of R-RHB for HPP and LPP was conducted at 80 °C using stainless steel reactor and jacketed glass reactor, respectively. During the delignification in the HPP, 5 bar pressure was applied; while atmospheric condition was used for the LPP. Delignification of HPP and LPP was run for 12 hours using aqueous solution of NaOH (4M) for the separation of cellulose from R-RHB by the dissolution of lignin and other amorphous impurities. Delignified samples were collected after delignification reaction, then washed, bleached and finally hydrolyzed in order to convert cellulose to NCC. NaOCl (20%) and H2SO4 (4M) solutions were used for bleaching and hydrolysis processes, respectively. The resultant NCC products of HPP and LPP were analyzed by FTIR, XRD, SEM, EDX, AFM and TEM. The chemical composition of R-RHB and NCC was estimated by TAPPI methods to observe the product purity. High purity NCC has been produced in HPP with crystallinity approximately 55 % and production rate of 62%



whereas LPP 51%. It was found that, while both processes produced NCC of diameter 10-20 nm and length 1-2 μ m, the HPP was faster and more efficient than the LPP to produce quality NCC from R-RHB. Keywords: Nanocrystalline Cellulose, High Pressure Process, Low Pressure Process, Rice Husk Biomass

S06-546

Fernandes Nassar Samira, Delpouve Nicolas, Guinault Alain, Sollogoub Cyrille, Domenek Sandra

Enhanced gas barrier properties due to confinement of PLLA obtained by the nanolayer coextrusion process

The development of biopolymers for foodapplications implies ecofriendly packaging character to specific industrial requirements as lowcost and good mechanical, thermal and barrier properties. Polylactide (PLA) is today the most used a biobased and biodegradable polymer due to its process ability and good mechanical properties [1]. As one of the major challenges for high performance PLA packaging at a large scale is the improvement of its gas barrier properties, the tailoring of the PLA microstructure. Methods, such as thermal crystallization [2,3] and drawing [4] have been strongly investigated in the recent years. New strategies are actually studied to obtained stronger effects. One of them consists in the geometrical confinement of the polymer at the molecular scale using the layer-multiplying coextrusion process combined eventually with annealing processes to create nanometric thickness layers. This technology is environmentally friendly and health secured and has already proved its efficiency to improve the gas barrier properties in case of other polymers [5]. In this work we propose to design multi-layer coextruded PLA to analyze the relationships existing between its microstructure, amorphous phase mobility and the resulting gas barrier properties. (1) Domenek S, Ducruet V. Characteristics and applications of polylactide, in "Biodegradable and biobased polymers: Environmental and biomedical applications", Kalila S, Averous L, eds, Scrivener Publishing.2015,171-224. (2)Guinault, A.;

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S06-566

Mhiri Sirine, Mignard Nathalie , Abid Majdi , Abid Souhir, Taha Mohamed

Synthesis of thermoreversible and biodegradable polyglycolic-acid-based networks

Poly(glycolic acid) (PGA) is one of the most promising biodegradable polymers owing to its good mechanical properties and its unique biological properties such as biocompatibility and biodegradability. Despite its high degree of crystallinity, its insolubility in all common solvents and its thermal decomposition, successful efforts are made to provide poly(glycolic acid) specific mechanical and architectural features and facilitate its handling such as synthesis of glycolide copolymers with varying compositions of comonomers, polymer blends and mesh network formation by crosslinking. Among these methods, cross-linking seems to be a good method to optimize the materials properties of PGA while maintaining its biodegradability. In this study, two different thermoreversible networks were prepared. First, PGA hydroxyl-telechelic oligomer with a well-controlled molecular weight was synthesized by ring opening polymerization of glycolide. Before approaching the synthesis of the networks, two precursors which are the Diels-Alder adduct and a coupling agent were synthesized separately for a better control of the conversion of the Diels Alder reaction. Thereafter, the networks were obtained by two methods: the first one in which the Diels-Alder adduct gives rise to the network and the one-shot process where the alcoholysis reaction of the coupling agent is responsible for the crosslinking. The formation of networks and their thermoreversibility through Diels Alder reactions have been identified over



32nd PPS International Conference 2016, Lyon, France several cycles following the thermal behavior of materials by dynamic mechanical analyses. This method of analysis is rapid and relevant for the detection of cross-linking and de-cross-linking of the networks. The biodegradation by aerobic microorganisms and the hydrolytic degradation at 37°C were studied on networks with different densities.

S06-640

El Kazzouli Saïd, El Brahmi Nabil, Mignani Serge, Cresteil Thierry, Bousmina Mosto, Majoral Jean-Pierre

Synthesis of new drug-phosphorus dendrimer conjugates and their evaluation as anticancer agents

Dendrimers which are nanosized polymeric molecules composed of a large number of perfectly branched monomers, have been studied for the delivery of both nontargeted and targeted drugs. In the targeted approach, the attachment of a targeting agent on the surface of the dendrimer allows preferential directing to, for example, cancer cell lines versus normal cell lines1. The small size of dendrimers enables their crossing through the gastrointestinal epithelium, tumor vasculature, and endothelium of cancer and inflammatory sites. While they are able to access the spleen and liver via fenestration, nanoparticles with 50–100 nm size are far too large to cross the endothelial barrier in all other healthy tissue but can reach some cancer cells and inflamed tissues2. In addition. nanoparticles have been shown to accumulate preferentially at tumor and inflammatory sites3. In this oral communication we will described our development recent concerning phosphorus dendrimers synthesis (generations Gc1 to Gc3) and functionalization using various drugs4. We will present also the anticancer activities of these drugloaded dendrimers. References: 1) a) R. K. Tekade, P. V. Kumar, N. K. Jain, Chem. Rev. 109, 2009, 49. b) S. H. Medina, M. E. H. El-Sayed, Chem. Rev. 109, 2009, 3141. c) D. Astruc, E. Boisselier, C. Ornelas, Chem. Rev. 109, 2010, 1857. 2) V. P. Chauhan, T. Stylianopoulos, Y. Boucher, R. K. Jain, Annu. Rev. Chem. Biomol. Eng. 2, 2011, 281. 3) J. Fang, H. Nakamura, H. Maeda, Adv. Drug Delivery Rev. 18,

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S06-644

Buchtová Nela, Bouvard Jean-Luc, Pradille Christophe, Budtova Tatiana

Cellulose aerogels and cryogels: structureproperties correlations

The use of cellulose, the most abundant renewable, biocompatible and biodegradable natural polymer, is nowadays reconsidered thanks to new non-toxic and powerful cellulose solvents which allow making materials with various functionalities. High value-added cellulose-based porous materials are thus very attractive for diverse applications, from (controlled bio-medical release, scaffolds) to engineering (thermal insulation) and electrochemical (when pyrolized). In this work, novel extremely porous and ultra-lightweight cellulose-based biomaterials are prepared via dissolution-coagulation route. Three drying ways were used: (i) supercritical CO2 drying (aerogel); (ii) freeze-drying (cryogel); (iii) vacuum-drying (xerogel), resulting in very different morphologies. Porous celluloses were characterised with bulk density and specific surface area via nitrogen adsorption; morphology was investigated by highresolution SEM and pore sizes were estimated when possible. Finally, the mechanical properties were also studied in details under the uniaxial compression. The influence of drying method, cellulose molecular weight and concentration on the structure and properties of the final porous materials will be presented and discussed. Acknowledgements: The work is part of «Aerowood» project financed by WoodWisdom Net+ EC program. The authors thank Prof. B. Saake from Hamburg University (Germany) for providing and characterisation of the native celluloses.

S06-656

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Turhan Kamile Nazan, Erol Ece

Use of Antimicrobial Methylcellulose Films During Storage of Salami

Antimicrobial packaging is an innovative way of inhibiting microbial growth on the foods. There has been a rising interest in the researches about biopolymeric materials and natural antimicrobial compounds which are environmentally friendly. Antimicrobial films reduce the growth rate of specific microorganisms by direct contact of the package with the surfaces of foods. Poor sanitation, unhygienic practices and unsuitable storage can cause growing pathogenic microorganisms on the surface of the food. Staphylococcal food poisoning caused by Staphylococcus aureus is a worldwide problem. Although S. aureus shows high sensitivity to thermal processing, they produce thermal resistant toxin, caused human poisoning. Naturally occurring antimicrobial compounds have good potential to be applied as food preservatives. Propolis is a brownish resinous material collected by worker bees and has antimicrobial effect on many food pathogens. Antimicrobial packaging can be prepared with polysaccharides which they have many advantages as biodegradability, edibility, biocompatibility. The usefulness of cellulose as a starting material for biodegradable films can be extended by its chemical modification to methylcellulose (MC), which is a nonionic, watersoluble ether with good film forming properties. The purpose of this study was to form methylcellulose films with propolis and demonstrate the physical properties and antimicrobial efficiency of the films. In this study, MC based antimicrobial films containing 3.75-6% (w/v) ethanolic extracted propolis (EEP) were produced. The effects of EEP amount on the water vapour permeability (WVP), mechanical and antimicrobial properties of the films were investigated. The EEP in the film solution caused a decrease in WVP and elongation, and an increase in tensile strength. The MC films containing 4.5% (w/v) EEP were applied on salami slices inoculated with S. aureus. The count of S. aureus was decreased 0.78 log cycle during 14 days storage.

S06-680

PPS[®]32

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Khemakhem Marwa, Lamnawar Khalid, Maazouz Abderrahim,

Biocomposites based on polylactic acid and olive solid waste: improvement of thermal stability, physico-chemical and rheological properties

A new valorization strategy for Olive Solid Waste (OSW) has been carried out which consists in incorporating this biomass as a filler in a biopolymer matrix. The aim of the present work is to gain a fundamental understanding of the between relationships structure, processing conditions and final properties of the obtained materials. In this study, biocomposites based on poly(D,L-lactide) (PDLLA) and two OSW fillers were prepared with various filler contents. It was highlighted that the inclusion of OSW under elevated temperatures resulted in the degradation of the matrix leading to a reduction of the viscoelastic properties and molar masses. Nevertheless, it was demonstrated that this degradation of the PDLLA matrix could be attenuated through two approaches. The first was chemical and consisted in using a chain extender agent named Joncryl containing glycidyl methacrylate (GMA) functions. The second route was physical and consisted in coating the OSW with the hydrophobic biopolymer poly(ecaprolactone) followed by mixing with PDLLA. Indeed, the processing conditions were monitored to produce composites with well controlled properties. The effect of OSW with and without Joncryl on the thermal stability as well as the melt and the crystallization properties was assessed. Furthermore, the rheological properties in linear the controlled viscoelasticity of systems PDLLA/OSW/ Joncryl and/or PDLLA/ (OSW) coated with PCL were investigated in the molten state. The improvement of the shear viscoelastic properties corroborated the measured molar masses. The physicochemical matrix/filler interactions had to be taken into account to explain the improved rheological, morphological and mechanical properties. The obtained materials with a tailored properties were fully recovered by two forming process as well extrusion and injection molding.

32nd PPS International Conference 2016, Lyon, France S06-684

Katir Nadia

Orthogonal synthesis of hyper-branched macromolecular microspheres by fusing classical and onion-peel phosphorus-based dendritic units

High molecular weight organic compounds are a class of pervasive materials at the borderline of molecular chemistry and materials science. Polymer synthesis, engineering and manufacturing have revolutionized the world of macromolecular chemistry at both academic and industrial basis. Among them, dendrimers are of particular interest owing to their structure reminiscent to natural trees and cells.1-2 Herein, the preparation of novel phosphorus-based architectures known as "onion peel" nanodendritic systems is reported. This construct is based on the versatility of synthetic methods and the capability of these systems to undergo regioselective reactions within the cascade structure.3 The "onion-peel" and classical dendritic units were fused within the same tectonic nanostructure by several polymeric condensation approaches including hydrazine-to-aldehyde Schiff-base formation and amine-to-carboxylic acid peptide-like coupling. These reticular, easy to run metal-free routes afford a new library of hyperbranched macromolecular materials featuring various phosphorus layers (both alternated and dissymmetrical), well-defined textured microspheres and controllable nanometric ordered substructures. The scope of the concept is successfully expanded to the integration of electroredox viologen units resulting in the synthesis of novel photo-active macromolecular materials. 1- N. Katir, A. El Kadib, J. P. Majoral, A. M. Caminade, M. Bousmina, Eur. J. Org. Chem., 2012, 269-273 2-N. Katir, A. El Kadib, V. Collière, J. P. Majoral, M. Bousmina, Chem. Comm., 2014, 50, 6981-6983. 3- N. Katir, N. El Brahmi, A. El Kadib, S. Mignani, A. M. Caminade, M. Bousmina, J. P. Majoral, chem. eur. J., 2015, 21, 6400-6408.

S06-695

Maffezzoli Alfonso, Ferrari Francesca, Velardi Rosario, Greco Antonio

Mechanical and durability properties of soft PVC plasticized by cardanol derivatives

The use of bio-plasticizers, derived from natural oil and modified to improve the compatibility with PVC, represents a valid alternative towards the use of phthalate plasticizers, aimed to reduce the environmental and toxicological impact. Nevertheless, the substitution of phthalates is still very difficult to attain, due to high cost of bioplasticizers. In addition, bio-plasticizes, contribute to the subtraction of resources to food chain, as is the case, for example, of epoxidated soybean oil. On the other hand, the potential of cardanol derivatives as PVC plasticizers was recently demonstrated. Compared to other bio-plasticizer, the cardanol derived plasticizers do not require the use of primary resources, and therefore do not contribute to the subtraction of resources to food chain. Therefore, this work is aimed to the development and property optimization of cardanol derived plasticizers. To this purpose, different plasticizers were produced though different epoxidation routes, characterized by low toxicological and environmental impact. The plasticizers are characterized by different yield of epoxidation of the alkyl chain double bonds. The properties of the cardanol derived plasticizers were compared to the properties commercial plasticizers, of either derived. phthalates or natural Mechanical properties were shown to be in the same range of other commercial plasticizers. The efficiency of the plasticizers was significantly improved by epoxidation. Also, the yield increasing of mechanical properties performed after ageing showed the excellent stability of the properties of the cardanol derived plasticizer characterized by the higher yield. Evaluation of the property retention index after ageing indicated that such plasticizers showed an improved stability of compared other commercial properties to plasticizer. The results obtained highlight the relevance of an high conversion of the double bonds into epoxies in order to produce high quality plasticizers.

S06-700

Bhati Pooja, Bhatnagar Naresh



32nd PPS International Conference 2016, Lyon, France

Mechanical Properties of PLA/PCL blend extruded tubes for the bioresorbable stent application

Significant studies are being done on the use of the poly lactic acid (PLA)/poly caprolactone (PCL) as a stents potential material for Bioresorbable manufacturing. Among the various manufacturing polymeric processes used for the stent manufacturing, the prevailing method is to extrude the tube and then subject it to post processing operations for enhancing its mechanical properties, so as to make it a better candidate for the stent. Subsequently, stent profile cutting by cold laser is required for changing the tube into a stent. The variation in manufacturing process employed for tube extrusion is an area not adequately reported. This study gives the insight into the effect of the manufacturing process variation on the mechanical properties of biodegradable PLA and PLA/PCL blend tubes. In this study the fabrication process of the tube is modified so that the post processing of the tubes can be eliminated. The tubes were extruded by three different ways 1). Simple Extrusion (SE), 2). Biaxial Expansion(BE) during extrusion 3). Delayed Crystallization (DC). Simply extruded tubes and delayed crystallized tubes exhibit lower tensile modulus and tensile strength as compared to biaxially expanded tubes for identical wall thickness and tube diameter. Also it was found that the tubes of PLA/PCL blend containing 8wt.% PCL have better tensile properties as compared to PLA/PC blend with 5wt% PCL, even though incorporation of PCL increases ductility. Further, burst strength of the simple extruded tubes and biaxially expanded tubes are compared and reported in this study

S06-711

Savitri Emma, Purwanto Edy

The Chitosan Degradation by Ozonation Process to Produce Oligomer Chitosan

Chitosan is a linier copolymer $(1\rightarrow 4)$ –linked 2acetamido-2-deoxy- β -D-glucan (GlcNAc) and 2amino-2-deoxy- β -D-glucan (GlcN) units in varying compositions. It is considered to be non toxic, reactive and abundant biodegradable material. Because of the advantages of chitosan, it has attention for many diverse received much applications in biomedicine, pharmaceutics, cosmetic, biomaterial, agriculture, food processing, and waste water treatment. Because chitosan has high molecular weight and also strong intra and intermolecular hydrogen bonding, ozonation becomes alternatives to degrade chitosan into chitosan oligomers and glucosamine. In this study, chitosan was treated with ozonation process with different composition and temperature process. After ozonation, chitosan was characterized by viscosimetry to determine molecular weight and the oligomers was analyzed by HPLC to determine the dissolved product. High molecular weight of chitosan was also characterized by FTIR to analyzed whether there was changing in side group of product.

S06-714

Sumarno Sumarno, Mayangsari Novi Eka, Trisanti Prida Novarita

Combination of sonication and hydrothermal for depolymerization of cellulose in ionic liquid pressurized with CO2 and N2

Cellulose is a polysaccharide compound having a crystal structure so difficult to dissolve in water. Degradation of cellulose to obtain useful substances (glucose, glyceraldehyde, and others) can be done by acid hydrolysis, ionic liquid, enzymatic / fermentation, and hydrothermal processes. In this study the degradation of cellulose is done with a combination of sonication pretreatment and followed by hydrothermal processing in ionic liquids (NaCl and oxalic acid). Hydrothermal conditioin was conducted under CO2 and N2 gas at 200 bar. Temperature processing was 125 oC and 200 oC for various degradation time from 30 -180 minutes. After the degradation process the sample was separated as liquid and solid part, where the liquid is analyzed by the dinitrosalicylic acid method (DNS method) using а UV-Vis spectrometer to determine the reducing sugar. The solids were analyzed by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) to



understand the structure change. The results show that the glucose concentration increase with time of hidrothermal proessing and have a maximum at 120 minutes, and 90 minutes for 200 oC. The crystallinity and morphology of cellulose shown by XRD results and SEM. Product substances resulted in the degradation process was showed by LC-MS. Keywords: Polysaccharide, sonication, hydrothermal, ionic liquid, CO2, N2

S06-715

Lusiani Cucuk Evi , Ningrum Eva Oktavia, Trisanti Prida Novarita, Sumarno Sumarno

Processing of Cassava Pulp to Glucose and Oligosaccharides by Sonication Process

Cassava pulp is solid waste of tapioca industry, having a high amount of biopolymer (65.5% starch, and 8.1% cellulose). This biopolymer could be processed to get starch, glucose and oligosaccharides by sonication. The method use ultrasound frequency to obtain H and OH radicals to attack glicosidic bond of starch and cellulose. The aim of this research is to study the effect of reaction time and temperature of sonication process to the resulting product and cassava pulp morphology change. The suspension of cassava pulp in water (1/20 w/v) was firstly heated up to 40° C and 50° C continued by sonication process for 10 to 60 minutes. Viscosity of suspension after sonication process increased with sonication time. It is caused gelatinization and solubilization effect on suspension. Sonication could break polysaccharide chains as shown by increasing concentration of reducing sugars with reaction time. Moreover, the morphology of native and treated cassava pulp showed that the starch granule can be liberated from fibrous matrix of cassava pulp after sonication. Keywords : Cassava pulp, sonication, glucose, oligosaccharide

S06-719

Walha Fatma, Lamnawar Khalid, Maazouz Abderrahim, Jaziri Mohamed

Reactive extrusion of sustainably sourced polymer blends based on Poly (lactic acid) and Polyamide

11: improvement of melt strength, toughness and enlargement of blown processability.

The objective of this study was to gain a true understanding of the effect of the composition and compatibilization on the properties of entirely sustainably sourced polymer blends based on polylactide (PLA) and polyamide 11 (PA11). The main focus of this study is to overcome the shortcomings of PLA including its thermal instability, poor shear and low elongation viscosities in order to enhance its processability and to expand its application area. Polymer blends were prepared with various compositions of PA11 and various amounts of a chain extender containing reactive epoxy functions. Results showed that a "self compatibilization" between PLA and PA11 chains can occur but it was found to be insufficient, contrary to recent work reported in the literature. The role of Joncryl as a compatibilizer for the PLA/PA11 system has been demonstrated by the significant decrease of particle size and interfacial tension as well as the improvement of ductile properties. Mechanical as well thermo-mechanical properties were also investigated. Experiment results revealed a significant improvement of meltstrength and toughness according to the in situ formation of PLA-co-PA11 copolymers in the presence of the glycidyl methacrylate functions. Based on the improved shear and elongational rheological properties, a great enlargement of the blowing processing window of PLA blends was demonstrated (i.e by the study of blow and tack up ratios (BUR and TUR)). Besides, the incorporation of PA1

S06-723

Nanthananon Phornwalan, Suttiruengwong Supakij, Seadan Manus, Pivsa-Art Sommai, Hiroyuki Hamada

Biodegradable polyesters reinforced with eucalyptus fiber: effect of reactive agents

The aim of this work was to investigate the effect of reactive agents on the rheological behaviors, morphology and mechanical properties of two biodegradable polyesters; poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) reinforced with



eucalyptus fiber. Two types of reactive agents, chain extender (Joncryl®) and peroxide (Perkadox® 14), were selected. Biocomposites consisting of a constant fiber loading of 10 wt% with and without reactive agents were prepared by one-step meltmixing methods via an internal mixer with the rotational speed of 60 rpm and the temperature of 150 °C and 190 °C for PBS and PLA, respectively. The biocomposite samples were then compressionmolded for tensile testing. Rheological and morphological properties of the biocomposites were also investigated by means of dynamical mechanical analysis (DMA) and scanning electron micrograph (SEM). The results revealed the presence of Joncryl® in PLA biocomposites caused the increase of mixing torque, complex viscosity, storage modulus and mechanical properties when compared to the addition of peroxide. The increase of complex viscosity of PLA biocomposites added Joncryl® was due to the increase in the population of the higher molecular weights as confirmed by GPC analysis. In the case of PBS biocomposites, it showed a dramatic increase in the complex viscosity and storage modulus with decreasing crossover frequencies when adding peroxide rather than adding Joncryl®. The SEM micrographs demonstrated that the compatibility between the polymer matrix and fiber was improved when adding a small amount of Joncryl® and peroxide for both polymers, except for 0.5 phr peroxide loading, leading to an improvement of their modulus and tensile strength.

S06-727

Seesorn Janjira, Suttiruengwong Supakij, Seadan Manus, YONG Kok Wee

Mechanical and Rheological properties of different plasticized poly(lactic acid) grades filled with Talc

Polylactide (PLA) is a biodegradable aliphatic polyester with a good transparency and high tensile strength. However, its brittleness and cost become major drawbacks. Balancing between the mechanical properties and cost is a key to making PLA more competitive to existing commercial plastics. The aim of this research was to study the effect of plasticizer content and filler on the mechanical properties of poly(lactic acid). The different poly(lactic acid) grades, PLA 4043D, PLA 2003D and PLA 3052D, were selected and meltmixed with 2 to 14 wt% of Polysorb®ID46 as a plasticizer via an internal mixer. The melt flow index increased with the amounts of plasticizes added. The tensile results demonstrated that upon increasing concentrations of plasticizers, it resulted in a decreased Young's modulus and tensile strength whereas elongation at break increased drastically when adding of the plasticizer above 12 wt% (~330%) for all PLA grades. PLA 4043D and PLA 2003D were showed slightly decreased Young's modulus when increasing plasticizer content, whereas elongation at break was still high. Tand peaks of plasticized PLA were shifted to the lower temperature with increasing plasticizer concentrations. 3-15 phr of Talc was then added to 12 wt% and 14 wt% of the plasticizer in PLA. Dynamic mechanical properties of Talc filledplasticized PLA samples were recorded. The results showed that when Talc contents were increased for both plasticized PLA ratios, the storage modulus and the complex viscosity tended to increase. The effect mechanical properties was on less pronounced for 12 wt% plasticized PLA compared to 14 wt% plasticized PLA because it showed the slow decreasing rate of Young's modulus and tensile strength whereas the elongation at break was still very high compared with neat PLA. For PLA 4043D, the addition of even higher amounts of Talc could increase Young's modulus and tensile strength while maintaining the elongation property.

S06-734

Jafaie Mahsa

Electrospun Core-Shell Nanofibers based on Thermoplastic Urethane elastomer and Gelatin: evaluation of cell behavior

Most of human organs are composed of fibrous structure with fiber size ranging from nanometer to millimeter scale. Therefore, nanofibers have now been extensively employed to mimic natural tissue matrixes. Electrospun scaffolds based on hydrophobic and biodegradable polymers exhibit



good mechanical properties but do not show acceptable cell attachment. In contrast, scaffolds based on natural polymers such as collagen and gelatin show an inherent tendency for cell attachment, but they are mechanically weak. Thus core-shell nanostructured scaffolds are expected to be the best candidate. In the present work, attempts have been made to design and fabricate nonwoven mat based on nanofibers with core-shell structure comprising thermoplastic urethane elastomer (TPU) and gelatin as the core and shell, respectively. Effects of micromorphology and viscoelastic behavior of the prepared scaffolds upon cell behavior such as cell attachment, generation and purification is another prospect. For this purpose, electrospun process used with a core-shell type needle, and the two polymers were processed in the form of solution in HFIP. Influence of solution and processing parameters on developedcorresponding nanofibers and mat micro morphology were investigated. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) evidenced formation of gelatin layer on top of TPU fiber as the core. The surface hydrophilic behavior of the prepared mats was examined using contact angle measurement. Degree of weight loss and water resistivity in aqua's media were evaluated by immersing the prepared mats in solution comprising water and PBS. Cell attachment and cytotoxicity of scaffolds were studied.

S06-767

Zhang Biao , Serghei Anatoli , Sudre Guillaume , Bernard Julien, Fleury Etienne, charlot Aurélia

Guar gum/poly(ionic liquid)/ionic liquid hybrid ionogels: rheology, morphology and ionic transport

With the aim to generate non-conventional biobased solid electrolytes, we exploit the synergistic interactions between galactomannan chains and hydrophilic imidazolium ionic liquids (IL). More particularly, we selected guar gum as galactomannan related to - its abundance, - nontoxicity, - its peculiar structure, - its high thermal stability and the commercial availability of very high molecular weights. We recently demonstrated that such guar/IL association leads to solid-like gels with relevant rheological, thermomechanical and conductive properties [1,2]. Based on these advanced research, we are now focusing on the development of ternary blends presenting a higher degree of sophistication by incorporating additional reinforcing building-blocks, such as imidazoliumbased poly(ionic liquid) (PIL), in view of generating biohybrid materials with enhanced properties. We synthesized a series of PIL by RAFT polymerization and we particularly showed the excellent control of the polymerization [3]. PIL are promising synthetic polymers which combine the unique attributes of ionic liquids (thermal and chemical stability, noninflammability, non-volatility and conductivity) with the ones of polymers in terms of mechanical reinforcement, and dimensional stability. Structure/properties relationships of the resulting multicomponent were in-depth systems investigated. The rheological, thermal and conductive properties were methodically studied and correlated with the morphology of the biohybrids by means of synchrotron scattering measurements [4]. The concept presented herein, based on biosourced polymer-containing multicomponent systems represents a promising route for the design of advanced conductive materials. [1] C. Lacroix, E. Sultan, E. Fleury, A. Charlot, Polymer Chemistry, 2012, 3, 538. [2] L. Verger, S. Corre, R. Poirot, G. Quintard, E. Fleury, A. Charlot, Carbohydr. Polym., 2014,10,932. [3] B. Zhang, E. Fleury, A. Charlot, J. Bernard, ACS Macro Letters, 2015, 4, 1008. [4] B. Zhang et al., submitted to J. Mater . Chem. A.

S06-775

Coltellia Maria-Beatrice, Mallegni Norma Mallegnia, Cinelli Patrizia, Kazem Fehria Seyed Mohammad, Gigante Vito Gigante, Aliotta Laura, Lazzeri Andrea

Opportunities and issues in extruding biodegradable polyester blends for packaging

Poly(lactic acid) (PLA) is one of the most promising and ready to market material for applications in

packaging. A right balancing of stiffness and impact resistance is however necessary for its properties modulation in both flexible and rigid items. The use of additives, also in combination, or the blending with other thermoplastic polymers gives the opportunity of controlling both processability and final properties of PLA based blends and compounds. Other biodegradable polyesters such as proteins, much affected by thermal degradation during processing, not yet developed on a large industrial scale, can offer opportunities for processing natural polymers coming from food or agro-waste. The advantage of this approach is the possibility of adopting traditional extruders for processing such blends, even if the modification of the process and the development of new technologies is often necessary. In the latter case, although this topic is still at an early stage of development, it seems evident that it is necessary the control of melt viscositv and compatibility to develop biodegradable blends with controlled and reliable properties. Keywords: polyesters, poly(lactic acid), biodegradable, renewable, proteins

S06-776

Mia Hao-Yang Mia, Jing Xin , Yu Emily, Peng Xiang-Fang , Turng Lih-Sheng

Fabrication of Multiple-Layered Vascular Scaffolds by Hybrid Electrospinning, Braiding, and Thermally Induced Phase Separation Methods

Fabrication of small diameter vascular scaffolds has been a challenge in recent years, especially scaffolds with multiple layers. In this study, two approaches were proposed to fabricate multiple-layered vascular scaffolds by hybrid electrospinning, braiding, and thermally induced phase separation methods. It was found that the electrospun fibers had a compact fibrous structure that provided good mechanical properties. The porous TIPS layer had high porosity and pore interconnectivity to facilitate cell penetration; however, this structure alone could not ensure sufficient mechanical strength for surgical applications. Double and triple-layered vascular scaffolds consist of different

layer materials with various structures were fabricated by applying different methods alternatively. The triple layered scaffolds comprised of nanofibrous inner layer, woven silk filament middle layer, and porous outer layer were found can mimic the structure of native blood vessels. They have a desirable toe region in tensile tests and sufficient suture retention and burst pressure for vascular graft applications. Endothelial cell culture tests showed that a cell layer could form on the inner surface of the scaffold with high cell viability and favorable morphology. Keywords: Multiplelayered vascular scaffolds, electrospinning, thermally induced phase separation, mechanical properties, human umbilical vein endothelial cells

S06-780

Liu Sijun , Li Lin

The sol-gel transition and scaling laws for κcarrageenan in aqueous solution

κ-Carrageenan comes from a family of linear watersoluble polysaccharides extracted from different species of marine red algae and is composed of an alternating disaccharide repeating unit of α -(1-3)-Dgalactose-4-sulphate and β -(1-4) 3,6-anydro-Dgalactose. The 1C4 conformation of the 3,6anhydro-D-galactose units allows a helicoidal secondary structure, which is essential for κcarrageenan to gel in water. The gelation of ĸcarrageenan in aqueous solution is generally accepted as a two-step model involving a transition of coils to helices followed by aggregation of helices. A κ -carrageenan solution changes its state from a liquid to a solid (= gel) in the vicinity of a critical value of a gelling parameter (e.g. temperature or concentration) which is referred to as the gel point. For k-carrageenan gels, a threedimensional network is composed of helical aggregates as the junctions, and flexible chains junction connecting the zones. However, rheological studies of k-carrageenan in aqueous solution did not explore the region of sol-gel transition and the detail of junction structure so far. Our studies verified that k-carrageenan hydrogels were formed by the formation of fibrils, and the fibrillar diameter increased with increasing ĸ-


carrageenan concentration. The formation and melting of k-carrageenan gels were thermally reversible and extremely sensitive to κ-carrageenan concentration. In comparison with the crossover of G' and G'', the extrapolation method based on multiwave oscillation and Winter-Chambon criterion were able to give more accurate critical gel temperature Tc. At the gel point, the critical relaxation exponent n was almost constant and independent of temperature and k-carrageenan concentration, whereas the critical gel strength Sg increased with increasing critical gel concentration cg. A constant gel strength Sg/cg was obtained by normalizing Sg with cg to eliminate the effect of temperature or cg, showing a unique character of ĸcarrageenan in aqueous solution during gelation. The molecular structure of the junctions at the gel point was analyzed using the modified Eldridge-Ferry model shown in Figure 1, which supported the similarity of the fractal structure in the κcarrageenan hydrogels k-carrageenan, scaling law, rheology.

S06-90

Guarás María P., Torres Nicolini Andrés, Alvarez Vera A., Ludueña Leandro N.

Pilot scale production of thermoplastic starch/bentonite nanocomposites and their blends with polystyrene.

The non-biodegradability of most plastics has caused many environmental problems. This fact has carried to an increased use of biodegradable polymers for industrial applications. The development of new materials for industrial applications consists of different stages. The first one is the design of synthesis routes and new material properties at laboratory scale matching the application requirements. Once this step is completed, the next step is the scaling of processes. In recent times, the development of starch-based products has a growing interest. Nevertheless, the TPS has low stability in high moisture conditions and has a fragile nature. The mechanical properties of TPS can be greatly enhanced with the addition of a small amount of nanoclays (usually less than 10 wt%). In addition, blending TPS with other

polymers has been used. Polystyrene (PS) is a polymer widely used in thermoformed products. TPS/PS blends could meet partial biodegradability, mechanical properties stability, and improved processability. The aim of this work is to scale up the synthesis of TPS nanocomposites and their blends with PS in order to obtain partial biodegradable products by thermoforming. Corn starch was used in powder form. The plasticizer used was glycerol. PS was purchased from INNOVA. Natural bentonite from Minarmco S.A. was used as nanoreinforcement. TPS/clay nanocomposites (TPS5B): corn starch, glycerol, stearic acid and 5wt.% of bentonite were extruded and pelletized in a twin screw extruder of D=18mm and L/D=25D at 25 rpm and 120/130/130/140/140ºC. TPS5B/PS and TPS5B/LDPE blends: blends 50/50 wt.% of TPS5B/PS were prepared by twin screw extrusion at 25 rpm. The temperature profiles used were 150/170/180/190/190. TPS5B/PS blends were thermoformed in a vacuum assisted machine.

S06-459

Verbeek Johan, Khanna Jai, Bier Jim

Reinforcement of Thermoplastic Protein Using Polymorphs of Titanium dioxide

Novatein thermoplastic protein is bio-based alternative to petrochemical thermoplastics but depending on the application, may not have the appropriate mechanical properties. Titanium dioxide is an effective reinforcement for Novatein, but its polymorphs (rutile and anatase) behave differently as reinforcements. The effect of composition and polymorph type was investigated for Novatein composites containing up to 3 wt% TiO2. Additionally, the effect of water as a plasticiser was investigated by conditioning samples at 50% relative humidity, thereby removing some water that would otherwise act as a plasticiser. The unconditioned results (i.e. high water content) showed that the tensile strength of unreinforced Novatein increased by 20% and 16% for rutile and anatase, respectively whereas the secant modulus increased by 60% and 30%. After removing excess water, the tensile strength increased by 30% and 13%, whereas the modulus



increased by 50% and 80% for each type. Impact strength showed the opposite behaviour and anatase generally lead to a greater increase. Impact strength increased by 15% and 70% for the rutile polymorh for high and low water content respectively, whereas it decreased by 30% and 40% for the anatase form. From these results, it can be understood that the rutile polymorh of TiO2 performed better with greater improvement in mechanical properties, most likely interacting differently with protein chains, leading to subtle changes in protein secondary structures.



Poster

S06-36

Li Ching-Feng, Wu Tzong-Ming

Electrocatalytic behavior of chitosan/polyaniline nanocomposite prepared via different acidic aqueous solutions for biosensing

A simple sensor based on glassy carbon electrode (GCE) modified by chitosan/polyaniline (PANI) nanocomposite has been studied. The casted nanocomposite film on GCE was prepared from formic acid, acetic acid and citric acid aqueous solutions. The morphology and electrocatalytic activity of chitosan/PANI nanocomposite were characterized by scanning electron microscope (SEM), cyclic voltammetry (CV) and differential pulse voltammetry (DPV). CV results revealed that the polyaniline in the chitosan/PANI film exhibited electrocatalytic activity to redox reactions of potassium ferricyanide (K3Fe(CN)6) used as probe. Among the three acids, chitosan/PANI casted by formic acid exhibited the most appropriate polyaniline dispersion in chitosan film, which resulted in the highest electrocatalytic activity. Therefore, chitosan/PANI nanocomposite casted on GCE via formic acid was used as working electrode to detect dopamine (DA). The biosensor provides a linear DPV response in the range of 0.25mM to 1.75mM for DA detection.

engineering materials such as structural materials and tribomaterials based on all plants-derived materials. Plants-derived polyamide 1010 (PA1010) was made from plant-derived castor oil. Hemp fiber (HF) was previously cut into length of 5mm, 10mm, 20mm and 50mm, and was surface-treated by two types of treatment: alkali treatment by NaOH solution and surface treatment by ureido silane coupling agent (HF-S). The volume fraction of HF-S in the composites was fixed with 20vol.%. HF-S/PA1010 biomass composites were extruded by a twin screw extruder and injection-molded. Their mechanical properties such as tensile, bending, Izod impact and Durometer hardness, and tribological properties by ring-on-plate type sliding wear testing were evaluated. It was found that the mechanical properties of HF-S/PA1010 biomass composites change with the initial fiber length of HF. The critical fiber lengths of various mechanical properties of these biomass composites decrease as follows: strength > modulus > elongation at break > Izod impact strength. Tribological properties such as frictional coefficient and specific wear rate also change with the initial fiber length. The frictional coefficient of these biomass composites slightly decrease with increasing the fiber length. On the other hand, the specific wear rate of these biomass composites dramatically improved with increasing the fiber length, and has a minimum peak at 20mm. It follows from these results that it may be possible to develop the new higher performance engineering materials by selecting the suitable fiber length.

S06-102

Nishitani Yosuke, Mukaida Jun, Yamanaka Toshiyuki, Kajiyama Tetsuto, Kitano Takeshi

Influence of Initial Fiber Length on the Mechanical and Tribological Properties of Hemp Fiber Reinforced Plants-Derived Polyamide 1010 Biomass Composites

The aim of this study is to investigate the Influence of initial fiber length on the mechanical properties of hemp fiber filled plants-derived polyamide 1010 biomass composites in order to develop the new

S06-129

Etxabide Alaitz, Uranga Jone , Urdanpilleta Marta, Guerrero Pedro

Promoting changes in protein structure as means of tailoring properties of fish gelatin biocomposites

The final properties of biopolymeric materials are directly related to the structure of the biopolymer at mirco- or nanoscale. With this regard, the extent of the cross-linking in biopolymers can be controlled



by the type of cross-linker but also by the conditions used during the preparation of biocomposites. In this work, the reaction between gelatin and lactose was analyzed as a function of lactose content and both processing methods and conditions. It was observed that soluble films can be prepared at acidic pHs, when the extent of crosslinking was lower, as shown by colour and UV-vis spectroscopy measurements, indicating the inhibition of cross-linking when pentosidine, a soluble compound, was formed. These results highlight the potential use of these films as active films in contact with gastrointestinal fluids, in which the pH is acid. In contrast, cross-linking reaction progressed at higher pHs, resulting in films with high UV-vis protection and tensile strength higher than 50 MPa, which could be used as packaging films. In all cases, the lactose-modified materials were transparent and hydrophobic, functional properties required for many applications.

S06-143

Zhang Zheng-Chi, Zhong Gan-Ji, Li Zhong-Ming

Preparation of PLLA/PDLA Blends with High Stereocomplex Crystals Content through an Efficient Thermal Treatment Method

Polylactides (PLA), produced by abundant renewable naturally occuring resources, is the most promising biodegradable polymer to replace conventional petro-based thermoplastics. However, the low heat resistance restricts its application in various fields. Fortunately, the stereocomplexe crystal (SC) formed in the blends of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) with melting temperature 50 °C higher than that of homochiral crystals (HC) provides a promising solution to high thermal resistant PLA materials. Nevertheless, it is not an easy task to obtain samples with high SC content especially in melting blened molecular weight PLLA/PDLA blends due to the microscopic phase separation into a PDLA-rich and a PLLA-rich phase. In present work, a simple and effcient method, i.e. thermal treatment, was applied to PLLA/PDLA blends. The thermal treatment conditions were carefully determined by using DSC

tests. The optimal thermal treatment temperature and duration is 210 °C and 10 min, respectively. Furthermore, the crystallization process was traced by in-situ WAXD during thermal treatment process under the optimal treatment condition. As a result, samples with exclusive SC and crystallinity of over 50% were obtained and a template effect is proposed to explain this phenomenon, i.e. newly formed SCs are induced by the surface of residual SCs. It is worthy to note that this simple and effcient thermal treatment method is open to almost all samples prepared through commercial processings to achieve high SC content and reasonable heat resistance. Keywords: PLA, stereocomplex crystals, thermal treatment.

S06-150

Bai Hongwei, Huang Chunmei, Zhang Huixian, Fan Mingfeng, Fu Qiang

Towards high-performance poly(L-lactide) products by tailoring crystallization with the aid of fibrous nucleating agent

As a "green" alternative for traditional petroleumbased polymers, bio-based and biodegradable poly(L-lactide) (PLLA) exhibits tremendous application potential in various fields because of its biocompatibility, excellent outstanding processability, and favorable mechanical strength. However, the large-scale adoption of PLLA as a commodity thermoplastic still faces some obstacles mainly associated with its poor heat resistance because the low crystallization rate makes it hard to crystallize during melt processing. In this contribution, we report a facile and robust strategy to address this obstacle via simultaneously tailoring crystal morphology and lamellae orientation with the aid of the nucleating agent (NA) that can be completely dissolved in PLLA melt and re-organize into fibrils upon cooling. These fibrils can act as nucleation templates to induce the crystallization of PLLA lamellae perpendicular to their long axis, thus inducing the formation of shish-kebab structure accompanied with the significantly accelerated crystallization. More importantly, by taking advantage of the preferred orientation of NA fibrils along the flow direction experienced in melt



processing, highly orientated PLLA lamellae is formed in injection molding articles and melt spun fibers. In this way, significantly improved heat resistance and tensile strength are achieved. This work provides a good example of preparing highperformance PLLA products by using a fibrous nucleating agent as a template to tailor the crystal morphology and lamellae orientation.

S06-154

Can Buse Nur, Ozkoc Guralp

PBAT/Thermoplastic Starch Blends: "Effects of Oxidized Starch and Compatibilizer Content"

In the last decade, the usage of plastics parallel to the modernization has increased in daily life. This increase of using plastics causes solid waste problems. Therefor many researches have focused on biodegradable polymers. In this study, the biodegradable blends of thermoplastic starch (TPS) and poly(butlylene adipate-co-terephtalate) (PBAT) were prepared in the presence of a styrene-acrylic multi-epoxy functional compatibilizer and oxidized thermoplastic starch (OTPS) using one-step meltcompounding process. The need for OTPS is to arrange the flow properties of starch phase and to balance the hydrophilicity. The compatibilizer is used to enhance the interfacial properties and the phase dimensions. The OTPS/PBAT ratio and the compatibilizer ratio were selected as material **OTPS/PBAT** parameters. The blends were characterized by performing tensile, impact tests; differential scanning calorimeter (DSC) and scanning electron microscopy (SEM). The physicochemical properties such as mechanical strength, glass transition and melting temperatures were investigated. The fracture morphology was studied by means of scanning electron microscopy (SEM). The rheological behaviour was investigated by means of oscillatory rotational rheometry. It was observed that the multi-epoxide compatibilizer improved the mechanical and rheological properties of the blends. The morphological investigations supported these findings. Keywords:

thermoplastic starch, poly(butlylene adipate-coterephtalate), compatibilization, blending

S06-16

Malfatti Andrea, Steuernagel Leif, Meiners Dieter

Improvement Of Mechanical Properties Due To Increased Fiber Matrix Adhesion In Flax Fiber Reinforced Polypropylene

The hydrophilic nature of natural fibers and the hydrophobic behavior of standard polymers such as polypropylene and other polyolefins are the major causes for the lack of adhesion between fiber and matrix in natural fiber reinforced plastics (NFRP's). To overcome this incompatibility of fiber and matrix, different coupling agents can be incorporated into the compound. Investigations at the Institute for Polymer Materials and Plastics Engineering (PuK) at Clausthal University of Technology revealed the bonding capability of three dendritic polyesters and one thermoplastic polyurethane in a flax fiber/PP compound. The treatment with different amounts of coupling agent led to an increase in mechanical properties such as bending strength, tensile strength and most of all CHARPY impact strength. In addition it was possible to make a correlation between IR spectra and the chemical and physical interactions between fiber, matrix and adhesive. Therefore a relationship between intermolecular forces and mechanical properties could be concluded.

S06-174

Lee Jungmin, Park Jongshin

Preparation and characterization of polysaccharide hydrogels based on modified starch

Hydrogels are hydrophilic, three-dimensional, and expandable matrices that are produced through chemical and/or physical crosslinking of certain polymers. In some cases, polysaccharides such as carboxymethyl cellulose, alginate, and starch were used in hydrogel preparation. In this study, chemical modification of starch was carried out in order to improve the functionality of the

compound. Epichlorohydrine and citric acid were used for crosslinking, respectively. Finally, polysaccharide hydrogels were prepared by chemical reaction of carboxymethyl cellulose and sodium alginate with modified starch and crosslinker. The structures of modified starch and polysaccharide hydrogels were established using FT-IR spectroscopy. The morphology and swelling behavior of hydrogels were studied. These polysaccharide hydrogels may have potential applications in the biodegradable superabsorbent polymer and controlled delivery of bioactive agents.

S06-198

Li Yang, Xu Jia-Zhuang, Li Zhong-Ming

Effects of Shear Flow on Crystalline morphology of Polylactic Acid

Manipulating the crystalline morphology of polylactic acid (PLA) is of immense concern in its endpoint application. In this contribution, evolution of crystalline morphology of polylactic acid (PLA) was investigated by combination of home-made fiber-pulling device with polarized optical microscopy (POM). By dint of this, the correlation between shear flow, always existed in the practical processing, and crystalline morphology was expected to be established. The shear rate calculated by Monasse's method was controlled by changing the pulling speed of the glass fiber (GF) in the PLA melt. In-situ POM results showed that the PLA spherulites were dispersed in the quiescent melt randomly, indicating no nucleation ability of GF. When the shear flow was imposed, that was GF was pulled, a large amount of cylindrulite appeared at the surface of GF. It was because high density of nucleation sites was induced by the shear flow around the GF surface. And these nuclei hindered the lateral extension and forced lamellae growth perpendicular to the GF axis. With the increase of shear rate, the nuclei density on the surface of GF was further increased, resulting in the formation of compact cylindrulite. Fiber pull out test confirmed that the interfacial strength was dramatically improved due to the interface crystallization between the PLA and GF.

S06-208

Kodal Mehmet, Elchekwis Abdulmounem, Özkoç Güralp

The Effects of Gamma Irridation on the Mechanical and Thermal Properties of Poly(lactic acid)

Poly (lactic acid) (PLA) is attractive as a substitute for classical polymers due to its biodegradability and sufficient mechanical properties. In the present work, various blend ratios of poly (lactic acid) (PLA) and triallyl cyanurate (TAC) were prepared compounding in by melt an Xplore microcompounder and molded by Xplore model microinjection molding device. TAC was used as a coagent. After compounding process, PLA/TAC composites were exposed to a gamma irridation at various adsorbed doses ranging from 0 to 100 kGy. The mechanical properties of PLA and PLA-TAC were performed by tensile testing. The chemical structure of PLA and TAC was visualized by Fourier Transform Infrared (FTIR) spectroscopy. The thermal properties of the composites were investigated by Differential Scanning Calorimetry (DSC). Results showed that neat PLA was strongly degraded by gamma irradiation while PLA-TAC composites are less affected because gamma irradiation promoted the TAC layer distribution within the PLA matrix. The elongation at break of composites decreased with the increasing TAC content. However, E-modulus has improved about 15% compared to pure PLA. DSC results indicated that a sharp decrease in degree of crystallinity (Xc%) of PLA/TAC composites was obtained for higher gamma irridation doses. FTIR analysis showed that gamma irradiation of PLA lead to oxidation reactions of ester groups inducing the formation of hydroxyl groups which can be present in hydroperoxides or alcohols. Keywords: PLA, crosslinking, gamma irridation

S06-255

Jaufurally Abdus Samad, Teixeira Andreia, Hollande Louis, Ducrot Paul-Henri, Allais Florent

Chemo-enzymatic synthesis and functionalization of a renewable lignin-derived bisphenol:



promising biobased antiradical additive and phenolic monomers

Lignins are the second most abundant natural polymer found in plants. They derive from the oxidative polymerization of three phydroxycinnamic alcohols (aka monolignols) in the presence of oxidative enzymes such as laccases1 and peroxydases. These monolignols differ from each other by the degree of methoxylation on the aromatic ring. During lignification, oxidized monolignols are coupled through different coupling patterns (e.g. b-b, b-5, 5-5 and b-O-4) resulting to C-C and C-O-C linkages2. Under specific conditions, one specific coupling has been favored to obtain a bisphenolic dimer as major product. With regards to the potentialities of this bisphenol as functional additive (e.g., antioxidant) or synthon, we optimized this biocatalyzed synthesis through design of experiments, and successfully obtained 93% yield of the pure bisphenol, without any further purification needed. TGA analysis of the dimer revealed high thermal stability Td5% (up to 281 °C). High antiradical activity was revealed by DPPH analysis3 and compared to that of commercial antioxidants (BHT, BHA and Irganox 1010). The bisphenol was then functionalized to obtain novel renewable phenolic monomers for polymer chemistry. References: (1) David M. O'Malley, Ross Whetten, Wuli Bao, Chen-Loung Chen, R. R. S. Plant J. 1993, pp 751–757. (2) Landucci, L. L. J. Wood Chem. Technol. 1995, 15 (3), 349-368. (3) Brand-Williams, W.; Cuvelier, M. E.; Berset, C. Food Sci. Technol.-LEB 1995, pp 25-30.

S06-266

Hollande Louis, Jaufurally Abdus Samad , Ducrot Paul-Henri, Allais Florent

ADMET polymerization of biobased monomers deriving from syringaresinol

Renewable a,w-dienes have been prepared from bromo-alkenes and syringaresinol, a naturally occurring bisphenol deriving from sinapic acid, using a chemo-enzymatic synthetic pathway then studied as monomers in ADMET polymerization with Hoveyda-Grubbs II catalyst. All monomers and polymers have been thoroughly characterized using NMR, GPC, DSC and TGA. ADMET polymerization was optimized with regard to catalyst loading and reaction medium (in mass vs. in solvent), which led to polymers with molecular weight up to 14.1 kDa. Thermal analyses of these new polymers showed excellent thermal stabilities (257-360 °C) and tunable Tg (18-70 °C) depending on the chain length of the alkene in the a,w-diene monomer. KEYWORDS: polyesters, ADMET polymerization, a,w-dienes, syringaresinol, bisphenol, lignin

S06-286

Calderas Fausto, Medina-Torres Luis, Nuñez-Ramirez Diola Marina, Sanchez-Olivares Guadalupe, Santiago-Adame Ruben, Manero Octavio

Minimizing Polymer Degradation In A Spray Drying Process Of Aloe Vera (Barbadensis Miller) Mucilage (Biopolymer

Rheological properties of Aloe vera mucilage reconstituted in aqueous solution by spray drying (SD) were evaluated on a shear rate range between 1 to 300 s-1, the rheological behavior was evaluated in function of mucilage concentration, temperature, pH and ionic strength. A decrease on shear viscosity was observed, showing non-newtonian behavior of the type thinning fluid (n<1) in all the increase imposed conditions. An in the pseudoplastic behavior was observed due to increased concentration of powder reconstituted in aqueous solution in the range of 3 to 6 g/100 mL. Viscosity values in the shear flows of the mucilage solution at 6 g/100 mL are higher than shown by a fresh solution mucilage, and 3 g/100mL xanthan gum at 25 °C. Cross model was properly adjusted to correlate viscosity data at shear-rate. The viscosity was found to be dependent on ionic strength, such as polyelectrolytic solutions, so, as the ionic strength increases, the viscosity decreases. This behavior was more remarkable when divalent cations are used. Aim, a marked dependence of viscosity on pH was observed, with increasing the pH of an acidic medium at an alkaline medium, viscosity increases. Aqueous solution of mucilage showed elastic flow similar at the Opuntia ficus



indica mucilage. The linear viscoelastic spectrum in a frequency range of 0.1 to 200 rad/s tends to have weak gel behavior, with a crossing point between elastic module G' and viscous modules G'', (G'= G''), which suggests a change in molecular conformation and a random coil arrangement in the molecule of reconstitute mucilage unlike fresh mucilage. Finally, fresh mucilage was let to spray drying at the best conditions of SD inlet: 1.5 L/ h flow, temperature of 150 °C and atomization rate of 27,500 rpm. The final powders were reconstituted in aqueous medium to compare the chemical composition and mechanical flow behavior with fresh mucilage, shown thickening and bioactive properties.

S06-299

Hammiche Dalila, Boukerrou Amar, Djidjelli Hocine, Grohens Yve

Effect of Fiber type on the properties of biobased polymer composites

Lignocellulosic fibers have gained a major interest in to use as reinforcement in polymer matrices due to their availability, low cost and compatibility with the environment. This work deals with the development of biocomposite materials based on polyhydroxybutyrate-co-valérate (PHBV) containing 20 w.% of natural fiber i.e., alfa fiber and olive husk flower (OHF). The effect of fiber type on thermal, mechanical and morphological properties of biocomposites was evaluated. Young modulus of PHBV was increased when alfa fiber and OHF each added either alone or both. From the SEM images, it was observed that OHF was uniformly dispersed in PHBV compared to alfa fiber. This may be due to the size of fiber. Indeed, the result obtained from a particle size distribution analysis showed that the size of particles of OHF varied between 1 µm to 150 um. More than 90% of OHF had a diameter lower than 96 µm, however, 90% of alfa fiber was obtained with a diameter between 100-110 µm. For OHF having lower particle sizes most of the fiber surfaces are covered with the matrix material attesting for adequate compatibility between the two phases.

Bai Dongyu, Bai Hongwei, Fu Qiang

Fabrication high-performance and optically transparent polylactide stereocomplex by lowtemperature powder sintering

Stereocomplexation provides an interesting way to greatly enhance performance of eco-friendly polylactide (PLA). Numerous studies have been carried out on stereocomplex formation and characterizations, but it is still a huge challenge to high-performance create stereocomplexed polylactide (sc-PLA) products from melt-processed high-molecular-weight poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) blends due to the poor melt memory effect of stereocomplex (sc) crystallites to restore exclusive sc crystallization after complete melting, which leads to the formation of a product with mixed homochiral (hc) and sc crystallites, and the substantial thermal degradation of PLA chains. Hence, we demonstrate a simple but robust strategy to address these obstacles by sintering of sc-PLA powder at temperatures as low as 180-210 °C for the first time. The results confirm that interdiffusion of enantiomeric PLA chain segments across interfaces of adjacent powder particles enable them to interact and co-crystallize into sc crystallites capable of tightly welding the interfaces during the sintering process, and thus sc-PLA products with 100% sc crystallites, excellent heat resistance and good transparency have been successfully fabricated. This work opens a new for the design and industrial-scale avenue of high-performance, fabrication optically transparent sc-PLA-based products via powder metallurgy inspired low-temperature sintering using conventional polymer sintering equipment. Keywords: polylactide; stereocomplex; powder; low-temperature; sintering

S06-343

Lai Sun-Mou, Liu Jung-Liang, Wang Chun-Chieh, Liao Wan-Lin, He Yu-Ting, Huang Yu-Wei, Yeh Hi-Ju, Luo De-Ting, Chang Chih-Ning



Preparation Of Natural Rubber (Nr) /Polycaprolactone (Pcl) Bio-Based Shape Memory Polymer Blends

PCL (polycaprolactone) is a biodegradable material exhibiting biodegradability and low processing temperature characteristic. NR (natural rubber) is a bio-based natural material without relying on petroleum resources. Shape memory NR/PCL biobased blends, where NR served as the reversible phase and PCL served as the switching phase, were prepared using a melt blending process. This work aims to further understand the various properties of NR/PCL eco-shape memory blends and foams. Only very limited NR/PCL blends were evaluated in the literature, but rare on their shape memory properties and fracture behaviors. In particular, the effect of crosslinking degree will affect the shape fixing and recovery behaviors in the different phases of the foam blends. The blend of NR and PCL could form thermoplastic elastomeric biobased blends for processing flexibility with elastomeric characteristics. effect The of crosslinking types including silane and sulfur on the thermal characterizations besides the one-way and two-way shape memory behaviors will be discussed. NR appeared to exhibit two-way shape memory behavior, but the addition of PCL greatly increased the actuation. This work paves the way for new development on the bio-based shape memory polymer blends.

S06-344

LOGIE Nicolas, DELLA VALLE Guy, DESCAMPS Nicolas , SOULESTIN Jérémie

Assessment of structural changes and rheological behavior of potato and pea starches under extrusion conditions.

Using conventional polymer processing techniques like extrusion, in presence of plasticizers, starch can be converted into a homogenous molten state. Process conditions may lead to different structural changes, or destructuration of starch, such as fragmentation of granules, crystals melting, molecular degradation which have an influence on final material properties. Therefore, a good understanding of starch melting and its rheological behavior is necessary to determine optimal processing conditions and better control of the products quality. That's why structural changes and starch destructuration have been evaluated depending on extrusion conditions in order to improve current rheological and melting understanding, optimize starch melting using extrusion and minimize material degradation. In this work, two starches of different botanical origin (pea, 33% amylose, and potato, 20% amylose) were processed on a twin-screw extruder under various specific mechanical energy inputs (SME). They were processed in presence of water contents (25, 30, 35%) in order to monitor the melting temperature of starch Tm, determined beforehand by DSC and at temperatures allowing to limit water evaporation and expansion at the die. Starch destructuration was investigated at different structural scales: molecular (chromatography), crystal (X-ray diffraction, DSC), granular (microscopy and paste rheology). Finally, the viscosity of partly molten starch was determined on a pre-shearing rheometer, Rheoplast® (simulating extrusion under controlled conditions). Combined with experimental methods development for destructuration degree evaluation, it enables to suggest interactions mechanisms between rheological behavior, extrusion parameter and transformation degree.

S06-358

Boukerrou Amar, Hammiche Dalila, Djidjelli Hocine, Beridi Maria José Fernandez

Effect of olive husk flower on the properties of biobased polymer composites

view of to higher production cost In of polyhydroxybutyrate-covalerate (PHBV) as compared to traditional polymers, we opt at the possibility to replace a quantity of PHBV by lignocellulosic fiber without damaging the properties of the composites. This study highlights the effect of fiber loading and pretreatment on properties of biocomposites based on PHBV. Thus, the biocomposites containing 10, 20 and 30 wt.% of olive husk flower (OHF) with and without pretreatment were prepared by using a co-rotation twin screw extruder followed by injection molding. Tensile modulus of biocomposites increased with fiber loading and with pretreatment but tensile strength decreased, whereas, the pretreatment of OHF enhances this property due to the better interfacial interaction of the PHBV biopolymer and the reinforcement after pretreatment. This result was confirmed by SEM analysis. Indeed, the surface of composites prepared with OHF pretreated had less voids and cavities suggesting a good adhesion between the two. Thermogravimetry analysis showed also that composites with pretreatment have enhanced thermal properties when compared with the composites without pretreatment.

S06-378

Boubekeur Bahia, Belhaneche-Bensemra Naima, Massardier Valérie

Jute fiber- reinforced PEBD/PLA biocomposites: Evaluation of Thermo-Mechanical properties and Morphology

The aim of the study is to enhance the natural fibers in the development of composite material. For this reason we opted for jute fiber as a reinforcement of blend of two polymers polylactic acid (PLA) and low density polyethylene (LDPE) in the presence of polyethylene compatibilizer glycidyl Methacrylate (PE-GMA) in the following composition PLA / LDPE / PE -GMA (80/20/5). The mechanical, thermal properties and morphology of the composites were investigated. the Were have prepared and characterized of jute fiber/composites. For that purpose, PLA/LDPE/PE-GMA blends reinforced of variable composition of jute fiber (0% - 40%) were prepared. They were characterized in terms of physical properties (density), mechanical properties. Their morphology was investigated by scanning electron microscopy. The results show that the properties of the fiber jute composites are better so the higher value of strength was obtained when the content of jute fiber 40%. Generally, a relatively good dispersion was achieved in composite with 20% of fiber jute. The results of thermogravimetric analysis show that adding 10% of fiber jute decreased the onset

temperature of degradation of composite beyond this percentage is found that this temperature remains more or less constant, The stability of fiber jute/composites was better. Keywords: poly (lactic acid), low density polyethylene, jute.

S06-400

Tiewtragool Phornkamol, Magaraphan Rathanawan

Bio-based Thermoplastic Elastomer Containing Polylactide and Natural Rubber via Admicellar Polymerization

Recently, the development of materials for reducing the environmental problems is an important issue. Bio-based materials from renewable resource gain lot of interests because they can be alternatives to petroleum-based materials. So to reduce the environmental impact from waste, bio-based materials should be used to produce thermoplastic elastomer materials. In this study, polylactide and natural rubber latex (NRL) were chosen as raw materials for a new thermoplastic elastomer via admicellar polymerization. Admicellar polymerization is the technique to coat polymer thin film onto the substrate surface by bilayer of surfactant which acts as a reaction template for polymerization. By using constant concentration of NRL substrate of 0.05 g/ml, the lactide monomer content (200, 500, 800, and 1000 mM) was varied to find the suitable concentration of lactide monomer for bio-thermoplastic elastomer applications. Fourier transform infrared spectra of the admicellar synthesized rubbers showed natural the characteristic peak of polylactide. The core-shell structure of polylactide coated onto natural rubber latex particles was revealed by transmission electron microscope (TEM). The bio-thermoplastic elastomers were characterized by dynamic mechanical analysis (DMA) for the glass transition temperature (Tg), behavior of materials and by melt flow index testers for measuring of the ease of flow of the molten bio-thermoplastic elastomers

S06-409

Shen Yucai, Wang Tingwei



Tailoring the oxygen gas barrier property in biodegradable poly(propylene carbonate) composites

Poly(propylene carbonate) (PPC) was melt mixed with poly(lactic acid) (PLA) and poly(butyleneadipate-terephthalate) (PBAT) in a laboratory internal mixer with a small amount of chain extender additive. Differential scanning calorimetry was used to measure their crystallization properties and crystallinity. Morphological characterization of composites was achieved by scanning electron microscopy. A comparative study of the oxygen gas barrier properties of PPC composites has been made. Tensile tests were also used to measure the mechanical properties. Results showed that there is a correlation between structure and oxygen gas barrier properties of the composites, and their structure mainly resulted from the loadings of different component of the composites and chain extender additive. Therefore, tailored oxygen gas barrier properties of the composites can be achieved.

S06-439

Li Zhong-Ming, Zhang Jin, Ding Jian-Xun , Liu He, Zhuang Xiu-Li, Chen Xue-Si, Wang Jin-Cheng

Ultra-High-Modulus Porous Polymer/Hydroxyapatite Composite Scaffold for Significantly Enhancing Cranial Bone Regeneration

A formidable challenge still exists nowadays in the fabrication of porous scaffolds with high mechanical performance essential for the regeneration of load-bearing bone tissues. Herein, high-pressure compression molding was utilized to structure a porous composite scaffold comprising poly(L-lactide) (PLLA), poly(lactide-co-glycolide) (PLGA), and hydroxyapatite (HA) aiming at enhancing the mechanical performance. The morphological observation indicates formation of a compact interpenetrating network structure and an optimized crystalline architecture in the highpressure compression molded (HPCM) scaffold. The yield load and Young's modulus of the HPCM scaffold molded under the condition of 1000 MPa/180 °C/45 min climb remarkably up to 71.45 N and 6.84 MPa, respectively, which become the highest values reported to date. The HPCM scaffold possesses an interconnected porous structure with a porosity of above 80%, an appropriate degradation rate, and an enhanced cellular proliferation. The HPCM scaffold is further investigated for the reparation of rat calvarial defect. Fascinatingly, all the data of high X-ray radiopacity, considerable bone density, enhanced biomineralization, excellent biomechanics, and upregulated osteogenesisrelated proteins demonstrate that the HPCM scaffold efficiently stimulates bone restoration and osseous tissue integration. The intriguing features suggest a prominent potential of our ultra-highmodulus scaffold for supporting the infiltration and reconstruction of bone in calvarial defects.

S06-458

Hopmann Christian, Facklam Martin, Schoengart Maximilian

Welding of Bio-Based Plastics for Applications in the Field of Injection Moulding

Due to intensive research in the field of material development considerable progresses in terms of processing and performance characteristics could be achieved during the last years. Therefore biobased plastics are increasingly being used for the durable production of injection moulded components. Several applications can be found in the automotive sector, in the field of consumer electronics or the sports industry. For an economic production, the joining technology often plays a key role to realise modular designed components. Detachable connections, which are frequently used in plastics processing (e. g. snap hooks or screw connections), often reach their limits with respect to the reliability and tightness of the joint. In order to meet the increasing requirements to the joint, plastics joining processes can allow a suitable component assembly. Bio-based plastics may differ from conventional plastics regarding their processing properties, such as the melting and solidification behaviour. Therefore investigations at IKV were carried out to get an extensive process knowledge in welding of bio-based plastics. To



perform a scientific examination of the influence of the moulding process on the weld seam quality, cellulose and lactic acid based plastics were selected and injection moulded with varying parameters like mass temperature, mould temperature and injection speed. In subsequent welding experiments using the infrared and ultrasonic welding method connections have been produced and analysed with regard to mechanical and morphological properties. The investigations show that all of the selected biobased plastics can be welded. Depending on the material and the welding method the choice of the moulding parameters can have different influences on the weld seam strength. For example, a higher mould temperature during injection moulding leads to higher weld seam strengths for ultrasonic welded test specimens made of lactic acid-based plastics.

S06-51

Aouachria Kamira, Massardier Valerie

Thermal, Rheological and morphological Properties of PLA/EVA – ATBC Blends

Polylactic acid (PLA) has attracted a lot of attention in recent years because of its good properties such as high transparency, high tensile strength and excellent biodegradability. However, high modulus and low strain slow down development of applications such as packaging. To overcome this limitation, PLA is mixed with various ethylene vinyl acetate (EVA) content (0-90% by weight) in absence and in presence of acetyl tributyl citrate (ATBC). The dynamical mechanical analysis (DMA) and thermal properties measured by differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) are fully investigated. By using scanning electron microscopy (SEM), it is demonstrated that ATBC increases the miscibility of PLA/EVA blends.

S06-667

Ben Hamou Karima, Kaddami Hamid, Dufresne Alain, Magnin Albert

Comparative study of nanocomposite materials reinforced with different cellulose nanofibrils: Morphologies, physical and interfacial properties.

Currently, numerous efforts are focused on the use of materials from renewable resources as reinforcement agents in nanocomposites. Among materials readily available, cellulose such nanfibrillated (CNFs) have attracted great interest due to their renewability, biodegradability, and spectacular mechanical properties. The effect of oxidation time on the morphology and the rmomechanical properties of polyvinyl acetate (PVAc) reinforced with cellulose nanofibrils (CNFs) was investigated. Two CNFs, prepared by 2, 2, 6, 6tetramethylpiperidine-1 oxyl (TEMPO)-oxidation of cellulose, were used and are presenting different morphologies and surface properties. The NFC-5min is more than 1 µm long and presents low surface energy and NFC-2h is 300 nm long and presents high surface energy (Benhamou, et al. 2014). Nanocomposites with various weight ratios of NFCs were fabricated by casting and vacuumdrying method using MeOH as solvent. These nanocomposite films exhibited high optical transparency and the MEB analyses have shown that the NFCs were dispersed homogeniously in the PVAc polymer. On the other hand the tensile strengths, elastic moduli are improved with increasing CNFs content. It appears that the size of the fibers has a greater influence as fiber composites having the larger size has the best mechanical properties. Dynamic mechanical analysis showed that the storage modulus of the CNF/ PVAc films increased significantly with CNF content above the glass-transition temperature of PVAc by the formation of an interfibrillar network structure of CNFs in the PVAc matrix. However, the thermal stability of both families of nanocomposites is lower compared to neat PVAc, based on percolation theory, only the smaller fibers seem to accelerate slightly the decomposition process. The outstanding and effective polymer reinforcement by CNFs results from their high aspect ratio, high crystallinity, and nanodispersibility in the PVAc matrix.

S06-686



Esmaeili Mohsen, Bagheri Reza, Pircheraghi Gholamreza

Effect of sorbitol/glycerol ratio on hydrogen bond formation and crystallization of co-plasticized starch

Thermoplastic starch (TPS) samples have been prepared in the present study using glycerol and sorbitol as co-plasticizers. Two different amounts of plasticizer, i.e. 36 and 42 wt.%, and sorbitol/glycerol ratios of 3:0, 2:1, 1:2 and 0:3 were incorporated for plasticizing granular corn starch using a laboratory co-rotating twin screw extruder. The hydrogen bond formation between plasticizers and starch chains was investigated by Fourier Transform Infrared Spectroscopy (FT-IR). X-ray diffraction (XRD) was also employed to study the crystalline structure of TPS over a period of two months to investigate the possible retrogradation process of starch. FT-IR results illustrated that the strength of starch-plasticizer hydrogen bond enhances by increasing the total amount of plasticizer and sorbitol/glycerol ratio. XRD spectra revealed A-type crystals of native starch are turned to anhydrous Va-type crystals after gelatinization. However, retrogradation and formation of hydrated Vh-type crystals may occur in the samples over storage time. Based on XRD results, glycerol plasticized starch samples are extremely prone to retrogradation as evidenced by formation of Vhtype characteristic peak. While, in the co-plasticized starch samples the mentioned peak is weakened and totally disappeared if only sorbitol is used for plasticization. In other words, the retrogradation can be effectively suppressed in the samples plasticized with higher amount of sorbitol. This is attributed to the strong hydrogen bonding between the starch chains and the sorbitol molecules.

S06-687

Hajlane Abdelghani, Kaddami Hamid , Joffe Roberts

Development of cellulose based polymer composite with enhanced through-the-thickness properties

The environmental concerns and public awareness of potential problems associated with growing consumption of oil and petroleum based materials boosted research on natural fiber composites. In particular plant fibers with high content of cellulose (e.g. flax, hemp) are of great interest due to their high stiffness and strength. However, these fibers properties which hinder their possess as reinforcement for structural composites (e.g. limited fiber length, sensitivity to moisture, high variability of properties). temperature, Therefore, another cellulosic fiber has attracted attention - manmade Regenerated Cellulose Fiber (RCF). This fiber is continuous with well-defined, consistent geometry and properties, which makes it reinforcement for composites. suitable The proposed Master Thesis project is continuation of the work carried out at LTU on development of natural fiber composites for structural applications. It is well known that composites usually exhibit excellent in-plane properties (e.g. tensile stiffness and strength) which are controlled by fibers that may be assembled in various 2-D reinforcements (e.g. uni-directional fabric, weave, non-crimp fabric). However, through-the-thickness properties are relatively weak because they are governed by the properties of the resin and in large extend by the strength of fiber/matrix interface. The objective of this study is to use hierarchical cellulosic reinforcement consisting of micro-sized RCF and cellulose nano-crystals to create composite with enhanced properties and durability to damage. The cellulose nano-crystals are grafted on the RCF assembled into non-crimp fabric in order to enhance the intra- and inter-laminar properties of the composite. Thus, the through-thickness performance is expected to be improved due to the nano-crystal network created on (and in between to) fiber.

S06-778

Stanescu Paul Octavian , Radu Ionut , Zaharia Catalin , Vasile Eugenia, Galateanu Bianca

DesignAndCharacterizationOfPolyhydroxyalkanoatesNanoparticlesLoadedWith Silymarin For Drug Delivery Applications

The design and production of efficient drug delivery systems (DDS) are of vital importance in tissue engineering and regenerative medicine.



Various polymers, either synthetic or natural, have been exploited for the production of drug delivery systems. Among them the class of biodegradable is of major compounds interest. Polyhydroxyalkanoates (PHAs) are a family of natural biodegradable polyesters obtained by numerous bacteria through the fermentation of sugars, lipids, alkanes, alkenes and alkanoic acid, as a unique intracellular carbon and energy storage compounds and accumulated as granules in the cytoplasm of cells [1-3]. Poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3hydroxyvalerate) (PHBHV) are the most studied natural polyesters and they are the first commercial thermoplastics from a bacterial source. This research paper is focused on the design of a delivery systems comprising polyhydroxyalkanoates nanoparticles (PHBHV) loaded with silymarin. Several approaches were employed to obtain an efficient DDS starting with oil in water emulsion and nanoprecipitation methods. PHBHV nanoparticles were characterized by FTIR and RAMAN. Morphological investigation of the particles was achieved through SEM and AFM techniques. Silymarin mass encapsulation in nanoparticle was determined from the amount of drug originally used and the amount remaining in the supernatant after harvesting. A validated spectrophotometric analysis method was used to assess encapsulation. In vitro release studies in PBS were performed in triplicate and the cumulative percentage release over time was plotted. Finally, biocompatibility of the nanoparticle system was assessed on human adipose stem cells (hASCs). References [1] S. Philip, T. Keshavarz and I. Roy, Review Polyhydroxyalkanoates: biodegradablepolymers with а range of applications, Journal of Chemical Technology and Biotechnology, 82, 2007, pp. 233-247 [2] Sang Yup Lee, Polyhydroxyalkanoates, Bacterial Biotechnology and Bioengineering, 49,1996, pp. 1-14 [3] Yu Ke, Yingjun Wang, Li Ren, Gang Wu, Wei Xue, Surface modification of PHBV films with different functional groups: Thermal properties and in vitro degradati

Quintana Robert , Persenarie Olivier , Lemmouchi Yahia , Bonnaud Leila, Dubois Philippe

Compatibilizing co-Plasticized Cellulose Acetate/Water Soluble Polymers Blends by Reactive Extrusion

The production of fully biodegradable materials is receiving large attention in the research community and industrial sector as the way out to produce environmentally friendly products. Biodegradable polymeric materials are an important alternative because they diminish the consequences of plastic waste through composting. In this communication, preparation and compatibilization the of biodegradable blends of cellulose acetate (CA) with two water soluble polymers; polyvinyl alcohol (PVOH) and the bio-sourced hydroxyethyl cellulose (HEC) will be presented. Like CA, HEC is advantageously both biodegradable and biosourced. For that purpose, plasticization of CA and PVOH was conducted by melt extrusion using triacetin and glycerol, respectively, while a twostep method consisting in a premixing step of HEC with plasticizer in presence of water, followed by the melt processing of the swollen premix was used and led to the successful plasticization of this biopolymer. Plasticized PVOH-based blends proved to exhibit better processability and properties. The prepared blends were characterized in terms of morphology and thermo-mechanical properties. The quality of blend interface was enhanced by reactive compatibilization using maleic anhydride grafted-polylactide (MAgPLA). An original procedure was conducted using two extruders connected in a T-configuration to prepare various plasticized CA-PVOH blends compositions. This advantageous set up allowed for in situ plasticization of CA which significantly reduces its thermo-oxidative degradation. The water-response of these blends was evaluated to settle on their potential as new water-dispersive biodegradable materials. Keywords: Cellulose acetate; Polyvinyl alcohol; Hydroxyethyl cellulose; Plasticization; Biodegradation; Biopolymer; Reactive compatibilisation/

S06-790

S06-792



Ozge Ozkoc Semin , Sungur Seval , Kaval Melike , Ozkoc Guralp

Comparison of Different Esters as Co-plasticizer in Edible Thermoplastic Starch Films

Production of environmentally friendly packaging materials getting increasing interest among researchers through consumer demands and regulations. Native polymers, such as starch alone do not meet all the requirements of synthetic polymer based food packaging materials. Therefore, thermoplastic starch films are obtained to meet most of the requirements. During this process, plasticizers are used to achieve ease of processing and in some studies co-plasticizers were used to prevent retrogradation of thermoplastic starch. In this study, different esters such as tributhyl citrate (TBC), triisodecyl citrate (TIDC) and ethyl benzoate (EB) were used to obtain edible thermoplastic starch films. Mechanical properties, clarity processing characteristics, and hydrophylicity measurements were done to compare films formulated with different esters. It is seen that the most compatible plasticizer was found to be TBC. The films produced using TBC elongates much higher than the others in tensile test, whereas their tensile strength and elastic modulus were lower. The mechanical tests showed that EB was incompatible with thermoplastic starch. The surface hydrophobicity of the thermoplastic starch films increased when co-plasticizers were used. The citrate esters having different molecular structures can be used as useful plasticizers to tune the properties of the thermoplastic edible films. Keywords: co-plasticizers, edible film. hydrophylicity, mechanical properties, thermoplastic starch.



S07- Process Modeling and Simulation

Keynotes

S07-18

Mitsoulis Evan, Konaganti Vinod Kumar, Hatzikiriakos Savvas G.

Extrudate Swell Of A High-Density Polyethylene Melt: Modeling Using Integral And Differential Constitutive Equations

The extrudate swell phenomenon of a highmolecular-weight HDPE is modelled using the following viscoelastic constitutive equations: the multi-mode Kaye–Bernstein-Kearsley-Zapas (K-BKZ) integral model with the Wagner and the Papanastasiou-Scriven-Macosko (PSM) damping functions, and multi-mode Phan-Thien-Tanner (PTT), Giesekus and Double Convected Pom-Pom (DCPP) differential models. The high-molecularweight high density polyethylene (HDPE) is rheologically characterized and the experimental data have been used to fit the parameters of the constitutive models. Experimental results on extrudate swell are compared with the numerical predictions. The simulation results showed that the integral K-BKZ model highly overpredicts and the differential PTT, Giesekus and DCPP models slightly under-predict the experimental measurements. When the capillary reservoir is excluded from the simulations, the predictions of the integral models are significantly reduced close to the experimental data, while those of the differential models remain practically unaffected. Although both integral and differential models used represent the rheological data equally well, an dramatically explanation of the different predictions of extrudate swell by the integral and differential models remains elusive.

S07-532

guzman-maldonado eduardo, Hamila Nahiene, philippe boisse

Simulation of thermoplastic prepreg thermoforming based on a visco-hyperelastic model

Thermoforming of thermoplastic prepregs is a fast manufacturing process. It is suitable for automotive composite parts manufacturing. In this paper, the simulation of thermoplastic prepreg forming is achieved by alternate thermal and forming analyses. The thermal properties are obtained from a mesoscopic analysis and a homogenization procedure. The forming simulation is based on a viscous-hyperelastic approach. The thermal coefficients simulations define the of the mechanical model that depend on the temperature. The forming simulations modify the boundary conditions and the internal geometry of the thermal analyses. The comparison of the simulation with an experimental thermoforming of а part representative of automotive applications shows the efficiency of the approach.

S07-649

Baird Donald, Chen Hongyu, Lambert Greg

Simulation of Long Fiber Orientation during Injection Molding in the Presence of Fiber Breakage

Long-fiber (lengths > 1 mm) thermoplastic composites (LFTs) possess significant advantages over short fiber (< 1 mm) composites in terms of their mechanical properties while retaining their ability to be injection molded. Mechanical properties of LFTs are highly dependent on the microstructural variables imparted by the injection molding process including fiber orientation and fiber length distribution. As the fiber length increases, the mechanical properties of the composites containing discontinuous fibers can approach those of continuous fiber materials. Long fibers have the ability to deform, bend and even break during any stage of the injection molding process. There is a lack of knowledge about the effects of fiber length and fiber length distribution (FLD) on fiber orientation kinetics. This lack of



information provides an opportunity to understand the length effect inherent in long fiber systems. The Bead-Rod fiber orientation model takes into account the flexibility of semi-flexible fibers that show small bending angles. In this model, a flexibility parameter representing the resistive bending potential is fiber length dependent. This work focuses on studying the influence of the fiber length variation on the performance of the Bead-Rod model. The Phelps and Tucker breakage model enables us to update the flexibility parameter based on the FLD data at each time step. From this aspect, the fiber breakage model is coupled with the fiber orientation model. The parameters within the stress tensor and orientation model are obtained via basic rheological measurements using simple shear flow in a sliding plate device and planar extensional flow in lubricated squeezing flow. Numerical simulation results involving a basic injection molding geometry are compared with the experimentally obtained fiber orientation and fiber breakage data. The bead-rod model shows significant improvement over the rigid rod model.

S07-669

Simacek Pavel, Sas Hatice, Advani Suresh

Process Modeling of Flow and Heat Transfer in Thermoset Pultrusion

The thermoset pultrusion generally consists of two steps: Resin infiltration into the dry reinforcement and Resin Cure. These two steps are carried in sequence and are coupled by the material motion. In the first step the dry reinforcement is impregnated with resin as it passes through a pressurized resin infusion chamber. Then, the reinforcement is compacted as it is pulled through a die which compacts the reinforcement increasing the fiber volume fraction and may complete the resin saturation due to the buildup of the pressure in the die. In the second step, the saturated tape moves into a heated die and resin cures before it exits the tool. The coupling between two stages is usually limited by the same material velocity, as the heated die tends to be thermally insulated from the infusion chamber. However, the common processing speed constitutes serious constraint to

process optimization. A process model is developed which is incorporated in an existing numerical simulation of resin infusion that can predict the relevant changes of the state in the dry fiber reinforcement tape as it passes through the tooling set, first during the infusion stage, then during the cure for complicated profiles. The simulation is used to identify a process window for the range of parameters for successful manufacturing without voids or dry spots. In addition one can use the virtual manufacturing simulation to optimize the entire process. The model considers the infusion dynamic in the pressurized chamber and relates the tape velocity with pressure, resin viscosity and reinforcement layup. For the cure stage, the limits are dictated in relation to prescribed velocity and applied heating. Experiments are also conducted to validate the cure and temperature profile during the process.

S07-89

Agassant Jean-François , Demay Yves , Castellani Romain, Abdesselam Yamina , Peres Richard, Gourdin Diego

Investigation of the knife-over-roll coating process for Plastisols coating applications

Plastisol formulations, composed of PVC particles of various sizes, calcium carbonate filler and several additives in a plasticizer, are widely used for flooring applications. The most commonly used coating process consists in shearing this plastisol formulation at room temperature between a substrate (a glassmat for example) disposed on a rotating cylinder and a fixed knife of varying geometry. The gap between the substrate and the knife is adjusted in order to deliver the prescribed coating thickness. The coated plastisol is then introduced in an oven for gelation. The coating ability of a plastisol formulation depends on its rheological behaviour. Several model plastisol formulations with varying PVC particle sizes and with or without calcium carbonate filler have been prepared and coated. Their shear rheology has been measured on a wide range of shear rates using a Couette rheometer and a capillary rheometer. Depending on the formulation, Newtonian, shear



thinning and shear thickening behaviours may be observed leading to non standard constitutive equations. A numerical model has been developed to account for these peculiar behaviours. It allows predicting the pressure distribution, the force exerted on the knife and the coating torque as a function of the processing parameters.



Oral

S07-103

Dubey Satya Prakash, Abhyankara Hrushikesh A, Mercchante Veronica, Brighton James L , Bergmann Bjorn, Trinh Giang , David Chantal

Alternative Energy Source Impact on Synthesis of Poly Lactic Acid through Continuous Reactive Extruder: Reaction kinetics modeling

Abstract¬¬-PLA is one of the most promising biocompostable and bio-degradable thermoplastic made from renewable sources. In the literature, the technique mainly developed for ring opening polymerization (ROP) of Lactide is based on metallic/bimetallic catalyst (Sn, Zn, and Al) or other organic catalysts in suitable solvent [1]–[3]. However, the PLA synthesized using such catalysts may contain trace elements of the catalyst which causes hazard and toxicity. Reactive extrusion experiments using stannous octoate Sn(Oct)2 and tri-phenyl phosphine (PPh)3 were considered to perform ROP of lactide monomer using ultrasounds as an alternative energy (AE) source for activating and/or boosting the polymerisation. Mathematical model of ROP of PLA was developed to estimate the impact of reaction kinetic and AE source on the polymerisation process. Ludovic® software was used for the simulation of continuous reactive extrusion of PLA. Experimental and simulated results schematic were developed to validate Figure 1. In this work we also investigated the usefulness and drawbacks of most conventional metal catalysts as well as effect of alternative energies on reaction mechanism and future aspects for safer and efficient bulk PLA production. Keywords: alternative energy, bio-degradable, Extrusion, metal catalyst, poly lactic acid (PLA), ring opening polymerization (ROP) [1] P. Dubois, C. Jacobs, Jerome, R. and Ρ. Teyssie, "Macromolecular engineering of polylactones and polylactides. 4. Mechanism and kinetics of lactide homopolymerization by aluminum isopropoxide," Macromolecules, vol. 24, no. 9, pp. 2266–2270, Apr.

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1991. [2] Y. Yu, G. Storti, and M. Morbidelli, "Ring-Opening Polymerization of l,l-Lactide: Kinetic and Modeling Study," Macromolecules, vol. 42, no. 21, pp. 8187–8197, Nov. 2009. [3] I. Banu, J.-P. Puaux, G. Bozga, and I. Nagy, "Modeling of L-lactide Polymerization by Reactive Extrusion," Macromol. Symp., vol. 289, no. 1, pp. 108–118, 2010.

S07-128

Huang Chao-Tsai, Hsu Chih-Chung, Chang Rong-Yeu, Tseng Shi-Chang

Cavity Dependence of Core Penetration in Co-Injection Multi-Cavity Molding

Co-injection molding is commonly used in daily accessories, car parts, and structural-reinforcement product. However, there are too many combinations of designs, materials, core/skin ration, and process condition, how to have suitable control of co-injection is very challenge. Furthermore, coinjection with multi-cavity system which is commonly applied in some forks structure products. However, due to the complicated nature, the inside mechanism for the combination of coinjection and multi-cavity is still not fully understood yet. In this study, we have proposed three kinds of multi-cavity systems to investigate cavity design influence on the core material penetration behavior. In Model 1 with three separated cavity system, the core penetration into individual cavity is strongly dependent on the timing of complete filled of the first cavity. Although flow rate conditions will affect the penetration history during the processing, it doesn't change the final core penetration shape too much. On the other hand, we have also considered different thickness of connection between cavities in Model 2 (with 3.5 mm thick connector) and Model 3 (with 1.75 mm thick connector). During the early filling age (less than 90% of total volume filled), in Model 3, it is Branch 2 dominant; while in Model 2 it has no preference for Branch 1 and 2. The flow rate conditions have no significant effects for core penetration in this period. However, as more melt keeps flowing into cavities till the end of filling, the core penetration behavior is dramatically different at low flow rate (10 cm3/s). These results



show that in the presence of different thickness of connector, the core penetration history and final shapes are significant different to that of separated cavity system (Model 1). Obviously, cavity design can alter the preference of core penetration from one side to the other. The results can help people for the management of skin/core distribution in coinjection molding.

S07-141

Mostafaiyan Mehdi, Wiessner Sven, Heinrich Gert

Application of the Least Square Finite Element Method in the Interface Tracking of a Two-Phase Flow

A least square finite element method is employed to solve the time dependent interface advection equation and to calculate the nodal values of the volume fractions (F) in a two phase flow, where the initial values of the volume fractions are determined by an imaginary control volume around each node. Then the quality of the reconstructed interface, which is obtained by the assumption of F=1/2, is evaluated using two different criteria and a highly satisfactory reconstruction is reported, before and after interface advection. Moreover, we benefited from a local least square method to calculate the tangent of the interface at its intersections with the element faces, which is considered to be an important parameter in the surface tension calculations. Finally, some explanatory examples are provided to assess the performance of the introduced method.

S07-145

Taniguchi Takashi, Harada Kohei

Multi-scale simulations of polymer melt flow in a contraction and expansion channel

We investigated a flow of a polymer melt with a molecular weight distribution in a channel with 4:1:4 contraction and expansion geometry by using a multi-scale simulation (MSS) method where a macroscopic model and microscopic molecular model are directly connected through the velocity gradient field and stress field. In the MSS method, we introduced Lagrangian particles, each of which contain many chains to precisely maintain the microscopic states. As the microscopic polymer model, a slip-link model is used. As a result, we clarified the relation between the macroscopic flow behavior and molecular level information such as a local polymer configuration and spatial distribution of number of entanglements per chain.

S07-160

Tran Thi Kieu Nhung , Colomines Gaël, Nourry Arnaud, Pilard Jean François, Deterre Rémi, Leroy Eric

A semi-mechanistic model for polyurethane cure thermokinetics : Application to a natural rubber based thermoset

The future of thermosetting polymers relies both on the formulation of biobased systems and on the energetic optimization of the molding processes. This second task more than ever relies on accurate thermokinetic modelling of the cure reactions involved. Nevertheless, bridging that gap between mechanistic knowledge and the production of simple kinetic equations that can be used in process simulation softwares remains a difficult issue. In the present work, we revisit the modelling of polyurethane cure kinetics taking the case of a partially biobased system : Isoconversional analysis was applied to non-isothermal bulk cure kinetics of uncatalyzed polyurethane (PU) resins based on telechelic hydoxyl natural rubber (HTNR) and poly[(phenyl isocyanate)-co-formaldehyde] (P-MDI). The dependency of apparent activation energy on conversion led to the identification of two different kinetic models, each involving two activation energies: a phenomenological model based on the Kamal-Sourour equation with non integer reaction exponents; and a new semimechanistic model. It assumes a main second order reaction between alcohols and isocyanates forming urethane linkages, and a secondary reversible reaction forming allophanates that is known to become significant above 120°C. Such a model based on mechanistic considerations gives more accurate simulation of experimental data, using less kinetic parameters and allows explaining the variations of reactivity of the HTNR polyols with its



average molecular weight. Keywords: bio-based polyurethane, natural rubber, calorimetry, kinetics, modeling

S07-223

Kech Armin

Evaluation of Fiber Orientation Prediction for automotive applications

The study presented started with a significance study of process parameters on resulting fiber orientation distributions of an injection-molded housing. The part is injection-molded from hydrolysis stabilized short glass fiber reinforced Polybutylene Terephthalate. It can be shown which parameter has most significant influence on fiber orientation, determined by X-ray micro computer tomography. Finally the fiber orientation is not the important data to measure, but mechanical properties for a part undergoing temperature changes as one of the operational loads. Another issue which is directly affected by the fiber orientation is warpage. So the study will show how accurate the fiber orientation distribution must be predicted to get data for thermo-mechanical loading as well as warpage which will be used for a pre-correction of the part before an initial sampling takes place. In order to show this behavior a decent analysis of material data as well as material models is required. Therefore, issues like solidification criteria, applied deformation laws for anisotropic shrinkage will be critically evaluated.

S07-230

Kaufman Miron, Fodor Petru S.

Erosion In Extruder Flow: A Numerical And Analytical Study

A detailed analysis of the fluid flow in Tadmor's unwound channel model [1] of the single screw extruder is performed by combining numerical and analytical methods. Using the analytical solution for the longitudinal velocity field (in the limit of zero Reynolds number) allows us to devote all the computational resources solely for a detailed numerical solution of the transversal velocity field [2]. This high resolution 3D model of the fluid flow in a single-screw extruder allows us to identify the position and extent of Moffatt eddies [3] that impede mixing. We further consider the erosion of particles (e.g. carbonblack agglomerates) advected by the polymeric flow. We assume a particle to be made of primary fragments bound together. In the erosion process a primary fragment breaks out of a given particle. Particles are advected by the laminar flow and they disperse because of the shear stresses imparted by the fluid. The time evolution of the numbers of particles of different sizes is described by the Bateman coupled differential equations [4] developed a century ago to model radioactivity. Using the particle size distribution we compute an entropic fragmentation index [5] which varies from 0 for a monodisperse system to 1 for an extreme polydisperse system. The time dependence of the index exhibits a maximum at some intermediate time as the system starts monodisperse (large size particle) and evolves through a polydisperse regime at intermediate times to a monodisperse (small size particle) at late times. [1] Z. Tadmor and C.G. Gogos, Principles of Polymer Processing, 2nd edition, Wiley-Interscience, Hoboken, New Jersey, 2006. [2] M. Kaufman and P.S. Fodor, Physica A 389, 2951 (2010). [3] H.K. Moffatt, J. Fluid Mech. 18, 1 - 18 (1963). [4] H. Bateman, Proceedings of the Cambridge Philosophical Society, 15, 423-427 (1910). [5] M. Kaufman, Nanoscale and Microscale Thermophysical Engineering, 11, 129–136 (2007).

S07-241

Costa Franco S, Cook Peter S, Zuo Zhihao

Enhanced Shrinkage Prediction Considering Cooling Rate Effects on PVT

The prediction of pressure decay, density and shrinkage of injection molded parts is based on the pressure-volume-Temperature (PVT) equation of state. The PVT of materials is typically characterized at equilibrium or near-equilibrium conditions which are far-removed from the rapid cooling rates occurring during injection molding. In this study, a cooling rate dependent PVT model for amorphous polymers is implemented as a user-PVT function interfacing to the Moldflow Insight



software. Predicted shrinkage values are compared to measured data for a number of amorphous materials at three different part thicknesses. Not only were improvements in the shrinkage magnitude observed, but also improvements in the trend of shrinkage changes with respect to part thickness (and cooling rate) were observed.

S07-252

Salazar Betancourt Luis Fernando, Laure Patrice, Silva Luisa, Sager Mustafa

On The Numerical Thermo-rheological-kinetical modeling Of Fibre-reinforced Composites

To improve the modeling of fiber reinforced composites, we present in this work numerical methods able to compute both fiber-reinforced composites deformation in squeeze flow and thermal-kinetic evolution. The homogeneous orthotropic model for fiber composites described the anisotropy of the in-plane fiber. Both physics are related since the kinetic evolution as well as the temperature profile modify the rheology of the composites. The model used here to account for the kinetics of reaction is the Bailleul's model. An study case is presented, where the mold temperature is set to 150C to a composite sample at 40C. Thermal transfer begins as well as sample compression at constant speed. The thermo-rheological-kinetical coupling is done by means of the viscosity. Here the kinetic impacts is shown by the evolution of the temperature, velocity and stress during reaction. Reaction begins in the surface and moves towards the center. However, reaction in the core of the material, once started, is much quicker than in the surface. This translates into a mapping of viscosity values presented during the reaction, modifying the usual nature of the squeeze flow pattern.

S07-256

Francois Guillaume, Ville Laurence, Gallier Stany

Two phases model for highly suspended viscous flow and 3D simulation

In this work, we aim to develop a numerical tool able to simulate viscous flows with large spherical suspensions at high concentration. Suspensions are described by their homogenized volumetric fraction. A two-phases formulation is used: the "suspension balance model" (SBM). This method introduces a particle stress to model the shearinduced migration and its effect on the flow equations. Concentration evolution is predicted by solving a new migration equation based on convection by flow and particle stress balancing. As particles interactions have a strong influence on the viscous flow, the new stress is also introduced into the Navier-Stokes equations. Its contribution is divided into a viscous stress, considered as a local viscosity increase, and a normal stress, considered as a volumetric force. The SBM model is then implemented into the Rem3D® injection simulation software. Migration and suspended flow equations benefit from the existing numerical stabilizations for 3D simulations. Migration accuracy is tested at each stage of its integration with simple validation cases. Finally, its robustness is proved with a more complex and three-dimensional industrial case, including moving free surface and complex flow as

S07-265

fluid-buckling.

LAURE Patrice, Nakhoul Rebecca, Silva Luisa, Vincent Michel

Multiphase and Multiscale Approaches for Modeling the injection of textured molds

Micro-injection molding is frequently used in micro-medical, micro-optic and micro-mechanics due to its effectiveness for mass production. This work focuses mainly on offering numerical tools to model the injection of textured molds. Such tools can predict the different filling scenarios of the micro-details and consequently offer optimal operating conditions (mold and melt temperatures, melt flow, stresses etc.) to judge the final part quality. To do so, a fully Eulerian approach is used to model the injection of textured molds on both the macroscopic and microscopic scales as usual industrial software cannot handle the filling the micro details. Since the thermal transfers with the mold are very relevant due to the cooling ratio, the coupling between micro- and macro- simulations are a must to insure a complete and accurate representation of textured molds injection. The influence most important parameters are studied and comparisons with experiment data are presented.

S07-291

Klein Daniel, Zimmer Johannes, Stommel Markus

This is a contribution to the optimization of packaging processes for plastic containers. It is common practice, to apply a stepwise packaging for a product. The so called primary packaging contains product, from the prevents it environmental influences and ensures that hygiene standards are fulfilled. A Secondary packaging facilitates the distribution of goods from the supermarket to the home of the consumer and a tertiary packaging is necessary for the shipment of the product on a pallet from the supplier to the customer. A widespread method for secondary packaging is the use of oriented Polyethylene (PE) shrink films. These films are designed to meet the individual requirements on their shrink behavior and thereby on the mechanical properties of the resulting secondary packs. The single layers of multilayer films can consist of material blends of Low Density-, Linear Low Density- and High Density PE (LDPE, LLDPE and HDPE). Within this high diversity of shrink films, the choice of an appropriate type depends on the individual mechanical properties of the product and on the desired pack size. Extensive testing in combination with a high level of expertise is afforded for that matter. The objective of this study is to simplify the packaging development using numerical methods. The procedure is described for the example of a pack consisting of six plastic bottles. A FE-Model of the shrink process is built up and calibrated experimentally. This Model predicts internal stresses, strains as well as shape and thickness distribution of the shrink film after it has been processed in the oven. In a follow-up FE simulation 166

a load is applied to the resulting six pack whereas the mechanical properties of the shrink film are described using a rate dependent elastoplastic material model. Parameters for the material model are fitted to uniaxial tensile test data. The result of the "load simulation" is compared with corresponding experiments and thus validates the numerical method

S07-305

BorzacchielloDomenico,Abisset-ChavanneEmmanuelle, Chinesta Francisco, Keunings Roland

A macroscopic model for predicting flow induced orientation of fibers in viscoelastic fluids

Most theoretical fibre suspension models currently used for predicting the flow-induced evolution of microstructure in the processing of reinforced thermoplastics are based on the Jeffery model of dilute suspensions in a Newtonian suspending fluid or phenomenological adaptations of it that account for fibre-fibre interactions. The viscoelastic behavior typical of thermoplastics is not taken into account by these models even though experimental results evidence radically different kinematics depending on whether the fluid is Newtonian or not. Even though few counterparts of the Jeffery theory exist for second-order fluids, they have been rarely considered and, to our knowledge, never taken into account for macroscopic scale modeling. In this work, we address the modeling of short fibre suspensions in rheologically slow flows of different viscoelastic fluids throughout the description scales, from microscopic to macroscopic. We propose a simplified modeling framework based on the concept of effective velocity gradient acting on the fibre. This is derived from the asymptotic analysis of the flow around the fibre at small Weissenberg numbers and allows the straightforward extension to viscoelastic fluids of the standard Folgar & Tucker model widely used in industrial simulation software.

S07-308

Park Jang Min

Phase-field models for partially miscible systems



In this work, phase-field models for partiallymiscible binary and ternary systems are presented based on the Cahn-Hilliard theory. A binary system is first studied by employing specific free energy function combining two smooth functions which have double-well and single-well structures, respectively. The binary model is then extended to a ternary model. In this case, particular attention is payed to satisfy algebraical and dynamical consistency with the binary system. Finally some numerical results will be presented which demonstrates usefulness of the present model.

S07-356

Spencer Paul, Caton-Rose Fin, Sweeney John, Coates Phil

Modelling of solid phase deformation

Solid phase polymer processing, such as diedrawing, is an establisted technique to produce highly oriented polymer products with a large enhancement in mechanical properties. The basic die-drawing process involves pulling a solid polymer billet through a converging die at elevated temperature, producing a large stretch in the axial direction, leading to orientation of the polymer chains. Here we use Finite Element Analysis to simulate free tensile drawing and the die drawing process. The parameters of the Material Law were determined from an extensive set of experimental tests. Large deformation 3D parametric analysis was performed in the commercial Finite Element package Abaqus. We investigated the effect of drawing speed, temperature, geometry, material properties, and the surface interaction between the polymer and die wall. The model predicts product dimensions and drawing force. The simulations were compared with experients performed on a small-scale die-drawing rig mounted on a tensile tesing machine. Here, strain and geometry were measured using image analysis, and combined with force measurement from the testing rig. We consider die-drawing both a rectangular crosssection and tube. By drawing a tube over a mandrel within the die, orientation may be induced in the hoop as well as the axial directions. Combining experimental and numerical investigation leads to a

more detailed understanding of the conditions required to produce orientation.

S07-416

Pachner Sophie, Aigner Michael, Miethlinger Jürgen

Modeling and Optimization of Melt Filtration Systems in Polymer Recycling

Introduction Melt filtration plays an important role in improving material quality, particularly in relation to polymer recycling, as it ensures that the melt stream is suitably clean and free of contaminants such as paper, metals, wood, foreign plastics, glass, dust particles, unmelted or degraded polymer formations. Optimization and Modeling The performance of a double-cavity piston screen changer was improved by rheological optimization of the flow geometry based on analytical calculations and numerical CFD simulations. We optimized the geometry of flow channels and breaker plate in order to increase their self-cleaning capacity, decrease residence time of the melt in the filter and reduce pressure drops, thus enabling gentle processing of various thermoplastic polymers. For the layout of a filtration process, the initial pressure drop of the polymer melt and the separation performance of the filter must be determined. An improved model allows the calculation of the pressure drop in a polymer melt flowing through woven screens as a function of mass throughput and polymer properties. Results Designing a melt filter with optimized flow geometry means balancing conflicting requirements. While achieving small pressure drops calls for increased diameters of the flow channels, short residence times and high wall-shear speeds for efficient self-cleaning require diameters to be reduced. The performed numerical und analytical calculations yielded an optimal design that takes into account all parameters. As a result, for a given pressure drop, the average residence time could be reduced by 13% and the wall-shear speed increased by 15%. In addition to the optimized flow geometry, we present a novel mathematical model for calculating the pressure drop based on heuristic algorithms. The model can be applied for polymers flowing through square-



woven and twilled-dutch screens, and was validated using a variety of in-house recycling materials, throughputs and filtration fines.

S07-440

Pignon Baptiste, Boyard Nicolas, Sobotka Vincent, Delaunay Didier

Crystallization Study Under Processing Conditions: High Cooling Rate And High Pressure

An accurate knowledge of heat transfer during forming processes (injection moulding, thermoforming...) is essential to predict shrinkage and warpage and consequently the quality of a thermoplastic part. Simulation requires the determination of both thermophysical properties and crystallization kinetics since they are intimately coupled and of the boundaries conditions at the part surface in conditions close to forming processes. Thus, we present the characterization of the crystallization at high cooling rate under high pressure conditions and also of the thermal contact resistance between the polymer and the mould, three complementary apparatus. The using crystallization kinetics at very high cooling rate is determined with a nanocalorimeter, the Mettler Toledo DSC Flash 1. The size reduction of samples allows the device to reach heating rates up to 20 000 K/s and cooling rates up to 10 000 K/s. The crystallization of a neat polypropylene or filled with black carbon, is presented. Avrami parameters are identified between 10°C and 140°C. The use of sample of several nanograms raises the question of the representativeness of the measure. In this context, the second device, called "Lagardère apparatus", allows the study of the crystallization at the surface of a bulk part. It consists to put suddenly into contact a piston at 30°C and a molten polypropylene at 210°C. This apparatus also allows the direct measurement of the thermal contact resistance between the polymer and the piston. The impact of the pressure on the crystallization kinetics is studied through specific volume measurements. The third device is the PvT-xT, a home-made multifunctional apparatus, which allows the measurements of PvT diagram

(Pressure–specific volume–Temperature), of the crystallization enthalpy and the identification of the crystallization kinetics under pressure. The applied conditions are close to processing conditions: high temperature up to 400°C and very high pressure up to 200MPa.

S07-466

Schaake Richard Pieter, Fan Jiying, Weigand Jeremy Joseph, Williams Jason Louis, Rhoades Alicyn Marie

Effect of crystallization on PEEK bearing components

Rolling element bearings are widely used machine The understanding components. of their performance has improved tremendously over the past century and simulations taking into account the dynamic behavior of individual bearing components are common practice. Such simulations allow product developers in the bearing industry to further optimize these components through better understanding of the dynamic loads the components are exposed to. However, to do this also requires more detailed knowledge of the actual material properties. Where components were originally developed based on datasheet properties and safety margins, it has now become necessary to the effect of process on understand the performance. In this presentation it is illustrated how fiber orientation, porosity and crystallization kinetics add up to explain knock-down factors used in bearing component analysis. The importance of modeling crystallization at high cooling rates is demonstrated.

S07-493

Yan Shiyong, Menary Gary, Nixon James

Characterization of the constitutive behaviour of aPET in the stretch blow moulding process

The stretch blow moulding (SBM) process is the main method for the mass production of PET containers. Understanding the constitutive behaviour of amorphous PET (aPET) during the blowing process is critical for designing the optimum product and process. However due to its



nonlinear viscoelastic behaviour, the behaviour of aPET is highly sensitive to its thermomechanical history making the task of modelling its constitutive behaviour very complex. This means that the constitutive model will be useful only if it is known to be valid under the actual conditions of the SBM process of interest. In order to characterize the constitutive behaviour of aPET during the blowing process, digital image correlation was employed to capture the actual deformation of material, thereby obtaining the corresponding stress-strain relationship by replicating this strain history via a biaxial stretching tester. Furthermore, an upgraded, in-situ characterization methodology based on both digital image correlation and implemented instruments was developed, which provides more efficiency and flexibility of determining the constitutive behaviour of materials during the blowing process.

S07-499

Hirschfeld Stefan, Wünsch Olaf

Experimental Study of Polymer Degassing in an Agitator Vessel

The controlled removal of volatile organic compounds (VOCs) is an important task in polymer processing because these substances impair the properties of polymer products and are typically harmful to health and environment. This devolatilization process is often performed in rotating devices like vessels or screw extruders, especially for the treatment of high-viscous polymer melts. Despite major commercial significance, this unit operation is not fully understand since different effects interact with each other. Mass transfer from the liquid phase into the gas phase is usually rate-controlled by diffusion in the polymer melt. Two mechanisms of devolatilization be distinguished: can film degassing and bubble degassing. Film degassing occurs on contiguous free surfaces. Models to describe this process are based on the penetration theory or surface renewal theory by Higbie and Danckwerts. refers Bubble degassing to devolatilization promoted by foaming in consequence of a supersaturation of the polymer.

This contribution presents the experimental investigation of devolatilization in a partial filled agitator vessel with a blade stirrer focusing on film degassing. The apparatus generate a wiped melt film on the barrel wall and a rotating melt pool at the stirrer blade contributing to mass transfer. A model substance system consisting of high-viscous polydimethylsiloxane as polymer and 1,1,2trichloro-1,2,2-trifluoroethane as volatile is used. Thus, all experiments can be performed at ambient temperature. The driving force for the degassing is provided by reducing the partial pressure in the gas phase with a nitrogen gas flow. The concentration of volatiles in the melt is measured by thermogravimetric analysis. The stripped volatiles were recovered and weighted by use of cold traps. The results of both methods are compared with each other. A model for the devolatilization is developed and the results of the model are compared to the experiments.

S07-530

Marschik Christian, Löw-Baselli Bernhard, Miethlinger Jürgen

Modeling Devolatilization in Single-Screw and Multi-Screw Extruders

The removal of residual volatile components such as monomers, oligomers, moisture, solvents or other impurities from polymers has gained growing attention as an important processing step. To meet the high quality requirements of the final product and to comply with the tight environmental regulations these undesired volatile components are usually removed by devolatilization during the extrusion process. The devolatilization process is carried out in partially filled screw sections and involves the diffusion of the volatiles to the polymer-vapor interface, evaporation of the volatiles at the interface and their subsequent removal by a vacuum venting system with condensation. To extend the understanding of the transport phenomena in single-screw or multiscrew extrusion units during devolatilization, a numerical model based on finite volume method is developed. The model investigates the twodimensional flow situation in a partially filled



venting section and analyzes the mass transport processes in the screw channel during devolatilization. Therefore, the velocity field describing the circulatory flow in the melt region of the screw channel due to drag flow is calculated and connected to Fick's diffusion equations. The residual volatile concentration is analyzed depending on various input parameters including residence time, material properties and processing conditions. Taking the simulation results into account, an analytical equation describing the course of concentration in the devolatilization zone is derived using a heuristic approach. The new analytical equation can be used to detect the influence of important testing parameters on the residual volatile concentration in the devolatilization zone. As a result, it offers a useful tool to design efficient devolatilization screw sections.

S07-571

Caton-Rose Fin, Hine Peter

Assessing A Completely Digial Component Design Of Short Glass Fibre Reinforced Composite Injection Mouldings

The continued exploitation and uptake of short fibre composites in a range of industrial applications would be greatly enhanced if the designer was able to carry out the complete design process within a computer. This would speed up the design process significantly and allow the materials to be used in a more cost effective, and greener, manner. In this paper we will aim to assess the state of the art in this process. For this study we have chosen a simple component, in this case a centre gated inverted cup with height 28mm and an outer diameter of 95mm. The side walls were 5mm thick and top moulded in three conditions with thicknesses of 1, 2 and 4 mm. Samples, for comparison with the computer predictions, were injection moulded from Rhodia 216 v40 40% wt short glass fibre reinforced nylon 6 and were produced using the manufacturer's moulding conditions. Autodesk Simulation Moldflow Insights was used to predict fibre orientation during the injection moulding process. Orientation data, along

with mechanical properties for the matrix and fibres, was then passed to ABAQUS finite element modeller for the analysis of a simple displacement at the centre of the disc using a 12.7 mm radius indentor. Results at all stages were compared with experimental data.

S07-59

Rudloff Johannes, Lang Marieluise, Kretschmer Karsten, Heidemeyer Peter, Bastian Martin, Koch Michael

Analysis of pellet diameter and inorganic filler influences on the polymer melting behavior in planetary roller extruders

The planetary roller extruder is well known for its superior mixing performance and its exact temperature control capabilities. Therefore it is widely used in the polymer industry for the compounding of shear- and temperature sensitive materials like PVC or Wood Plastic Composites. In contrast to the considerable amount of scientific work that deals with investigation, modeling or simulation of the process behavior of single and twin screw extruders there are only few publications about the planetary roller extruder. Due to increased quality requirements and the trend to cost reduction by process optimization, this is increasingly becoming a problem for plant construction and processing companies. In our former work first analysis of the plastics melting process in planetary roller extruders were conducted and models describing these processes were published. However the influences of pellet diameter and inorganic filler were not considered. As a consequence the process models are only valid for a partial amount of the materials processed on planetary roller extruder. This paper presents experimental melting behavior investigations of powder, micro pellets and standard pellets. Furthermore the influence of filler amount is examined with standard pellets. At these experiments the melting initiation and the melting propagation is determined. Based on the experimental results, a theoretical consideration for the melting in planetary roller extruders is proposed.



S07-602

Karim SAIDI, ELOTMANI Rabie, MONKADE Mohamed, kandoussi Khalid, CHHITI Younes, AMRANI Hicham

Karim SAIDI, ELOTMANI Rabie, MONKADE Mohamed, kandoussi Khalid, CHHITI Younes, AMRANI Hicham

The present study concerns the analysis of the numerical simulation of filling phase of a micro gear in the micro molding process. In this process, the non-isothermal molten polymer flow is injected from the gate of the cavity which initially occupied by the air, giving a two-phase flow. In this model, the Navier Stokes and energy equations were coupled with the level-set equations in order to track the melt polymer front evolution versus time. The molten polymer is considered as a generalized Newtonian fluid and his viscosity dependent of shear rate and temperature is modeled by the Cross-Arrhenius model. The effect of thermal contact resistance was investigated. The velocity, temperature, pressure, and viscosity field are calculated versus time and discussed.

S07-614

Babenko Maksims

Evaluation of Melt Cooling Prediction and Determination of HTC Values for Microinjection Moulding

The work presented is focused on the heat transfer coefficient (HTC) in microinjection moulding, a parameter which describes the heat flow between the polymer melt and the mould wall. The HTC is a dominant parameter in cooling simulation predictions. Understanding of heat flux during cooling phase is essential, as cooling behavior can have a significant influence on internal structure, morphology and resulting physical properties, yet the availability of HTC values for microinjection moulding is limited. A range of cooling curves were obtained for two materials, namely carbon black filled polypropylene and carbon black filled polystyrene using a special mould with a sapphire window which allowed surface temperature

measurements during the cycle using a high speed infrared camera. The obtained cooling curves were statistically analysed and compared to simulation results. Microinjection moulding simulations were performed using Moldflow software where processing conditions were matched to the experimental parameters, including different melt temperatures, mould temperatures, injection speeds and packing pressure. Within Moldflow software two solvers, namely the conduction and flow solvers, were employed to obtain cooling profiles of the melt surface temperature. For both materials improvements in cooling prediction were observed with an increase of HTC values from 2500 W/m2C (default) to 7700 W/m2C.

S07-616

Maia Joao, Boromand Arman

A Computational Study of the Rheology and Structure of Surfactant or Co-Polymer Covered Droplets

The use of different types of surface-active agents and co-polymers is ubiquitous practice in different industrial applications ranging from cosmetic and food industries to polymeric nano-composite and blends. Moreover, the presence and self-assembly of these species on an interface will display complex dynamics and structural evolution under different processing conditions. Analogous to bulk rheology of complex systems, surfactant of copolymer covered interfaces will respond to external mechanical forces or deformation differently depending on the molecular configuration and topology of the system constituents. Although the effect of molecular configuration of the surfaceactive molecules on the planar interfaces has been studied both experimentally and computationally, it remains challenging to track the efficiency and effectiveness of different surfactant molecules with molecular different geometries on curved interfaces. In this study we use Dissipative Particle Dynamics to study the effectiveness and efficiency of different surfactant molecules on a curved interface in equilibrium and far from equilibrium. DPD is particularly suited for this problem because it is capable of capturing microscopic phenomena



and provide comparison to macroscopic simulations and experiments much faster than Molecular Dynamics. Also, DPD being an off-lattice simulation technique, makes it unnecessary to use any algorithms to track interface position in time, unlike in lattice-Boltzmann simulations and interface deformation will not depend on availability of a suitable interfacial constitutive equations, as is the case of Boundary Integral Methods. In particular, in this work we calculate the interfacial tension for linear and branched surfactants. Deformation Parameter and Taylor plots are obtained for individual surfactant molecules and co-polymers under shear flow.

S07-633

Rao Rekha R, Hariprasad Daniel, Ortiz Weston, Secor Robert, Schunk P. Randall

3D Viscoelastic Flow with Free and Moving Boundaries Using a Stabilized Finite Element Method

One standard method for viscoelastic (VE) finite element method is the discrete elastic-viscous stress-split method of Guenette and Fortin (J Non-Newt. Fluid Mech., 1995) which uses the Galerkin method for the momentum equation requiring a velocity-pressure space that satisfies the LBB condition, a Petrov-Galerkin method for the differential stress constitutive equation, and the addition of a least-square interpolation of the velocity gradient tensor to a continuous space. Adding the smoothed velocity gradient to the momentum equation acts to stabilize the stress space, allowing for low order stress interpolation. These simulations are computationally demanding since in addition to the standard Navier-Stokes unknowns, we must also solve a symmetric stress tensor and a non-symmetric velocity gradient tensor. Multimode calculations require even more unknowns, adding a stress tensor for each mode. The matrices arising from the discretized problem are poorly conditioned, requiring direct Gaussian elimination methods. Here we investigate methods to speed up multimode viscoelastic flow calculation in both 2D and 3D, including free and moving boundaries represented arbitraryby an

Lagrangian-Eulerian method. Applications of interest include extrusion, coextrusion of layered polymers, and blade coating of polymeric solution on flexible substrates. Results have shown that decoupling the momentum equations from the stress and velocity gradient equations can greatly reduce solution times. Stabilization of the momentum equation using Dorhmann-Bochev stabilization allows for use of Krylov-based iterative solvers in place of direct solvers, even for mixed velocity-pressure formulations. The method is fully parallelized using MPI and a GMRES solver preconditioned with ILUT. Comparison of solution times and scalability for the monolithic and decoupled solve will be discussed.

S07-67

Trippe Jan, Schöppner Volker

Investigation of the influence of material and pellet shape on the dissipation in the solids conveying zone of single-screw extruders based on the Discrete Element Method (DEM)

In polymer processing, there are existing currently established models for the conveying and melting behavior of polymer materials. These models record the majority of relevant industry applications well. In the field of conveying solids the models especially relate to Darnell and Mol (1956), who postulate a plug flow in the solid area. The following melting process implies a heat input exclusively from heat conduction at the barrel and from dissipation energy which results from the contact between pellets and screw / barrel. The frictional heat, resulting from relative motion in the solid bed, is being neglected in the models. This is why an overestimation of melting efficiency by the actual models is to be expected. Furthermore, the models do not take the influence of pellet shape and size into consideration, which is why there are expected higher internal frictions from sharp-edged pellets than from round ones with a smooth surface. In terms of cylindrical pellet, alignment and unroll effects play an important role. In order to mathematically describe and analyze complex motions in a solid bed correctly, numerical simulations based on the Discrete Element Method



(DEM) have been carried out. In order to do so, a 60 mm solid conveying test stand has been built up in the simulation. The test stand can be fed with pellets of various shapes and sizes. Pellet and material parameters, which have been defined in preliminary investigations and were implemented in the simulation, play a decisive role. Because of the variation of dimensionless geometry and process index, a modelling approach arises, with which now the description of the influence of various pellet sizes and shapes on the dissipation in the solid conveying area is possible for common extruder sizes.

S07-696

CHENG Gang, Barrière Thierry, Gelin Jean-Claude, Sahli Mohamed

Experimental characterisation and identification of elastic-viscoplastic polymer properties used in hot embossing process

Micro hot embossing process is widely used for manufacturing of polymeric components with complex surfaces. The physical properties of polymer plate in hot embossing process could be considered as viscoelastic or viscoplastic, depending on materials and temperatures. A large number of hot embossing experimental results have been published, the material modelling and processes simulation to improve the quality of micro replication by hot embossing process are still lacking. This paper consists to characterize the physical behaviours of amorphous polymers used in hot embossing process. The compression tests at the temperature range lightly above Tg have been carried on and an elastic-viscoplastic law has been proposed to describe the polymers' behaviours in the tests. The experimental data fits well by the model with the identified parameters. It shows the further application for the numerical simulation of hot embossing process in the future.

S07-704

Tanoue Shuichi, Uematsu Hideyuki, Iemoto Yoshiyuki

Prediction of Cross-Sectional Shape at Die Exit on Film Casting Process by Viscoelastic Flow Simulation

On the film casting process, the following phenomena occur, 1) neck-in, the film width becomes smaller than the die width, 2) Edge bead, the film thickness at edge becomes larger than that at the film center. One of the requirement points on the film casting process is to manufacture the film with uniform thickness. In this study, we tried to predict the cross-sectional shape of die exit on the film casting process in order to manufacture the film with uniform thickness by using a viscoelastic flow simulation. The Phan-Thien Tanner (PTT) model was employed as the constitutive equation. By this simulation, we could get the cross-sectional shape of die exit in order to manufacture the film with uniform thickness. The width of this die exit except at edge became large and the thickness at edge of this die exit became small when the draw ratio increased because the neck-in and edge bead phenomena occurred on the film casting process. The width of the die exit at same draw ratio was almost independent of the fluid characteristics, i.e., the viscosity ratio of uniaxial elogational viscosity to planar elongational one at same elongation rate. However, the die thickness region with same value became increased when this viscosity ratio increased. And the deformation from rectangular cross-section became prominent at high draw ratio.

S07-718

Elias-Birembaux L. Hélène, Arif Nadia, Rosu Iulian, Lebon Frédéric

Modeling and characterization of Bush aircraft tire

Landing and take-off operations are the most critical phases of an aircraft flight. Indeed, the high speed, the violent impact, and eventually bounces, when the aircraft touches the ground, the need of braking efficiently, the ground irregularities (the absence of landing runway for bush airplanes), the climatic conditions (snow, freeze, crosswind, contaminations, etc.) as well as other parameters can make these ground maneuvers very complex.



In this paper, some numerical models are proposed for simulate the aircraft tire behavior on the ground in critical situations. Fully coupled thermomechanical analysis procedures taking into account visco-elasticity properties of the rubber, finite strains, dynamics, frictional contact and the roughness of the ground are proposed.

S07-789

Schäfer Christian, Osswald Tim A.

Simulation of the Micropelletization Process using the Corotational Maxwell Model

Understanding and modeling of viscoelastic fluid flows is essential for several industrial applications. Simulations of internal viscoelastic flows as well as of viscoelastic free-surface flows are quite complex and it is necessary to utilize advanced material models. A series of free-surface viscoelastic flow simulations are performed in order to model the mechanisms associated with the flow and breakup of a polymer melt in a Micropelletization process. This method is an alternative way of producing powders with physical properties demanded in polymer processes such as sintering, rotomolding and extrusion. Micropellets are achieved by extruding a polymer melt strand through a capillary and perturbing it with a stream of hot air. This causes the development of Rayleigh disturbances that result in breakup of the strand into particles. Experimental work has demonstrated that the viscoelastic response of the extruded thread influences the breakup process. Therefore, affecting final shape and size distribution of the pellets. A free surface viscoelastic solver implemented in the OpenFOAM fluid dynamics package allows visualization of viscoelastic effects on the melt as it leaves the extrusion die and meets the stream of air. In this work the single relaxation time Corotational Maxwell Model (CRM) is applied as part of nonlinear differential constitutive models. This model is able to predict shear-thinning, normal stresses and other qualitative effects. The focus is on changing the relaxation time λ ; one of two variable parameters in the CRM. Simulations with four different relaxation times are performed while other material and process conditions are kept

constant. When the relaxation time is short compared to the overall processing time, the polymer chains are able to relax more quickly and it can be shown that the elasticity does not have a significant effect on the flow behavior. However, if the relaxation time is longer, the polymer chains are not able to relax to a great extent and the melt seems to be more elastic. Keywords: Extrusion, Rheology, Relaxation time, OpenFOAM, Powder, Micropellets

S07-85

Sporleder Federico, Carella José M., Dorao Carlos A., Ludueña Leandro N.

Novel Approach for Modeling the Dynamics of Fiber Breakage in Polymer Matrix Composites during Capillary Extrusion

Many high performance products are made with thermoplastic/fiber composites by injection molding processes. The shear forces induced in injection molding produce fibers breakage which detriments the final mechanical properties of the material. Therefore, the prediction of the evolution of the topology of the fibers during the molding process is a critical aspect for obtaining an optimal final product. The runners of the injection molds are the critical zones where fiber breakage takes place. The fiber breakage process inside the mold runners can be more easily studied from capillary extrusion. The fibers can be characterized as a population of entities that break as they move along the capillary. As such, the population balance equation (PBE) can be used to study the breakage of the fibers. This equation makes a statistical description of the evolution of a group of entities. The PBE uses a density function as its main variable, defined as function of time, physical coordinates, and internal coordinates. The latter are used to represent properties of the entities, such as size, mass, temperature, composition, etc.. In the case of fiber capillary extrusion, the density function is affected by breakage events. The aim of this work is to analyze the applicability of the PBE for predicting the evolution of the fiber breakage in polymer/short-fiber composite during capillary extrusion. The least squares spectral method will be



used to solve the resulting integro-differential PBE equation. The main goal of this work is to show the evolution of a density function predicted with different breakage kernels and to validate the modeling results with experimental data. Four intrinsically different breakage kernels and two redistribution functions are tested.



Poster

S07-56

Santos Wilson Nunes dos

Behaviour Of The Thermal Conductivity Of Amorphous Polymers

The thermal conductivity of four amorphous polymers was determined within a wide range of temperatures, starting at room temperature up to above the glass transition temperature (Tg). In this work, the hot wire technique was adopted for the experimental measurements and the thermal conductivity was directly determined in the temperature interval analyzed. As expected, the experimental results show that Tg exerts a measureable influence on the thermal conductivity of amorphous polymers. For such materials, the dependence of the thermal conductivity with the temperature is quite different from that foreseen by dieletric materials. The thermal conductivity behaviour with temperature displays two distinct regions: in the glassy state before Tg and in the rubbery state after Tg. The influence of this transition temperature on the thermal conductivity behaviour with temperature has been analysed in terms of phonons conduction process, specific heat variations with temperature and modulus of elasticity of the analyzed polymers, in order to explain this apparently anomalous behaviour. This effect is hardly detectable for semi-crystalline polymers, since only the amorphous phase is responsible for this behaviour, and the crystalline phase overrides this influence. Keywords: Thermal transition temperatures, thermal conductivity, phonons heat conduction, hot wire technique. *Corresponding author.

S07-64

Pyshnograi Grigory, Naud Jean-Charles, Kondratieva Olga, Tregubova Julia

Polymer Film Production And Rheological Characteristics Of Forming Solutions In the present mathematical model, the process of film formation from polymer solution is described. Rheological parameters of the model were determined by comparing theoretical curves and experimental data measured for simple shear in chitosan solutions. Dimensionless similarity criteria were found for the rheological characteristics of the process. This work considers the effect of these criteria on the dependence of the velocity, concentration and width of the film on the distance from the exit of the die. Mathematical modeling used in the design and manufacture of products made of polymer materials gives a number of benefits, such as the ability to control the quality of polymer products and to solve a number of production optimization problems. Such problems are based on a mathematical model, which should be fairly simple but reflect all relevant characteristics of the process. The fabrication of polymer films is one of the common processes in polymeric material processing. The process of obtaining films from polymer solution is twostaged and is so complex. This complexity is caused by the fact that an increased polymer concentration results in a sharp increase in the polymer system's viscosity. Thus, while developing mathematical models to describe the processes of polymeric film formation, the characteristics of each forming step should be considered. The set of dynamics and mass transfer equations is written in a onedimensional approximation, when the elongation velocity, the concentration of the solvent, and the non-zero components of the stress tensor are functions of the distance to the die exit, and the rheological parameters of the model are known

rheological parameters of the model are known functions of concentration. A set of ordinary differential equations for the dependence of the width and thickness of the film on its longitudinal velocity for the case of uniaxial tension was obtained and solved.

PPS[®]32 32nd PPS International Conference 2016, Lyon, France

S08- Process Monitoring, Control and Sensors

Keynotes

S08-271

Coates Phil, Caton-Rose Phil, Spencer Paul, Vgenopoulos Dimitris, Thompson Glen

Neck profile geometries in solid phase processing of polymers: indicators of molecular features

Solid phase deformation of polymers provides a major route to enhancement of polymer properties, exploited in our laboratories particularly for biomedical (e.g. soft tissue and joint fixations, arterial stents) and structural engineering applications. An underpinning understanding of polymer deformation is important for optimisation and control of solid phase orientation processes. Using in-house software routines, we measure free tensile drawing behaviour of polymer tensile test specimens, including measurement of neck profile geometries and draw load versus time, at selected temperatures above Tg but below the melting point of the polymer. This provides detailed information on the development and stability of neck profiles and neck profile velocities, and using previous mechanical modelling, the stress, strain and strain rate fields along the specimen can be obtained. The neck profile geometries have previously been found to be sensitive indicators of particular molecular features (e.g. the effect of high MW fractions in a polymer on strain hardening and strain rate sensitivity) and morphology (e.g. slow cooled versus quenched morphologies). High MW materials tend to have shallower necks, reflecting a higher strain hardening and strain rate sensitivity. Neck profiles can also provide insight into optimising processing geometries in solid phase processing. The neck profile presented by a polymer can be interpreted as the polymer indicating its preferred, minimum energy route to

deformation in response to the specific tensile drawing conditions, consequently metrication of the neck geometry can inform die geometries for solid phase processing techniques such as die drawing. We report polymer necking behaviour for selected polypropylenes, and link this to the observed die drawing behaviour of these materials, with finite element modelling of the deformation behaviour in tensile free drawing and die-drawing, using data generated from the above experiments.



Oral

S08-175

Hopmann Christian, Theunissen Matthias, Heinisch Julian

Compensating viscosity fluctuations in injection moulding

A conventional control of the injection moulding process is based on machine values like the position and speed of the plasticising screw. Modern machine technology can reproduce these values with a high precision. However, systematic disturbances fluctuating like environmental conditions or variations in material viscosity still affect the reproducibility of the injection moulding resulting process and the part quality. Consequently adaptive and self-optimising control algorithms have to be applied for a further improvement of product quality. pvT-А optimisation allows a material-tailored online control of the holding pressure. Based on an online determination of the temperature state of the melt in the cavity, the cavity pressure can be closed loop controlled in order to achieve a constant specific volume of the moulded parts. Therefore a pvToptimisation enables a compensation of thermal disturbances during injection moulding. However, fluctuations of material viscosity have a strong impact on the resulting profiles of the cavity pressure. Therefore under the influence of viscosity disturbances the specific volume and other related quality values cannot be reproduced homogenously using a pvT-optimisation. For the compensation of viscosity fluctuations an online measurement of the current viscosity in the process is necessary. For this purpose an indicator based on the pressure loss within the mould cavity is defined and analysed. On this basis a control of the viscosity is implemented. Within this concept the injection speed is adapted to the current process viscosity. First results of compensating viscosity fluctuations inflicted by the use of recycled material show the feasibility of the concept. In the future this concept

has to be validated in combination with the pvToptimisation. This enables an injection moulding process which is less sensitive to changing boundary conditions.

S08-224

Moritzer Elmar, Huettner Matthias, Henning Bernd, Webersen Manuel

An Approach to Non-Destructive Testing of Aged Polymers

Because of the variably modifiable material qualities, plastics are used in every area of life nowadays. Thereby, the polymers have to meet various requirements to be able to guarantee the suitability for the use of the respective components. Besides, during their operation time the plastics are exposed to steadily changing environmental influences, which lead to the aging of the polymers. Frequent temperature changes, dampness, saline media and mechanical loads belong to it among others. The aging effects, caused by the interaction with the surrounding media, are not quantifiable to detect in the components applications. Strength losses, changes in the material behavior, for example embrittlement, or a degradation of the molecular weight resulted from the aging process, can only be detected after the components' failure. To be able to prove these qualities in aged plastic components, besides, destroying testing methods are necessary, so that the checked components cannot be used anymore and are to be exchanged, in any case. Hence, in the following a measuring procedure will be introduced, with which aging effects in plastics can be non-destructively detected. In addition, polyamide 6 specimens are aged hygrothermal artificially and their macromolecular changes are made visible by means of ultrasonic testing.

S08-235

Chiu Tzu-Heng, Yao Yuan, Wang Kai-Hong, Qi Wei

Online Estimation of Permeability in Resin Transfer Molding Using Parallel-Plate Capacitor



Resin transfer molding (RTM) is a popular liquid composite molding technique, which has been widely used for manufacturing polymer RTM, composites. In permeability of fiber reinforcement is a crucial factor affecting the property of resin flow and consequently influencing the final product quality. Hence, it is essential to estimate the permeability of the fiber during the manufacturing process. In past research, the permeability is estimated online using the flowfront information captured by a CCD camera and the local pressure measured by a pressure transducer array. However, the feasibility of such method relies on the visibility of the melt flow. When even the mold is not transparent or the color of the resin melt is similar to that of the fiber, this method is not applicable. To overcome the limitation of the existing method, a parallel-plate capacitor is developed in this research for measuring the flow front, where the capacitance keeps an approximately linear relationship with the position of flow front. The principle of the measurement is as follows. Before mold filling, the medium between the capacitor plates is mainly air. Then it is gradually replaced by resin melt during filling. Therefore, the dielectric constant of the medium is continually varying, resulting in the variation of the capacitor value, i.e., the capacitance. Based on the resin flow-front position, the flow velocity is calculated and substituted into the Darcy's law together with the injection pressure. In doing so, online estimate of permeability is available. The proposed method is illustrated with experiments on an RTM process using glass fiber reinforced plastic (GFRP). Keywords: resin transfer molding, permeability estimation, parallel-plate capacitor, Darcy's law, glass fiber reinforced plastic.

S08-558

Dropsit Elise, Chapron David, Bourson Patrice, Hoppe Sandrine, Durand Alain

On the exploitation of optical signal from Raman spectroscopy for in situ monitoring macro and molecular parameters of emulsion polymerizations emulsion polymerization reactions is a real current challenge. First, it may help establish relations structure, the between the physicochemical properties and the performance properties of final latexes. Moreover, it brings a better understanding of chemical and physicochemical phenomenon that occur. Easy installation, performance of measurements and abundance of information gathered (from molecular to material scales) make Raman spectroscopy the adequate technique for this kind of issue, as shown in recent studies [1] [2]. The main goal of this work is to demonstrate the ability of this technique to control the polymerization of styrene via macroemulsion process. Firstly we proved that Raman spectroscopy could be a suitable technique for real time in situ conversion monitoring. Indeed, we demonstrated that normalized Raman signal was ideal to answer this demand because independent of optical parameters but sensitive to processes ones. Raman data were correlated with off-line thermogravimetric results for quantifying the conversion of styrene in polystyrene. Then an indepth study of its raw signal revealed the sensitivity of Raman spectroscopy the to heterogeneity of the reaction medium. Indeed some peaks of interest seemed to be influenced by optical and chemical parameters. Among these parameters, there are for example the depth position of the analyzed volume in the reactor and the number of particles synthesized during the nucleation step. Off-line studies on samples have already been carry out in order to establish links between physical and chemical phenomenon [3]; our in situ studies could bring additional information. Literature Cited [1] M.C. Chevrel et al. Ind. Eng. Chem. Res. 2012, Vol 51, 16151-16156. [2] N. Brun et al. J. Raman Spectrosc. 2013, Vol 44, 909-915. [3] M. van den Brink et al.J. Raman Spectrosc. 2002, Vol 33, 264-272.

Development of in situ monitoring techniques of

S08-783

Aktaş Demet

Swelling And Drying Process In Ionic Hydrogels For Low And High pH Using Fluorescence Technique 179


Steady-state fluorescence (SSF) technique was employed for studying swelling and drying of poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)) composite gels for low and high pH. Disc shaped composite gels were prepared by free-radical crosslinking copolymerization of P(AAm-co-AAc). N, N'- methylenebis (acrylamide) (BIS) and ammonium persulfate (APS) were used as crosslinker and initiator, respectively. Pyranine 4 (4sPy) was introduced as a fluorescence probe. P(AAm-co-AAc) composite gels dried before using for swelling experiments. Fluorescence intensity of 4sPy was monitored during in situ swelling and drying processes of composite gels. It was observed that fluorescence intensity values decreased as swelling is proceeded. Li-Tanaka equation was used to determine the swelling time constants, τ and cooperative diffusion coefficients, D from intensity variations during the swelling processes. It was also observed that fluorescence intensity values increased as drying is proceeded. Gravimetrical and volumetrical experiments were also performed. It was shown that swelling time constants, τ decreased, diffusion coefficients for swelling process, DF increased and diffusion coefficients for drying process DG decreased as the pH values are increased.

Poster

S08-462

Hopmann Christian, Klein Jan, Schoengart Maximilian

Tensile Impact Testing on Polymer Materials Considering the Force-Oscillation Phenomenon

Thermoplastic materials are extensively used as a light weight replacement for metal alloys, especially in automotive applications. Furthermore polymer materials can be used to enhance the safety of passengers and pedestrians in a car accident. The state of the art design process for plastics parts is based on Computer Aided Engineering (CAE), especially for automotive applications. Using Finite Element Analysis (FEA), highly dynamic systems can be simulated with a very high accuracy. Considering crash applications, the influence of strain rate on the mechanical behaviour is of paramount importance. То determine the impact of strain rate on the mechanical behaviour, tensile impact tests are conducted at different haul-off velocities. With an increase of the haul-off velocity, the forceoscillation phenomenon becomes significant. The force-oscillation phenomenon is an artifact caused by the dynamic load application in highly dynamic tests. It can be monitored as a superimposition of measured force characteristics with oscillations which increase in amplitude to higher impact velocities. This study looks at the phenomenon of force oscillation in tensile impact testing on viscoelastic materials and its dependency on longitudinal stress wave propagation. Aside a detailed analysis of its origin, a new approach is presented to measure a nearly oscillation free force signal in tensile impact testing on polymer materials, basically independent of the considered haul-off velocity. For this purpose a modification of a standard dumbbell specimen was designed.

S08-463

Hopmann Christian, Wipperfürth Jens, Schoengart Maximilian

S08-87

Spatially Resolved Temperature Measurement in Injection Moulding Using Ultrasound Tomography

Current simulations of the injection molding process insufficiently consider the thermal interactions between melt, solidified material and mold. To improve the prediction accuracy in terms of shrinkage and warpage these interactions cannot be neglected and require a precise observation of the temperature field within the ongoing process. Nowadays temperature measurements at the transition of the polymer melt to the mold or near the surface of the polymer melt are applicable and do not allow either a non-invasive analysis or a determination of the temperature field. In the approach of ultrasound tomography presented here, an ultrasound beam is emitted into the melt and the time-of-flight (TOF) is detected by a set of transducers, which are radially arranged around the melt. Subsequent the measurement is repeated different directions. from Using algebraic reconstruction techniques, a distribution of the ultrasound velocity can be calculated based on the TOF-dataset. With additional information about the polymer from pvT-curves, the distribution of the ultrasound velocity can be converted into a temperature field. To evaluate the applicability of ultrasound tomography, а prototypical measurement device was set up. The device consists of a hollow cylinder in which eight brass forerun elements are integrated in order to scatter the ultrasound beam. A polymer melt can be placed within the hollow cylinder and ultrasound tomography can be performed. The results show the applicability of commercially available transducers and the operability of the brass forerun elements, since each of the seven transducers was able to detect a signal that was sent out from the one remaining transducer. However, a useful reconstruction of the temperature distribution is, due to the inhomogeneous melt in the prototype, not yet possible. Currently an injection mold is designed which fulfills all prerequisites for and overcomes the ultrasound tomography difficulties from the prototype.



Hopmann Christian, Fecher Marc Linus, Boettcher Arne, Fischer Kai

Development of a novel and adaptable injection unit for an automated and quality controlled manufacturing of RTM parts for aerospace applications

Fibre reinforced plastics (FRP) are increasingly being implemented in aircraft and automotive applications for structural lightweight components. A decisive problem for the high volume production of structural parts made of FRP with high fibre volume contents of up to 60 % is, that applied processes are only partly automated and have a low process robustness. Additionally the processes are typically not controlled and for a quality controlled qualification of the parts, time consuming post processes are necessary. In order to increase process robustness and reduce time consuming post processes a novel injection unit has beed developed by the Institute of Plastics Processing (IKV) at RWTH Aachen University together with Airbus Operations GmbH, Stade, and FILL GES.M.B.H., Gurten, Austria. This injection unit shall enable a fully automated and quality controlled manufacturing of Resin Transfer Moulding (RTM)for aerospace applications. parts Therefore, different sensors will be integrated into the injection unit to fulfill the quality assurance: pressure sensors, thermocouples and dielectrical sensors. This allows for a measurement of all necessary process parameters and such process parameters which cannot be measured and controlled by common injection units or in-mould sensors. For example, the selected arrangement of the pressure sensors will enable the build-up of an online rheometer, which makes an injection of the resin system depending on the current viscosity possible. Furthermore, an online determination of the parts porosity and the permeability of the preform are envisaged. This paper explains the functionality of the developed injection unit with all integrated measurement systems. Additionally, current results of investigations regarding the verification and validation of the injection unit are presented and discussed.



S09- Reactive Processing

Keynotes

S09-6

Bergmann Bjoern, Diemert Jan

InnoREX – European project reveals impact of microwave and ultrasound energy on polymerisation of PLA via reactive extrusion

The demand for biobased polymers is growing rapidly. However, due to production processes consisting of several batch processes, biopolymers such as polylactic acid (PLA) still have the potential for an increased commercially exploitation. In order to overcome these problems, twelve partners launched the InnoREX project in December 2013. This FP7 EU-project aims at the continuous, highly precise, metal-free polymerization of PLA using alternative energies for reactive extrusion. In this presentation the projects innovations regarding impact of microwave and ultrasound incorporation on the process opportunities and its influence on process performance and material characteristics will be show. The consortiums work to simulate the overall polymerisation kinetic, alternative energy input, and to model the drastically changing viscosity during polymerisation will be further presented. This comes together in a Ludovic® user module able to simulation polymerisations in a twin screw extruder under alternative energy input. By the date of this talk the project has ended 1 month ago, such this talk will cover all the InnoREX developments throughout the value chain, from findings regarding catalysts, process optimisation, according simulation to material performance from end-user point of view.

S09-739

JI Wei-Yun , ZHANG Cai-Liang, HU Guo-Hua, FENG Lian-Fang , HOPPE Sandrine

The use of a reactive compatibilizer-tracer to probe reactive polymer blending processes

Most polymer pairs are immiscible. It is common practice to use a block or graft copolymer known as a compatibilizer to promote the dispersion of the one of the phases in the other and stabilize it. Such a compatibilizer can be either premade or generated in-situ during the blending process upon reacting two reactive polymers at the interfaces. The latter case, called reactive compatibilization, is mostly practiced in industries. It is very challenging to investigate a reactive compatibilization process because both mixing and interfacial reactions between reactive polymers are highly coupled. Most importantly, the amount of the in-situ formed copolymer is often too low to be determined in a relatively accurate manner, especially for an industrial scale process. For this reason, we propose a concept called reactive compatibilizer-tracer. It bears reactive groups capable of reacting with its counterpart upon forming a copolymer in-situ, and fluorescent labels allowing determining very small amounts of the in-situ formed compatibilizer. This paper reports on an unusual and highly undesirable phenomenon which may occur during a reactive polymer blending process. When a critical amount of the in-situ formed compatibilizer is reached, the dispersed phase domains undergo a drastic increase in size with a further slight increase in the amount of the compatibilizer, instead of continuing to decrease or leveling off as one may expect. This phenomenon is revealed owing to the concept of reactive compatibilizer-tracer. It indicates that a reactive compatibilizer can be a very efficient compatibilizer under certain thermomechanical conditions and may become inefficient under other ones. It also shows how challenging it may be to design and optimize the molecular architecture of a reactive compatibilizer as a function of thermo-mechanical conditions under which a reactive blending system is processed.

S09-772

Tian Ming , Wu Hanguang , Ning Nanying, Tian Hongchi , Wu Youping , Zhang Liqun



New Understanding on the formation of phase structure of Thermoplastic Vulcanizate (TPV) During Dynamic Vulcanization

In our study, the minimum size of the rubber phase in the EPDM/PP blend at the early stage of dynamic vulcanization was firstly calculated to be in the range of 25 nm and 46 nm by using the critical breakup law of the viscoelastic droplets in matrix. Meanwhile, the real size of rubber phase in Thermoplastic Vulcanizate (TPV) at both the early stage and the final stage of dynamic vulcanization were observed by using Peak Force Tapping Atomic Force Microscopy (PF-AFM). The results indicated that EPDM phase indeed broke up into nano-scale particles at the early stage of dynamic vulcanization, consistent well with the calculated result. More interesting, it was firstly revealed that the micro-meter sized rubber particles commonly observed in TPV were actually the agglomeration of nano-scale rubber particles with a diameter of 40-60 nm. We further revealed a new mechanism for the morphological evolution and microstructure formation of TPV during dynamic vulcanization as following. First, the breakup and crosslinking of the rubber phase mainly occured at the early stage of dynamic vulcanization. The phase inversion of the rubber phase and thermoplastic occured when all the rubber nanodroplets transformed into interconnected nanoparticles, which formed a strong rubber network. At the later stage, these rubber nanoparticles agglomerated more densely because of the requirement of thermodynamic stability, leading to the formation of larger and more regular agglomerates and significantly weakened rubber network. Our results indicated that the occurrence of phase inversion of the dynamically vulcanized blend was dominated by the formation and agglomeration of rubber nanoparticles rather than the increased viscoisty ratio of EPDM and PP as previously reported. This study provides guidance to control the microstructure of TPV to prepare high performance TPV products for a wide range of industrial applications. Keywords: thermoplastic vulcanizates; dynamic vulcanization; microstructure; mechanism.



185

Seo Yongsok

In-situ polymerization of epoxy based thermotropic liquid crystalline polymers by reactive extrusion and its liquid crystalline behaviors.

A new series of thermotropic liquid crystalline polymer (TLCP) containing three phenyl ring connected by an ester mesogenic unit are synthesized by reactive extrusion method. In twin screw extruder, main chain TLCP had been in-situ polymerized from the liquid crystalline epoxy (LCE) monomer reacted with monoamine in several minutes. The chemical structure of TLCP was characterized by means of Fourier-transform infrared (FT-IR) spectrometer, 1H and 13C nuclear magnetic resonance (NMR) spectroscopy. The thermal properties and thermotropic liquid crystalline behaviors were investigated by Thermal gravimetric Analysis (TGA), Differential scanning calorimetry (DSC), 2-D high temperature X-RAY Diffraction (2-D XRD) with GADDS (General Area Detector Diffraction System) program and Polarized light Optical Microscopy (POM) with hotstage. All the series of TLCPs revealed nematic LC transition behavior and exhibited Shlieren or marbled texture depended on their chemical structures. The nematic-to-isotropic transition temperatures were existed in the range of 175•Ż to 240•Ž, and TLCPs were thermally stable up to 350•Ž. The molecular weight of TLCPs were determined by Gel permeation chromatography (GPC) and the values of Mn were in the range of 8,600 to 24,100.

S09-164

Sobkowicz Margaret, Farahanchi Azadeh , Gug JeongIn

One-step Reactive Twin Screw Extrusion Process for Compatibilizing Polymer Blends

Polymer blends can combine the properties of two materials for more versatile high performance plastic products. In addition, increasing packaging complexity requires new blending solutions for recycling multicomponent feedstocks. Twin screw

Oral

S09-109

Battegazzore Daniele, Lavaselli Matteo, Frache Alberto, Li D, He J, Yang R

Reactive Extrusion of Sol-Gel Silica as Fire Retardant Additive In Ethylene-Vinyl Acetate Copolymer (EVA) Composites

Ethylene-vinyl acetate copolymer (EVA) is a widely used material, particularly in the cable industry. It is frequently formulated with large quantities of inorganic filler material, such as aluminium trihydroxide (ATH). EVA is known to form a protective layer which can inhibit combustion, especially at low heating rates but, unfortunately, this effect is not observed when used in formulations with ATH. Moreover, to be efficient, a high amount of such inorganic filler is necessary (60 wt.%). This fact is an important drawback that lead to a reduction of the mechanical properties and of the processability. Aiming to improve these aspects, this research is focused on the use of sol-gel reactions to synthesize inorganic fillers in a polymeric matrix. The sol-gel method is based on a hydrolysis-condensation reaction of a metal alkoxide, which allows the synthesis of particles well dispersed in the polymer matrix. These reactions were done inside the extruder during the processing of the polymer matrix. The presence of sol-gel silica increases the Time To Ignition and also improves self-extinguishing ability, thanks to a better thermal stability at higher temperatures, and reduces the maximum Heat Release Rate in cone calorimeter tests. The flame retardant mechanism of silica in the EVA is mainly due to the physical process of silica acting as enhanced char/silica layers in the condensed phase which prevents the heat and mass transfer in the fire. A synergistic flame retardant mechanism have been evidenced by adding sol-gel silica inside EVA/ATH composites.

S09-117



compounding is the standard technique for achieving well dispersed composites and blends, and incorporating in situ reaction yields further property improvements. In this work, a unique ultra-high speed extruder was used to simultaneously blend and compatibilize a variety of biobased and recycled polymers. Increasing the compounding speed increased the surface area available for interchange reactions; however, the high rate of mechanical energy input also led to depolymerization and side reactions. Reactions were tracked using nuclear magnetic resonance spectroscopy and the morphology of the blends was linked to the changing interfacial tension as reactions progressed. A simple rheological model was developed for predicting processing-structureproperties relationships. Process simulation was used to tie the effects of shear rate to droplet breakup and coalescence depending on chosen screw design. The work shows that the combination of experiment and simulation helps to establish greater control over this novel one-step process.

S09-272

LI Jingping, CASSAGNAU Philippe , BOUNOR-LEGARE VERONIQUE

Carbonyl hydrosilylation reaction in polymer processing conditions: Toward PBT/PMHS crosslinking and compatibilization

Carbonyl hydrosilylation reaction was developed to prepare either polybutylene terephthalate (PBT)/polysiloxane (PMHS) crosslinking network or compatibilized polymer blends. It is focused on the addition reaction of hydrogenosilane groups (SiH) from polysiloxane onto carbonyl groups from PBT catalyzed by trirutheniumdodecacarbonylRu3(CO)12 An approach on PBT model compounds was carried out to investigate the potentiality and efficiency of carbonyl hydrosilylation reaction with 1H NMR. During kinetic study, at lower temperature100oC, the hydrosilylation reaction can reach 3 mol% after 4 hours. Some side reaction can reach up to 23 mol%, especially at high temperature such 180oC Hydrosilylation reaction was extented to PBT modification. The formation of PBT network was

investigated by rheology and SEM, the gel fraction was measured in a mixed solvent HFIP and chloroform. The impact of both shearing and hydrosilylatio reaction on the final morphology was deeply studied. In addition, the reaction is also applied to Polyamide12 (PA12). Since the process temperature of PA12 is lower than PBT, the side reactions are inhibited, we get PA12/PDMS blend with better dispersion and stability. References [1]P. Cassagnau, F. Fenouillot, Polymer 45 (2004) 8019-8030. [2]U. Sundararaj, C.W. Macosko, Macromolecules 28 (1995) 2647-2657. [3]K. Prakashan, A.K. Gupta, S.N. Maiti, J. Appl. Polym. Sci. 105 (2007) 2858-2867 [4]J. Bonnet, V. Bounor-Legaré, P. Alcouffe, P. Cassagnau Materials Chemistry and Physics 136 (2012) 954-962

S09-277

Massardier Valerie, Fel Elie, Khrouz Lhoussain , Bonneviot Laurent, Cassagnau Philippe

Properties of gamma-Irradiated PP/PE blends obtained by reactive processing.

t: Three commercial formulations of polypropylene (PP) and two of polyethylene (PE) were airradiated with 25 kGy integral dose in air atmosphere and investigated using X-band electron paramagnetic resonance (EPR). The free radicals were identified and their concentrations were related to both formulation and crystallinity of the polymers. The recombination of each species was monitored versus temperature. The concentration decay versus time concentration was monitored and simulated as a mixture of zero or first order mechanism for HDPE and of one for the PP polymers. In order to improve impact and tensile properties of PP based blends containing PE, reactive extrusion has been carried out with radicals obtained by a-irradiation. The addition of a ã-irradiation step in the processing sequence, between extrusion and injection, can be considered as an efficient way for improving the properties of blends. The improvement of mechanical properties has been discussed in terms of creation of secondary interactions or covalent bonds at the interface of the a-irradiated polymers, a-PP and a-PE. Mechanical, rheological properties and Electron



Paramagnetic Resonance (EPR) studies of the extruded blends after a-irradiation reveal that reactions of ã-PP and ã-PE macroradicals are likely to occur. On one hand, the rheological measurements have highlighted an increase of the complex viscosity of the ã-irradiated blends at low frequencies. On the other hand, the EPR spectrum simulation shows that the radicals are not the same in the blend and in the genuine a-PP and a-PE. Besides, the increase of temperature in the sample affects the shape of the EPR spectra, revealing that some macroradicals react one to another, which creates new macroradical structures of rather alkoxyl type. Key words: Polyolefin blends, radicals, reactive extrusion, high shear, ãirradiation, electron paramagnetic resonance (EPR), simulation, reinforcement, lightening.

S09-279

Schawe Jürgen E.K.

The interplay between molecular dynamics and reaction kinetics during curing reactions

According to the viscosity change during curing reaction the glass transition temperature increases. At isothermal conditions or slow heating, a thermosetting resin vitrifies during curing reaction if the reaction temperature is lower than the actual glass transition temperature of the reacted material. This is indicated by the heat capacity change during reaction. Due to the vitrification process the kinetics become diffusion-controlled and the reaction rate decreases dramatically. The transition between chemically controlled and diffusion controlled reaction can be described using a diffusion control function. The actual reaction rate can be expressed as a product of the reaction rate of the chemically controlled reaction and the diffusion function. It is shown that the chemically controlled kinetics can be evaluated using iso-conversional methods DSC (model-free kinetics) from heating experiments at sufficiently high heating rates. Several approaches of the diffusion function exist. However, most of them need a large number of parameters or measured data of the vitrification process. Using such approaches the material behavior during diffusion control cannot be

predicted, because the parameters have to be measured before. To overcome such drawback we introduce a phenomenological expression for the diffusion control function, which is independent of reaction temperature and requires the the conversion dependence of the glass transition temperature. The presented approach can be used to predict the kinetics of complex reactions, including the change from chemically controlled to diffusion-controlled kinetics and the behavior in the diffusion controlled regime, on the basis of a small number of experiments. The tested system is a thermoset and consists of an epoxy resin (DGEBA) and a cross-linker (DDM). This system is studied by DSC, Temperature Modulated DSC and Dynamic Mechanical Analysis (DMA).

S09-441

Amine El Sayed Achraf

An engineering approach to improve the prediction of melt flow behaviour for injection moulded rubber parts

While injection molding simulation softwares are becoming more and more popular in thermoplastic industries due to their ease of use and advantages, many rubber molding companies have not yet fully benefit from this technology, known as reactive injection molding (RIM). This is mainly due to the complexity of material characterization, the lack of material data and appropriate description of the material behaviour. Specifically, the analysis of the filling stage of the RIM process requires the determination of the cure kinetics and the rheological, PVT, and thermal behavior of the material. Often one of the hurdles is characterizing and modeling the viscosity of rubber compounds reinforced with particulate fillers. This type of compounds usually does not obey to the Cox-Merz rule [1] due to the presence of fillers [2]. In addition, the cure rate dependence of viscosity has to be properly addressed. In this work, we have shown that the destruction of filler network at high shear rates makes the steady state shear viscosity, ç, measured by capillary rheometer, lower than the complex viscosity, ç*, obtained via RPA. In order to obtain an effective methodology to model



compound viscosity, an engineering approach has combines been developed. It material characterization modeling, numerical and simulation, and experimental verification. By applying this methodology, numerical simulation results have shown good prediction of melt front time and sprue pressure for different injection molds and rubber compounds. References: [1] W.P. Cox and E.H. Merz, Journal of Polymer Science, 28, 619 (1958) [2] J. E. Mark, B. Erman and C. M. Roland, The Science and Technology of Rubber (Fourth edition), pp. 322

S09-522

Yao Zhen, Xu Lin-jie, Qiu Shao-long, Li Yan, CAO Kun

Preparation of Long Chain Branched Polypropylene by the Silane-grafting Reactive Extrusion and its Foaming Behavior

The silane-grafting branched long chain polypropylene(Silane-LCBPP) was prepared by the means of the coupling reaction between maleic anhydride grafted Polypropylene(PP-g-MAH) and 3-aminopropyltriethoxysilane(APTES) in a twin screw extruder. The assistant regulation role with introducing supercritical carbon dioxide(scCO2) as the in-situ plasticizer and effect of the molar ratio of silane and maleic anhydride were mainly investigated. Fourier transfer infrared resonance(FTIR) was adopted to analyze the chemical structure change of the siloxane and maleic anhydride bonds. Differential scanning calorimetry(DSC) measurement showed the higher crystallization temperature. Based on the higher dynamic modulus, increased low-frequency complax viscosity and lower loss angle etc., the rheological results confirmed the existence of LCB structure. Moreover, the Silane-LCBPP could suppresse the cell coalescence and rupture more effectively during the foaming process assisted with scCO2. The silane-modified PP exhibited more homogeneous cell structure, higher cell density and larger expansion ratio.

S09-542

Bernardeau Fabien, Perrin Didier, Caro Anne-Sophie, Benezet Jean-Charles, Ienny Patrick

Surface modification of bakelite particles: enhancement of their performance as a filler

Phenolic molding compounds are the oldest synthetic plastic produced and used by mankind. Despite their old age, they are still in use today. Due to their excellent thermal and electrical properties, and fair price, they find use in various applications. However, one major drawback of phenolics is their lack of recycling option, landfilling being the main route of disposal. An alternative recycling method is proposed in this work. It relies on the use of comminuted phenolic compounds as a filler in a thermoplastic matrix. When this phenolic filler is incorporated without modification in a non-polar or polar polymer, poor adhesion is observed between the two phases as well as a decrease of the mechanical properties of the composite. In order to obtain a reactive organic filler by improvement of interfacial functional group reactions, different types of surface modification of the filler were performed. They depend on chemical reaction of two potentially reactive sites of the phenolic compound surface. On one hand, attempts were made to graft organosilane on phenolic hydroxyls. Two types of silane were used: an aminosilane and a vinylsilane. On the other hands, reaction of unsubstituted ortho and para carbon position of aromatic ring were attempted to graft β -amino-carbonyl molecules onto phenolic molding compound (Mannich reaction). Formaldehyde and various diamine were used. All reactions were carried out in a three necked round flask with a stirrer under reflux. The efficiency of the grafting reactions was evaluated with different techniques. Fourier transform infrared spectroscopy was used to assess the formation of the expected chemical bonds, as well as 13C NMR. In the case of silane treatment, the amount of grafted silicium was evaluated with EDX and 29Si RMN. The surface energy of the modified fillers was also measured. Finally, the modified fillers were incorporated in a polymer matrix and the mechanical properties of the composites were measured.

S09-548

Ji Weiyun, Feng Lianfang, Gu Xueping, Zhang Cailiang, Hu Guohua

Using a concept of reactive compatibilizer-tracer to probe mixing performances of a twin screw extruder for reactive compatibilizing blending processes

Reactive compatibilizing blending, called also as insitu compatibilization, involving interfacial reactions leading to in-situ formation of graft or block copolymers as compatibizers is a convenient and effective way to produce new materials with combinations of properties not available in a single polymer. Twin screw extruders (TSE) are often used for carrying out polymer blending processes. It is very challenging to investigate a reactive blending process in TSE because both mixing and interfacial reactions are highly coupled. Most importantly, the amount of the in-situ formed copolymer is often so low that it is very difficult to determine it in a relatively accurate manner. In this work, we propose a new concept called reactive compatibilizer-tracer, which bears reactive groups capable of reacting with its counterpart upon forming a copolymer for in-situ compatibilization of a reactive polymer blend and at the same time fluorescent labels allowing determining very small amounts of the in-situ formed compatibilizer. To show its usefulness and potential applications, blends based on polystyrene (PS) and polyamide 6 (PA6) are used. The reactive compatibilizer-tracer is a random copolymer of styrene (St), 3-isopropenyl- α , α' -dimethylbenzene isocyanate (TMI) and 9-(methylamino-methyl)anthracene (MAMA), denoted as PS-TMI-MAMA. Using the reactive compatibilizer-tracer together with transit experiments, the influences of various parameters including screw configuration, feeding mode, blend composition and screw speed on the evolution of morphology and interfacial reaction. Those results provide many fundamental insights into reactive blending processes in TSE.

S09-601

Radusch Hans-Joachim, Hübner Matthias, Röber Friedhelm, Wutzler Andre

Reactive Compounding of Polydimethylsiloxane-Polyurea Copolymer based Masterbatch Colorants

Optical and esthetic modification is a basic need for polymer application in all technical and consumer fields. Colorants are used in broad volume to satisfy the demand of costumers for that purpose. Mainly, colorants are included in a carrier polymer, which should help to dose the colorant precisely, to mix it homogeneously, to be compatible with the matrix, and it should not influence the mechanical and rheological properties unfavorably. A colorant masterbatch on the basis of polydimethylsiloxanepolyurea copolymer (PDHC) was proposed, which should warrant these demands in high manner. The masterbatch was generated by a specific twin screw extruder with liquid feeding unit for the liquid initial components polydimethylsiloxane (PDMS) and diisocyanate, and an optimized segmented mixing screw. As PDMS a pigment containing PDMS prepared in a pre-dispersion process was inserted. The precise adherence of the stoichiometric ratio of the initial components as well as the optimization of residence time of the polymer in the extruder in concern to the reaction time of the components allowed the generation of the PDHC based masterbatch. Different isocyanates and aminopropyl terminated PDMS with different molecular mass were used. The investigation of coloring effectivity and homogeneity was realized by a single screw extruder with flat die and chill roll device. A higher number of thermoplastics was involved into the investigation of the suitability of the generated masterbatches. Beside the nearly universal applicability of the masterbatch, the improvement of processability - expressed by lowering of the viscosity and reduction of energy consume of the extruder - could be demonstrated. The good dispersion of the pigment particles is demonstrated by optical microscopy. Stress-strain measurements proved that no significant negative influence of the new masterbatch in concentrations < 5 % on the mechanical properties of the investigated thermoplastics could be observed.

S09-676



Rondin Jerome

Adhesion development and water ageing resistance in multilayer pipes for sanitary and hot water transport

PVDF has a high resistance to most chemical compounds, which makes it suitable for transporting numerous chemicals. Its resistance to chlorinated agents (chlorine dioxide, chloramines, sodium hypochlorite ...) makes it a prime candidate for hot water transport applications, including hospital and public environment where aggressive treatments using chlorinated agents are commonly used. The technical challenge to achieve here is to ensure the integrity of the piping system exposed to chlorine treatments while maintaining a high quality of the water transported through the pipes (low accumulation of biofilm on the inner layer surface). Arkema® has developed a technical solution consisting of a 100% thermoplastic multilayer tube (MLT) comprising: i) a primary layer made of polyolefin (HDPE PP ...), ii) functionalized tie layers to ensure good compatibility between the layer structure and the inner layer and iii) a PVDF layer providing resistance to chlorinated agents and resistance to hydrolysis while in compliance with European regulations for potable water transport (ACS, KTW, KIWA...) This presentation aims to explain the adhesion mechanisms in multilayer structures obtained by coextrusion. The impact of the coextrusion conditions, the surface chemistry of the tie layers and the PVDF barrier layer on the adhesive properties of the multilayer structure will be discussed. The final part will present the last results obtained after immersion and ageing of these multilayer pipes in hot water (T = $80 \circ C$, P = 6bars, t = 2000h) and in chlorinated hot water ([ClO2] = 70 ppm, T = 70 $^{\circ}$ C).

S09-728

Lucas Antoine, Bounor-Legaré Véronique, Cassagnau Philippe, Boisson Fernande, Crépet Agnès, Martin Gregory, Vanhille Aurélie

Elucidation of complexes structures created by reactive extrusion through coupling rheology, DOSY NMR and SEC analysis

Chemical reactions carried out by reactive extrusion usually lead to complexes created structures with mixtures of modified and non-modified polymers and in some cases to chain scissions and thus evolution of molar mass distribution. Face to such structural changes in the melt, a main challenge is to adapt physico-chemical analysis to deeply identify the new species formed. Some specific techniques can answer to such requirements: i) The use of Multi-Angle Laser Light Scattering (MALLS) for the determination of branching is usually processed on star-branched polymers synthetized from a multifunctional initiator; ii) The diffusion Ordered Spectroscopy (DOSY) is commonly used to witness the grafting of an additive or a polymer block onto polymer chains.; iii) and classically, the molar masses are measured by size-exclusion chromatography (SEC). However to our knowledge the coupling of rheology, MALLS and DOSY technics in order to observe the grafting of a multifunctional additive on a polymer and the resultant branching has never been studied. To evaluate such approach, reactive extrusion of a polymer with a multifunctional additive had been carried out with a twin screw extruder. These formulations were analyzed by frequency sweep measurements on an ARES rheometer to estimate the change of viscosity. Besides the significant drop of the copolymer molar mass confirmed by SEC, the analysis by 13C NMR and DOSY evidenced the grafting on the polymer. Hence, MALLS experiments performed on formulations obtained by playing on the functionality of the additive highlighted significant structure difference and allowed to differentiate the behavior of linear polymers from branched systems. In conclusion, these original coupling experiments demonstrate the possibility to understand in details the complexes structures created during reactive extrusion process.

S09-735

Zschech Carsten, Gohs Uwe, Heinrich Gert



Electron induced reactive processing of polypropylene/ethylene octene copolymer blends – a new method to produce toughened polypropylene

Polypropylene (PP) belongs to one of the most used commodity polymers due to its exceptional properties including good chemical resistance, mechanical properties and processability at low price level. In addition to traditional applications, it is increasingly used as functional material in automotive industries, but its low impact resistance limits this application. Consequently, it is blended with a rubber in order to increase its toughness. PP/ethylene octene copolymer (EOC) blends show higher impact strength in comparison to other PP/rubber blends. The main drawback of this method is a reduction of E-modulus and tensile strength. In addition, the weak interfacial interaction between EOC and PP phases negatively effects the final properties of this blend. Thus, the PP/EOC interface has to be modified. Based on our PP/EOC works on thermoplastic previous vulcanizates, we firstly tested our continuous pilot plant for electron induced reactive processing (EIReP) to prepare EOC based toughened PP. This novel reactive processing method offers a high efficiency as well as a local and temporal precise generation of radicals. We investigated the mechanical, morphological and rheological properties of toughened PP. The tensile strength of toughened PP is at the same level compared to virgin PP due to increased interfacial adhesion between sub-micrometer EOC phase in the PP matrix.

S09-763

Scholtens Boudewijn J.R., Loontjens Ton, Ozkoc Guralp

Micro compounding for reliable screening of reactive extrusion (REX) processes

Recycling of PET and PA is hampered by inferior mechanical properties due to aging during previous application, hydrolytic and/or thermal degradation. Chain extension by reactive extrusion (REX) can become new way to repair these deficiencies in an economically attractive way. Process optimization of REX needs many variables to be tested such as chain extender type, concentration and many process conditions. In this presentation we show a new way of very fast screening of many REX conditions and catalysts. This enabled us to study many more variables within the same budget and in a shorter time. In addition this study led to new insights of efficient use of process control data of a micro extrusion process

S09-768

faridi rad Farzaneh , Ahmadi Shervin, Barmar Mohammad

Insitu Polymerization of Laurolactam towards Polyamide 12: Investigating the Effect of Catalyst And Activator

Insitu ring opening anionic polymerization of Laurolactam towards polyamide 12 (PA12) was successfully performed via the melt polymerization of Laurolactam as monomer in the presence of sodium caprolactam as a catalyst, and toluen diisocyanate as an activator during reactive melt blending. This reaction takes place at a significantly faster rate and gives a narrower molecular-weight distribution than those obtained with other techniques. The effects of various concentrations of catalyst and activator on the rate of reaction and the amount of residual monomer were determined. In order to characterize the synthesized samples, DMTA, TGA and DSC analysis have been done. Also the existence of amide groups was proved by ATR and XRD spectrums accordingly

S09-771

Ning Nanying , Ma Qin , Liu Suting , Zan Xiaoqing , Tian Ming, Zhang Liqun

Improving the actuated performance of graphene/dielectric elastomers composites by using some new methods

Dielectric elastomers (DEs) can can give rise to surprisingly large deformations by applying an electric field. 1-3 Because of the lightweight, large strain, and high energy density etc., DEs find many applications in industry such as artificial muscles 191



and sensors. Among various DEs, graphene based DEs have attracted much attention because of its high dielectric constant (k) and unique layered structure. In this study, some new methods were used to improve the electromechanical performance of graphene based DEs. First, we prepared thermoplastic polyurethane (TPU) DE with high k and low dielectric loss by disrupting hydrogen bonding between TPU chains and in-situ thermal reduction of graphene oxide nanosheets (GONS). Second, we prepared GONS-encapsulated carbon nanosphere (GO@CNS) hybrid/XNBR dielectric composite with high k, low dielectric loss and large actuated strain at a low electric filed by latex compounding. Third, we prepared poly (dopamine) encapsulated GONS/elastomer composites with low dielectric loss and improved breakdown strength and actuated strain at a low electric field. in the The improvement electromechanical performance of graphene based DEs facilitates the wider application of DEs. Key words : Dielectric elastomers (DEs), dielectric properties, grapheme

S09-774

Gigante Vito G, Coltellia Maria-Beatrice Coltellia, Phuong Vu than , Cinelli Patrizia, Lazzeri Andrea

Reactive extrusion of PLA/PC blends and composites

Poly(lactic acid) (PLA) is one of the most promising renewable polymer to be employed in injection molded parts. However, the heat deflection temperature and the impact properties should be improved. The reactive blending with polycarbonate (PC) in the presence of an interchange reactions catalyst was demonstrated to be a successful strategy. This process was applied to both virgin and recycled-PC/PLA blends and interesting differences were evidenced as a function of different viscosity in the melt, of the polymers. The blends were prepared in a laboratory extruder, tensile and impact properties were measured, and the phase morphology was investigated even by electron microscopy. Cellulose/polymer composites were also prepared by using PLA/PC blends as polymeric matrix. Fibres having different thickness and aspect ratio were selected and used as fillers in

extrusion trials. The elastic modulus increased thanks to the reinforcing behavior of the fibres and several models were applied to fit the experimental trends as a function of composition. Keywords: poly(lactic acid), polycarbonate, recycling, renewable, catalyst.



Poster

S09-111

Tuna Basak

Effect of reactive extrusion conditions on the properties of PA6 organoclay nanocomposites

Effect of melt processing conditions on the reactive extrusion of PA6 organoclay nanocomposites Basak Tuna (1), Hadj Benkreira (1), Adrian Kelly (1) (1) R&KT Centre of Advanced Engineering Materials, School of Engineering, University of Bradford, UK b.tuna@bradford.ac.uk Polyamide-6 (PA6) undergoes thermal degradation during melt processing. The organoclays accelerate chain scission of the PA6 matrix which leads to a matrix of lower molecular weight. In this work we employed a novel chain extender to rebuild the molecular weight which can react with end groups of PA6 during the limiting time of extrusion. Joncryl® ADR 3400 was used as the chain extender and Cloisite® 30B was employed as organoclay. The experiments were performed in APV twin screw extruder (L/D=25) at different temperature profiles and screw speeds and a laboratory scale mixer Haake Minilab Microcompounder to understand effects of melt processing conditions and extruder type on the reactive extrusion of PA6 organoclay nanocomposites. Rheological, thermal and mechanical methods were used to characterise samples. Keywords: Thermal degradation, melt processing, chain extender, reactive extrusion, polyamide organoclay nanocomposite.

S09-190

Fontanier Jean-Charles, Lortie Frédéric, Gérard Jean-François

Monitoring the polymerization of an acrylic-based formulation in a RTM process: application to thermoplastic-based composites

Nowadays, polymer matrix composites are widely used for aerospace, automotive and railway

applications. For equivalent properties, these materials are lighter than metallic parts that makes them very attractive. In this context, thermoplasticbased composites, especially acrylic-based ones, deserve to be considered as they exhibit good mechanical properties in terms of stiffness and resilience. Furthermore, they can be more easily recycled as opposed to thermoset polymers. Manufacturing structural composites requires to produce good qualities parts with complex geometries while maintaining short processing cycles to stay cost-effective. For this purpose Resin Transfer Molding (RTM) has been selected to process these composites. Indeed it is a low temperature closed-mold process allowing for manufacturing complex continuous fibersreinforced parts. However, it requires precursors with a very low viscosity (η <1Pa.s) to ensure a good dry preform impregnation. Thermoplastic polymers which own a very high viscosity in molten state cannot be directly injected. Idea is to use an acrylicbased reactive formulation exhibiting a very low initial viscosity and which can be subsequently polymerizes via a radical mechanism once the mold filled and the preform fully impregnated. To envision the mass production of high quality TPbased parts, it is necessary to ensure the reliability of the process. In particular the exact conversion and viscosity have to be monitored all along the RTM processing step. Indeed if these parameters are not well controlled, preform impregnation and polymerization rate can be unsatisfying which may decrease final properties. Therefore, our strategy was to fit an RTM mold with several dielectric sensors in order to in-situ monitor electrical properties upon cure. Conversion and viscosity evolution versus time have also been determined ex-situ. Finally in-situ and ex-situ measurements have been related to build abacus. Thus it was possible to track conversion and viscosity evolutions of the acrylic-based system with time at different locations of the RTM mold.

S09-318

Li Miao



The Study of Preparation and Heat Stabilization of Complexes of Calcium,Zinc,Lanthanum (Ⅲ)With N-(2-amino ethyl) Maleamic Acid Radical on PVC

Abstract: Due to the limitation of thermal degradation of PVC, thermal stabilizer must be added when processing, it makes thermal stabilizer becoming a rapidly growing field. However, The rare earth stabilizer have a unique electronic structure, so they can form complexes with such compounds many organic including the coordinated atoms: N and O which used as PVC thermal stabilizer. Amide type open chain of rare earth ions have a strong ability of coordination and high selectivity, we can obtain with new structure complexes at the same time, which has received the widespread attention. In this paper, maleic anhydride, ethylene diamine, sodium hydroxide, lanthanum chloride, zinc chloride and calcium chloride as the raw material, adopts the direct legal system had not reported three kinds of complexes, the N-amino ethyl maleamic acid lanthanum(LaL3), ZnL2,CaL2.And through their recombination to study the synergistic effect between them and the impact on the thermal stability of PVC. By melting point determination, element analysis, infrared spectrum, such as the composition, structure and properties were studied. Congo red test and TG analysis shows that the three kinds of complexes have good thermal stability of PVC. By these three composite heat stabilizers, suggests LaL3/ZnL2 and CaL2/ZnL2 composite heat stabilizer on PVC thermal stability increased significantly, and could effectively suspend "zinc burning". Key words : complexes of lanthanum(Ⅲ); N-(2-amino ethyl) maleamic acid radical (L-) Lanthanum (III) ; Polyvinyl chloride (PVC) ; Heat stabilizer

S09-658

Yang Mingtao, Li Jiang, Guo Shaoyun

A reactive extrusion process with the aid of ultrasound for preparing cross-linked polypropylene

Introducing the long chain branching or crosslinked structure in polypropylene (PP) is highly desired to meet the requirement of high melt strength, which is a key for the application of PP in thermoforming, blow molding and foaming where elongation flows dominate. In this work, the power ultrasound was introduced into the reactive extrusion at the exit die of an extruder for preparing the long chain branched or cross-liked PP. The main goal was to maintain the highly branched and cross-linked structure during reactive extrusion process in superior process-ability case of low peroxide concentration. The results of the dynamic rheological property, melt flow index, dynamic mechanical spectrum and extensional viscosity measurement showed that the crosslinked extent and melt strength of PP increased obviously with the employment of a ultrasound of 300 W while the content of functional monomers and peroxide was constant. FTIR analysis, DSC characterization, and GPC measurement proved that the increase of cross-linked extent and melt strength was attributed that the ultrasonic waves can induce the chain scission and recombination reaction when the PP melts flowed through the exit die assembled with a ultrasonic probe.

S09-785

Shin Hyeon Jeong , Go Cheol Wan, Jeong Han mo

Waterborne polyurethane modified with silicone macromer and the nylon airbag coated with it

A waterborne polyurethane (WPU) with a double bond in the main chain was modified with a poly(dimethylsiloxane)(PDMS) macromer having a terminal methacrylate group (PDMS methacrylate macromer) by using a radical mechanism, and the changes in various physical properties were examined. Although the crystallinity of the soft segment domain increased, the cohesion of the hard segments was weakened as a result of the modification with the PDMS methacrylate macromer. The adhesion between the WPU and nylon decreased due to the hydrophobic/low polarity of the PDMS component, and this improved the flexibility and the tear strength of the nylon-6,6 textile coated with WPU. The air permeability of the coated textile also increased as a result of the modification



PPS®32

S09-88

Hopmann Christian, Karatzias Christos, Boettcher Arne, Fischer Kai

Production of CFRP components with clear surface layer in the PU spray impregnation process

The high volume capable production of continuous carbon fibre reinforced plastic (CFRP) components for visible areas with high fibre volume contents still presents a challenge. One of the most important disadvantages is low economic efficiency due to the required subsequent work (grinding, painting). To overcome this disadvantage, a process for a high volume capable production of such visible components with polyurethane (PU) matrix systems is being developed at the Institute of Plastics Processing (IKV) at RWTH Aachen University. Two approaches based on the manufacturing processes PU spray impregnation and wet pressing are pursued. Both approaches rely on the generation of a clear PU surface layer (coating) on the visible component surface. As process variants, a one-step pressing process with an application of the coating directly on the noncured PU-impregnated preform has been developed, as well as a process with an application of the coating on the pre-cured or on the final-cured CFRP component. This paper describes the results of the process analysis for the process integrated application of the coating material. The investigations include a variation of the process, material and preforming parameters. The focus of the investigations was the generation of a low surface waviness and a good adhesion between the coating and the CFRP component. The results of investigations regarding the surface quality for the combination of an aromatic PU system as matrix system and an aliphatic lightfast PU system as coating material show, that the coating material can compensate the characteristic waviness of the neat CFRP component. In this paper, the influence of the process parameters on the surface quality is analysed and optimum process parameters for the developed one-step pressing process are concluded.



S10- Rheology and Rheometry

Keynotes

S10-169

Kashi Sima, Gupta Rahul K, Bhattacharya Sati N

Anomalous Effect of Temperature on Rheology of Poly Lactide /Graphene Nanoplatelet Nanocompsoites

Biodegradable poly lactide (PLA)/ graphene nanoplatelet (GNP) nanocomposites were prepared by melt intercalation. Morphological studies were carried out via scanning electron microscopy and Xray diffraction. Results showed good dispersion of GNPs in PLA at low filler concentrations. Semicrystalline structure of PLA was found to change under the effect of GNP incorporation which was also confirmed by differential scanning calorimetry measurements. Dynamic viscoelastic nanocomposites exhibited properties of the significant enhancement with increasing GNP loading. In particular, storage modulus showed less frequency dependency in the low frequency region leading to a percolation threshold of between 6 and 9wt% at 180 °C. Increasing the temperature of measurements showed that nanocomposites with high GNP loadings not only did not obey the timetemperature superposition but exhibited an unusual behaviour. In the low frequency region, viscoelastic properties of the nanocomposites increased with increasing temperature in contrast to the ideal melt behaviour. This was attributed to the changes in the different interactions present in the system with increasing the temperature resulting in occurrence of physical gelation at lower GNP concentrations.

S10-21

Räntzsch Volker, Özen Mürüvvet Begüm, Ratzsch Karl-Friedrich, Guthausen Gisela, Wilhelm Manfred

Low-Field RheoNMR: Newly Developed Combination of Rheology and Time Domain (TD)-NMR to Correlate Mechanical Properties with Molecular Dynamics in Polymer Melts

NMR is a useful technique for characterization of the microscopic dynamics and structure of polymeric material, while rheology provides access to the macroscopic mechanical properties of polymer melts. To achieve greater insight into the interplay of these two domains, especially with regard the microscopic effects of nonlinear shear fields, it is desirable to combine these two methods in one setup. To this end, new developments with permanent Halbach magnets were used to shrink NMR magnets to under 20 cm and a few kilograms [1], making it possible to integrate into a commercial high-end strain-controlled rheometer (Rheometrics/TA ARES), together with a convective sample heating system. This unique low-field RheoNMR setup can simultaneously make a full rheological shear characterization (G', G'', LAOS, I3/1, FT-Rheology [2]) while monitoring molecular dynamics via 0.7 T 1H TD-NMR up to temperatures of 210 °C [3, 4]. Possible applications for low-field Rheo-NMR include the measurement of quantitative composition in crystallizing polymers [5] and multiphase systems [6] during the application of non-linear mechanic deformations, e.g. shear induced crystallization. It enables to directly correlate changes in rheological moduli with the degree of crystallinity. To display the possibilities of this new technique, the studies on crystallization of isotactic polypropylene and variating molecular polyethylene weight, crystallization temperatures, additives and applied shear are presented. The results are compared to the findings of other groups [7]. Keywords: Rheo-NMR, crystallization, polymer melts References: [1] B. Blümich, F. Casanova, S. Appelt, Chem. Phys. Lett., 2009, 477, 231-240. [2] M. Wilhelm, Macromol. Mater. Eng. 2002, 287, 83-105. [3] V. Räntzsch, M. Wilhelm, G. Guthausen, Magn. Reson. Chem. 2015, DOI 10.1002/mrc.4219. [4] V. Räntzsch, K.-F. Ratzsch, G. Guthausen, S. Schlabach, M. Wilhelm, Soft Mater. 2014, 12, 4-13. [5] A. Maus, C. Hertlein, K. Saalwächter, Macromol. Chem. Phys. 2006, 207, 1150-1158. [6] K. Saalwächter, Prog. Nucl. Magn.



Reson. Spectrosc. 2007, 51, 1-35. [7] G. Lamberti, G. W. M. Peters, G. Titomanlio, Int. Polym. Proc. 2007, 22, 303-31.

S10-229

Yamaguchi Masayuki

Modification of rheological responses under elongational flow

It has been recognized that rheological responses under elongational flow affect the processability greatly at various processing operations. Therefore, numerous efforts have been carried out to control the elongational viscosity. The evaluation of the rheological responses under uniaxial elongational flow is, however, often carried out by measuring the force required to stretch a molten polymer after passing through a die, which is defined as drawdown force. The drawdown force is known to be greatly enhanced by the addition of rigid fibers by the excess shear deformation of a matrix between fibers, although the system does not show marked strain-hardening behavior in transient viscosity. Furthermore, elongational the crystallization behavior plays an important role on the drawdown force for a crystalline polymer, because it is evaluated at the non-isothermal condition. For example, the drawdown force of isotactic polypropylene (PP) and high-density polyethylene (HDPE) is found to be sensitive to the length of dies. This is attributed to the prompt crystallization of a polymer melt with fewer entanglement couplings by the exposure to the prolonged shear stress in a long die, which provides the steep increase in the elongational force. Therefore, the drawdown force can be enhanced by the addition of a nucleating agent, which is proved using PP. Finally, the addition of a small amount of poly(methyl methacrylate) (PMMA) with low molecular weight is found to enhance the drawdown force of PP. Because of the very fast cooling rate at the drawdown force measurement, the solidification of PMMA occurs faster than the crystallization of PP. Consequently, deformed PMMA domains act as rigid fibers in the PP melt, leading to the enhancement of the drawdown force.

S10-540

Teixeira Paulo F, Hilliou Loic, Covas Jose A

In-process rheo-optical characterization of polymer systems at constant extrusion conditions

As it is increasingly important to minimize costs and time-to-market when developing polymer systems with improved performance, in-process characterization methodologies become more attractive. Indeed, it is important to make available fast response characterization tools which, albeit using small amounts of sample, are capable of generating relevant data on the rheological response, process-induced material structure and properties. Recently, authors product the developed a prototype modular small-scale single / twin-screw extrusion system with outputs in the range of grams/hour that was coupled to a rheooptical slit die adequate to measure shear viscosity and normal-stress differences and perform rheooptical experiments, namely small angle light scattering (SALS) and polarized optical microscopy (POM) [1]. As with most similar attempts, the generation of a range of shear rates implied operating the extruder with varying screw speeds or feed rates. However, this changes the thermomechanical experience of the material inside the machine and, henceforth, may change the characteristics of the material in the die inlet, which in turn may jeopardize the validity of the measurements. To circumvent this problem, the authors adopted a design concept that has been seldom utilized, consisting of a die with two parallel channels, each fitted with an output control valve at its inlet, the total pressure drop remaining constant. While one of the channels can be utilized for conventional extrusion, the other has a slit configuration adequate for rheo-optical characterization. This solution is validated and several case studies are discussed. [1] P.F. Teixeira, J.M. Maia, J.A Covas, L. Hilliou. A small-scale experimental extrusion set-up for exploring relationships between process-induced structures and characteristics of multiphase polymer systems. Macromr Mat.Eng., in print, (2015). DOI: 10.1002/mame.201500196.



Oral

S10-153

Li Huijun, Li Lin

Rheological analysis of 3D printability of alginate hydrogel

With advanced 3D bioprinting technologies, fabrication of complex tissues or even organs becomes possible. One of the challenges for successful 3D bioprinting is the selection of a suitable scaffold material with a good printability. Hydrogels have attracted great attention as printing three biomaterials for dimensional scaffolds for tissues or organs. However the relations between rheological properties of hydrogels and 3D printability have not been extensively studied. In this study, alginate-based hydrogels were prepared and used as a printing material for 3D printing of scaffolds using an extrusion-based printer. Rheological studies were performed for the hydrogels with different formulas. We deduced the shear rate range for the hydrogels that bore during the 3D printing process. Furthermore, thixotropic properties the of hydrogels were investigated by applying and removing a shear rate. The measureable parameters for quantifying the quality of printing have been defined. The results will be shown and discussed. This presentation will provide some new understanding of the relation between rheological properties of hydrogels and 3D printability.

S10-171

Tae Joon-sung, Yim Kyung-gyu, Kwak Jae B., Gim Jinsu, Rhee Byung-oh

Effect of the wave length and the intensity of UV LED on UV-curable LSR

UV-curable LSR can be molded at relatively low temperature condition, which has advantages for an over-molding with inserts of temperaturesensitive materials. As the light sources for the radiation-cure process, halogen or mercury UV lamps have been used conventionally. However, the conventional lamps dissipate a lot of heat and their service life is relatively short. As substitution for the lamps, UV LED lamps provide a longer service life and a lower heat dissipation. In this research, UV LEDs were tested to analyze the rheological behavior of UV-curable LSR during curing process. UV-LEDs of various wave lengths and intensities were tested. The steady shear test was applied to find the starting time of cure and the SAOS was applied to find the ending time of cure. In addition, the hardness change along the curing

S13-195

Maeda Shuichi

Unusual Tiger-striped Flow Mark Patterns Appeared in Injection Moldings of Polypropylene/Talc Compounds

time was compared with the rheological test result

to make sure the reliability of the rheological test.

Relationships among tiger-striped flow mark patterns appeared in injection moldings, molecular characteristics, especially molecular weight distribution of polypropylenes (PP) and rheological properties of PP/talc compounds have been investigated. Usual tiger-striped flow mark pattern observed on one side of injection moldings of PP/talc compounds shows alternately bright and dark areas in the direction of flow and the pattern on the other side reverses out-of-phase with brightness. But the flow mark patterns of some PP/talc compounds are quite different from the usual one. The patterns on both side of injection moldings are in-phase and/or change halfway from in-phase to out-of-phase. We speculated the different flow mark patterns appeared in the injection moldings would result from the different flow behaviors of flow front during the injection stage of injection molding process. We also found that the flow mark of PP/talc compounds composed of PP with wide molecular weight distribution was in-phase pattern. In this study we will discuss the relationship the flow behaviors of flow fronts and tiger-striped flow mark patterns of PP/talc



compounds and also propose an improvement of tiger-striped flow mark of PP/talc compounds.

S10-217

Oblak Pavel, Gutierrez Joamin Gonzalez, Zupančič Barbara, Aulova Alexandra, Emri Igor

Processability and rheological properties of extensively recycled high density polyethylene (HDPE)

In plastics industry it is common practice to mechanically recycle waste material arising from productions. However, mechanical recycling affects material inherent structure and consequently its rheological properties and processability; therefore it needs to be quantified. Mechanical recycling of high density polyethylene (HDPE) was simulated by one-hundred consecutive extrusions. During the extrusion also processing parameters, namely melt pressure and torque were recorded. After every cycle, portion of material was removed for the purpose of characterization. After the processing, rheological properties of the material were characterized in terms of measuring melt flow index and viscosity. In addition, gel permeation chromatography and solubility tests were performed in order to study structural changes. The results of rheological measurements, i.e. MFI and complex viscosity, showed unfavourable effect of mechanical recycling on HDPE processability. With increasing number of the reprocessing cycles MFI drops practically to zero after 30th extrusion cycle. Further, viscosity significantly increases between 5th and 20th cycle. Moreover, changes in processability were directly monitored through the melt pressure and extrusion torque. Both values rise in first 30 extrusion cycles, pressure reaches more than 500% in respect to first extrusion. GPC measurements and solubility tests suggest that chain-scission branching and chain occur simultaneously from the start of the reprocessing. Through the first 30 extrusion cycles the molecular structure is being dominated by chain branching, while after 30th extrusion cycle chain scission becomes predominant over the chain branching. After 60th extrusion cycle, the branched molecule chains begin to cross-link. More can be read in 11.

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S10-268

Manero Octavio

Measuring the Effects of Filler Variations on Compound Viscoelastic Properties as Measured by the Capillary Rheometer and the RPA

The die swell and other viscoelastic characteristics imparted to a rubber compound by different elastomers and reinforcing fillers are very relevant to compound performance in extrusion, calendering, molding, and other factory operations. In this study, an ARC 2020 capillary rheometer was used to measure the die swell and other rheological behavior at different shear rates. Model rubber compounds were prepared and tested. Processability characteristics were also measured for these mixed stocks using the RPA 2000 with EDR. Comparisons were made of the performance behavior for these compounds. Statistical analyses were performed on running die swell and relaxed die swell vs. tan delta and G' under a wide range of frequencies and strain amplitudes. applied Observations were made and discussed for the tan delta inversion crossovers which may prove useful in quantifying state of mix and degree of in-situ silanization during the mixing process.

S10-294

Hajiraissi Roozbeh, Jahani Yousef

Low Frequency Region as a Finger print to Trace Droplet Deformation

Droplet deformation throughout polymer processing induces various morphologies which causes sundry characteristics. It is well known that rheology plays a key role in polymer processing. Appearing a secondary plateau at low frequencies implies existence of longer relaxation times compared to samples manifesting terminal behavior. The objective of this work is to trace



droplet deformation by conducting fiber spinning process. In this regard, two types of polymer blends (PP)/Polyamide6 Polypropylene (PA6) and Polypropylene/Polytrimethylene terephthalate (PTT) with various ratios (99/1, 94/6, 90/10, 80/20) were melt blended on twin screw extruder and thereafter, were spun. Morphological characterization was obtained by scanning electron microscopy (SEM) and as-extruded samples manifested droplet morphology and spun blend fibers showed fibrillar morphology prevalent throughout the PP matrix. Linear melt viscoelastic data were gathered by performing rheological approaches in linear region. Dynamic storage modulus of fibers represented a secondary plateau at low frequencies which was distinct from asextruded samples and complex viscosity showed a viscosity upturn upon fibril maturation.

S10-350

Jugo Viloria Miren, Domejean Hugo, Valtier Michel, Vergnes Bruno

Quantification Of Volume Defects Encountered During The Extrusion Of Rubber Compounds

During extrusion process, rubber compounds frequently present volume defects which alter the quality of the product. In the present study, we have systematically studied the flow of such compounds in capillary rheometry. Compounds made with two types of rubber, butadiene (BR) or styrene butadiene (SBR) rubber, silica and two types of additives (coupling agent and covering agent) have been prepared in an internal mixer. The flow behavior of these various compounds has been characterized using a pre-shearing capillary rheometer, with dies of different lengths and diameters. BR compounds exhibit the classical behavior of linear polymers, with two stable branches separated by an oscillating area. SBR compounds show a transition above a certain shear rate, indicating the onset of strong wall slip. Except at very low shear rates, all the extrudates present volume defects. Even though these specific features are not modified when varying filler content or

type of additive, it appears clearly that instabilities increase with the coupling agent. For each extrusion condition, samples have been collected and analyzed. The geometry of the extrudates has been quantified using a high-resolution scanner and image analysis. We show that the diameter distribution of the extrudates allows a global description of the severity of the volume defects.

S10-426

Luger Hans-Jürgen, Köpplmayr Thomas, Sobczak Lukas, Haider Andreas, Miethlinger Jürgen

Elongational rheology of glass-fiber and naturalfiber reinforced polypropylenes with a novel online rheometer

The aim of the present work was to study the influence of fiber content and fiber length distribution on the shear and elongational viscosity of polypropylene compounds measured with a novel online rheometer. The recently developed device consists of two slit sections and a hyperbolic contraction part in between, which allows for monitoring of both shear continuous and elongational viscosity during an extrusion process. Due to the favorable design of the hyperbolic contraction, pressure transducers can be incorporated directly into the flow channel, which prevents material accumulation in pressure holes. A polypropylene homopolymer intended for thermoformed packaging applications was compounded with different fiber content of either glass or cellulose fibers. While the measured shear viscosity only changed slightly, the elongational viscosity was found to be sensitive to the fiber content. Furthermore, the variation of fiber length distribution in а glass-fiber reinforced polypropylene random copolymer, intended for pipe applications, was detected by the elongational viscosity. Therefore the developed elongational rheometer is recommended as online process rheometer for quality control as well as for R&D. These results were confirmed by other methods such as Cogswell analysis of High Pressure Capillary Rheometer (HPCR) data or measurement on a wedge-shaped slit die. In addition, fiber length distributions of selected compounds were



determined to study the fiber shortening during processing before the rheological measurements.

S10-438

Marcourt Marjorie, Fulchiron René, Cassagnau Philippe, Rousseaux Dimitri, Lhost Olivier

In Situ Conductivity Measurement During Extensional Deformation Of HIPS Filled With Carbon Nanotubes

The addition of Carbon Nanotubes (CNT) to polymer has paved the way to ultra-low filled nanocomposites characterized with both electrical and mechanical properties. They have, amongst other, made their way into specific packaging with Static Dissipation protection. Electrical The privileged process is the sheets thermoforming of High Impact Polystyrene (HIPS) filled with CNT. This process presents major advantages for packaging such as efficiency and its cost-effective thermoforming tools and molds. However, during thermoforming the parts experience elongation flow which strongly deform the parts and may orientate the filler and then drastically impacts the electrically properties of the final part. Indeed, electron conduction requires filler percolation and good connection between filler aggregates. The challenge is then to reduce to a maximum the CNT amount keeping a percolating enough filler network to obtain complex parts with ESD properties. The deformation of the CNT network in polymer melts has been investigated by a combination of in-situ conductivity monitoring and extensional deformation analysis. For this particular purpose, an Extensional Viscosity Fixture put in a rotational rheometer ARES has been modified to allow the sample conductivity measurement during the extensional experiment. This new setup permits the observation of the conductivity variation under uniaxial deformation. We have experienced conductivity increase under specific condition and observed the conductivityinsulated transition and that before the sample break illustrating the filler network disconnection. stronger Moreover, а sensitivity to both

deformation and temperature contribution than extensional rate has emerged. To fully understand the mechanism of the filler network behavior during thermoforming we have in addition characterized the nanocomposites systems through improved contrast charge SEM method and rheological combined with conductivity measurement analysis.

S10-451

Rueda Martha Margarita, Fulchiron René, Prebe Arnaud, Martin Grégory, Cassagnau Ph

Rheological Properties Of Highly Filled Ferrite/Polypropylene In The Molten State

The objective of the present work is to study the linear and non-linear viscoelastic behavior of molten polypropylene filled with ferrite particles at different concentrations. Formulation, rheology and process interplay as a whole matter in this study. The effect of adding a commercial dispersant on the flow properties has been investigated by rotational and capillary rheometer. In rotational rheometry, an accurate study about structural material changes can be performed, while, in capillary rheometry the material is subjected near to real processing conditions and thus its non-linear behavior can be investigated. In rotational rheometry, a pre-shear was applied (1s^-1 for 160 s) and was followed by a time sweep experiment (w=1rad/s) at different deformations. The measurement of G' and G" over time showed that such materials were not stable, so that the composite structure changed a lot over time. Interparticle interactions together with a slight sedimentation effect might be the origin of this effect. It has been observed that particles can reorganize into a network under dynamic and quiescent conditions and thus a gel point can be determined. Adding a dispersant to these formulations stabilizes the morphology and thus the moduli and the viscosity remain constant over time. In capillary rheometry, two process windows were investigated: extrusion window (10⁰ to 10²) s^-1) and injection moulding window (10² to 10⁵ s^-1). No evolution of the structure has been observed in capillary rheometry. The effect of adding a dispersant on the flow properties is more



visible in the dynamic state than in the steady state. In the extrusion window, the addition of the dispersant agent decreases the inter-particle interactions and thus a decrease in viscosity is observed. Nevertheless in the injection molding window, no change in viscosity was perceived. Wall slip phenomenon may be the origin of this hide effect.

S10-471

Scheffler Thomas

Determination of the rheological behavior from highly filled phenolic injection molding compounds

Thermosetting molding compounds feature a high material and substitution potential for high temperature thermoplastics in technical applications due to their excellent thermomechanical properties. As a result of their high filling rates up to 80 percent (fibers, beads, particles) their mechanical properties are mainly dominated by the fillers. For example, particles with an aspect ratio (fibers) can cause an anisotropic behavior due to their process-induced orientation. The orientation of the fillers is among others a result of the viscosity depending on time, temperature and shear rate. The aim of this study is to determine the rheological properties of highly filled thermosetting molding compounds. An oscillating plate-plate-rheometer was used to examine the rheological behavior within the range of low shearing rates of a phenolic molding compound by varying the degree of filling and content of water.

S10-474

PPS[®]32

Sukumaran Sathish K., Komuro Ryohei, Takuya Ito, Sugimoto Masataka, Koyama Kiyohito

Slip and Roughness at the Interface between Polymeric Liquids during Capillary Flow

Studies that use only rheological data to deduce the slip velocity between immiscible polymer melts usually involve applying shear deformation to a stack of parallel multilayers. The maximum stress at which the slip velocity can be measured in these experiments is limited by the distortion of the parallel layers. However, polymer extrusion involves flow at significantly higher stresses than that accessible in these experiments. In order to understand slip in the context of extrusion, we have investigated slip at the interface between two immiscible polymer melts undergoing pressuredriven capillary flow. To enable the measurement of slip velocity at the polymer/polymer interface we have adapted the Mooney method, a method originally developed to study wall slip. Using the method, we measured the dependence of the interfacial slip velocity on the interfacial shear stress for cylindrical core-sheath samples of Polypropylene and Polystyrene. In agreement with prior work on multilayer sandwiches, we found two distinct power-law regimes in the relationship between the interfacial slip velocity and the interfacial shear stress. The power-law exponent changes from a value of approximately 3 at low shear stress values to approximately 2 at high shear stresses. We then investigated the effect of varying

S10-496

polymer/polymer interface.

Fasching Michael, Friesenbichler Walter, Leitner Eduard, Berger Gerald

the temperature on the slip velocity and explore the

consequences of time-temperature superposition

for the two polymers. Interestingly, the interfacial

slip velocities can be superposed using the WLF

parameters of one of the polymers but not the

other. Finally, I will discuss the connection between interfacial slip and the roughness observed at the

A New Device for Measuring Shear Viscosity of Rubbers on a Rubber Injection Molding Machine

The measurement of shear viscosity for rubber compounds is a challenging task, as the contribution of the fillers like carbon black or silica to the measurement result is dependent on the material prehistory. Thus, the capillary rheometer and especially the rubber process analyzer show different measurement results compared to what is

observed in the actual injection molding process. This work presents the development of a new rheometric injection mold which is mountable on a standard rubber injection molding machine and therefore allows the measurement of the material condition of the actual injection molding process (taking into account effects of shear forces of dosing screw). The fixed half, where the shear viscosity measurement is carried out, is equipped with a rectangular slit and 4 pressure sensors as well as 2 heat flow sensors to be able to detect and correct frictional heat occurring during the measurement. Frictional heating might also initiate the curing reaction for rubbers equipped with curatives. Consequently, the upper part of the measurement slit is attached to the movable mold half to enable the demolding of the rubber compound. The moveable half comprises of a cylindrical shape and a hydraulic plunger, which is able to (1) measure the actual flow rate (corresponding with the shear rate in the slit) via a displacement transducer and (2) allows the application of counter-pressure to enable the evaluation of the pressure dependency of shear viscosity. The demolding of the rubber compound in the movable half is enabled by angular sliders which compose the cylindrical cavity. As first results obtained with this new measurement concept, shear viscosity curves of a NBR compound filled with carbon black in configuration with and without curatives are presented compared conventional and to measurements on a capillary rheometer.

S10-503

Uitto Jussi, Verbeek Johan, Lay Mark

Rheological modification of Novatein Thermoplastic Protein

Polymers from industrial byproducts and waste streams show great potential as low-cost biomaterial resources. Novatein Thermoplastic Protein (NTP) is a bio-derived alternative for fossilfuel based plastic products. Its main component is dried bovine blood which is a low value by-product from the meat processing industry and is at least 90 % protein. Rheological properties, such as shear and extensional viscosity, are critical in defining polymer's thermo mechanical processability properties. In comparison to conventional polymers, extensional viscosity of protein plastics is typically drastically higher. Thus, applications of more advanced processing methods such as sheet extrusion and injection molding are limited. In this study, extruder driven capillary rheometer was used to determine rheological properties and its modification possibilities of NTP. Pressure requirements for different mass flow rates were collected by using three different length capillaries and these values were used to calculate true shear stress, shear rate and viscosity values by using Bagley and Rabinowitsch corrections. Extensional viscosity properties were calculated from the entrance effect properties. Aim of the study is to determine the effect of different plasticizers and understand which of the processing parameters affects extensional properties the most.

S10-637

Genoyer Julie, Yee Marcio, Soulestin Jérémie, Demarquette Nicole

Effect of the addition of organoclay on the morphology and rheological behavior of PMMA/PS blends

Nowadays, blends of polymers are an important matter of research in the plastic materials. In particular, blends of immiscible polymers are technologically interesting as their morphology can be tailored to tune their mechanical, thermal, electric, magnetic, or optical properties. The interplay between flow, morphology, and rheology is therefore a key point if one aims at tailoring the final material properties. Block copolymers are commonly used to compatibilize the polymers forming the blend and therefore have a better control on the morphology. However, the use of block copolymer has non negligible drawbacks: each type of blend needs to have a block copolymer with a tailored chemistry adapted to the blend chosen, and the block copolymer employed is often expensive. More recently, immiscible blends have been shown to be stabilized by nanofillers as well. At the present time, the influence of fillers on polymer blends morphology is a matter of intensive



investigation. In this work, the effect of adding organoclay (Cloisite 20A) to a blend of poly(methyl metacrylate) (PMMA) and polystyrene (PS) was evaluated. The clay was introduced using three different methods: direct mixing of the three components, mixing with PS or PMMA prior to the extrusion of the blend. The morphology of the blends was analyzed by scanning and transmission electron microscopy. Their rheological properties were evaluated carrying out small amplitude oscillatory shear tests from which the relaxation spectrum was inferred. The morphological results indicated that the addition of the clay resulted in a decrease of the size of the dispersed phase and that the clay was located at the interface between the blend phases. The relaxation spectra of the blends to which clay was added showed the presence of three relaxation times, one which was originated from the relaxation of the phases, one from the relaxation of the shape of the dispersed droplets and another one which could be due to the Marangoni stress.

S10-639

Ponton Alain

Structural and multi-scale magnetorheological investigation of simple magnetic fluids and nanocomposites biopolymer based networks

A new magnetorheological cell is designed to investigate the flow and the viscoelastic properties of complex ferrofluids. In a first part water-based and oil-based ferrofluids in various states of stabilization are synthesized, characterized and studied by stationary flow measurements at constant temperature $(25.0 \pm 0.2 \circ C)$ under different magnetic field strengths. Various soft magnetorheological behaviors are thus encountered here evidencing the determinant role of the size-sorting of the NPs size-distribution able to eliminate nanoaggregates in aqueous solvents, an efficient surfaction process of individual NPs in organic solvents and the interparticle colloidal interaction, which tunes the microstructure probed in parallel by small angle neutrons and X-Rays measurements.

nanocomposite biopolymer-based materials have been designed and studied. Magnetic nanoparticles of maghemite have been synthesized either by coprecipitation of a mixture of ferrous and ferric chlorides in an ammonium hydroxide solution and then stabilized by the adsorption of negatively charged citrate ions on the surface of nanoparticles with sodium counter-ions (Na+) or by the polyol process and further functionalized with ligand bearing NH2 functional groups and able to bind the nanoparticles through the ethoxy groups. Enhancement of viscoelastic moduli and viscosity at low shear rate has been clearly evidenced. In the first case it could be explained by the formation of liquid and deformable under magnetic field submicron or micron-sized droplets of demixing and by intramolecular electrostatic interactions between the positively charged NH3+ groups present at the surface of the magnetic nanoparticles and the negatively charged carboxylate groups (COO-) of sodium alginate chains in the second case. C. Galindo-Gonzalez, A. Ponton, A. Bee, J. Chevalet, D. Talbot, R. Perzynski, E. Dubois, Rheologica Acta (2015) S. Roger, Yan Y. Cheung Sang, A. Bee, R. Perzynski, J.-M. Di Meglio, A. Ponton, European Physical Journal E(2015) C. Galindo Gonzalez, S. Gantz, L. Ourry, F. Mammeri, S. Ammar-Merah, A. Ponton, Macromolecules (2014)

second part novel magnetic sensitive

S10-732

In a

Lafforgue Olivier, Poncet Sébastien, Seyssiecq Isabelle, Favier Julien

Rheological characterization of macromolecular colloidal gels as simulant of bronchial mucus

Mucus is mainly composed of water (90-95%) and mucins (2-5%), these mucins being high molecular weight macromolecules forming a 3D cross-linked matrix. It makes it a complex non-Newtonian fluid, with viscoplasticity, viscoelasticity, shear-thinning and thixotropy (Lai et al., 2009). These properties were qualitatively and separately tested by different authors. Due to the difficulties to collect samples and the extreme sensibility of the tested materials, the results are widely variable. A

complete and intrinsically consistent characterization remains to be done to develop a reliable rheological model for future numerical simulations of mucus displacements in airways, in the case of pathologies such as cystic fibrosis. For this purpose, samples of mucus simulants were tested using a controlled stress rheometer. The material consists of macromolecular colloidal gels at different concentrations in macromolecules to the variability in mucin production mimic depending on the disease state and environmental factors. The rheological properties at rest were investigated using small amplitude oscillatory shear tests as a function of stress amplitude, frequency and temperature. They revealed that mucus simulant behaves as a gel within a defined linear viscoelastic region and as a viscoelastic liquid above the yield stress zone. To characterize the behavior of mucus in response to in vivo shearing induced by cough or by air flows produced by clearance helping devices, steady state flow tests have been performed. The steady state flow curves for various polymer concentrations are well fitted using a Herschel-Bulkley law. To account for the time dependent behavior of mucus, 3 intervals thixotropy tests were also implemented to monitor structure breakdown and buildup processes. The combination of all of these measurements finally design a reliable procedure accounting for the rheological complexities of mucus, that now needs to be applied to real mucus for validations.

S10-77

Lu Bo, Lamnawar Khalid*, Maazouz Abderrahim

Dynamic Heterogeneity of PMMA/PVDF Blends: Composition Dependance and Role of Interphase

Dynamic heterogeneity in PMMA/PVDF blends was systematically investigated with insights from microscopic dynamics to macroscopic properties. In this work, an initial attempt was made to understand the weak thermorheological complexity in the framework of chain entanglements. Intriguingly, the degree of thermorheological complexity displayed a composition dependence: PMMA-rich blends and PVDF-rich blends showed a slight thermorheological complexity, whereas blends with intermediate compositions exhibited a moderate one. Notably, inter-chain entanglement prevailed over the intra-chain entanglement in the former series of blends, whereas intra-chain entanglement dominated in the latter. The molecular entanglements were accordingly supposed govern the scenario to of thermorheological complexity. Local heterogeneity was observed to exist in the melt-state blends by insitu dielectric relaxation spectroscopy (DRS); its molecular origin was depicted mainly due to the presence of interphase in the melt manifesting in the distinct Maxwell-Wagner-Sillars (MWS) relaxation. Further, the interphase in the melt was demonstrated to be evolved from the crystalamorphous interphase in the solid crystalline blends and the corresponding molecular dynamics were evaluated by the electric modulus formalism. The relaxation dynamics in the interphase were found to be confined by the PMMA segments and vary as a function of composition: they were completely absent in PMMA-rich blends, but prominent in blends with intermediate compositions and reduced in PVDF-rich blends. This clearly indicates that interphase associated local heterogeneity in the melt also contribute to the overall dynamic heterogeneity. In addition, the glass transition temperature for blends appeared to satisfactorily follow the "self-concentration" model, suggesting the distinct distinct relaxation dynamics in and therefore dynamic components of dynamic heterogeneity. Lastly, the effect heterogeneity on the dynamic mechanical properties was further assessed. Zhang Н., Lamnawar K., Maazouz A., J. Rheol., 2016; Lu B., Lamnawar K., Maazouz A., Soft Matter, 2016.

S10-788

Führer Roman, Läuger Jörg , Arnold Gunther

Humidity Controlled Rheology for the Study of Polymers

n this work combined rheological techniques with novel parameters were investigated. One of these additional parameters for rheological measurements is humidity control. Rheology combined with temperature and humidity control



is a powerful tool to characterize polymers. The influence of relative humidity on mechanical properties of films was investigated using the humidity option of a CTD (convection temperature device). Humidity step tests and humidity ramp tests at constant temperature as well as temperature scans at constant relative humidity were performed to study the influence of temperature and humidity independently. This feature can be extremely useful when measuring poly condensation products such as polyamides that can be influenced from relative humidity on the modulus value and the glass transition temperature due to moisture absorption. Furthermore adhesive sealant formulations especially in regard to curing and hardening behavior were investigated with a new measuring geometry. This Plate Partitioned Ring geometry shows the advantage of a higher surface to volume ratio in comparison to the plate-plate geometry. Because of this and the low sample volume, the entire sample will be much more affected by the ambient humidity conditions. In addition to chemical composition, ambient conditions are key influencers on the curing and hardening behavior of sealants and adhesives. While the influence of temperature on the rheological behavior of adhesives has been extensively investigated, the impact of relative humidity on the mechanical properties of such materials is of increasing interest recently. It could be shown that the water uptake of polymers caused by humid ambient air has major impact its thermo-mechanical and rheological properties. The complex shear modulus of polyamide strongly decreases over time, when the humidity of the surrounding air is increased. Furthermore the glass transition temperature also strongly depends on the humidity of the measuring environment. The rheological behavior and curing rate of adhesives is also strongly affected by relative humidity. It could be shown that the crossover of G' and G'' of silicone based adhesives decrease with increasing relative humidity. Hence, the impact of the ambient humidity as well as the temperature on the determined rheological parameters can be used to characterize the curing process of resins and mechanical properties of solid polymers at various ambient conditions. Keywords: Humidity, Rheology, DMTA.



Poster

S10-17

Stanciu Ioana Stanciu Ioana

Rheological Behavior Modelling for the Copolymer Hydrogenated Poly (isoprene-costyrene) Solutions

Viscosity is the most important physical feature of the lubricants for it varies with the temperature and the shear rate and determines their performance. Multi-grade oils contain organic polymer additives to improve the viscosity index. The organic polymers are base oil soluble, have molar mass from 104 to 106 g/mol and are able to reduce the dynamic viscosity's dependence on the temperature. The viscosity index additives are those polymers whose chains may be blocked by twisting them either in between or with the oil's, which alters the speed, the geometry and the molecular movement of the both components and varies along with the temperature. The chains get blocked by twisting and therefore cannot move easily at high temperature as compared to no twisting and thus we have a loss in viscosity. In this paper I undertook to determine the rheological characteristics of the copolymer hydrogenated poly (isoprene-co-styrene) solutions. I have studied the 3, 6, 10, and 12% concentrated solutions for a temperature interval from 40°C and 90°C in 10 degree steps, and for the shear rate from 3 to 1312 s-1 in the second domain. The measurements were performed using a Haake VT 550 rotational rheometer with a HV1 sensor. The rheology of the solutions has been impacted by the shear rate, the temperature and the concentration of the copolymer hydrogenated poly (isoprene-costyrene). I have found two models that successfully describe the rheological behaviour of the solutions compared to other models that do not consider the copolymer's concentration.

S10-354

ranjbar behnaz, Ghiassinejad Sina, Nazockdast Hossein

The aim of the present work was to study the effect of nanoparticle flexibility onincreasing the storage modulus after cessation of shear flow field. For thispurpose polyethylene oxide (PEO) was utilized as a matrix and multi-walledcarbon nanotube (MWCNT) and cloisite 30B were used as the nanoparticles thesamples above percolation threshold different were pre-sheared at shearrates/times. Then the shear was stopped and the re-structuring was monitoredas a function of rest time. In order to better understanding of structural recovery process, the structure parameter evolution was calculated as afunction of time. The first time derivative of structure parameter showed thatdisorientation process for MWCNT containing nanocomposite samples weredone within two steps, where the first step was carried out faster. While, for the cloisite 30B containing nanocomposite samples, the structural recovery wascarried out in one step. We proposed a physical model for these processes and finally we related the change in the rate of in MWCNT recovery containingnanocomposite samples to the two governing mechanisms for structurerecovery and nanoparticle disorientation.

S10-372

Dranebois Clemence Noemie Elvire, Smith Dawn Alison, de Silva Karnika, Taylor Mark

Using Torque Rheology to Characterise Cure of Bio-based Powder Coatings

Powder coatings have the great advantage to emit fewer volatile organic compounds (VOC) when compared to traditional solvent-based paints. To reinforce the ecological interest of this technology, recent research efforts have developed polyester resins from renewable resources. However, these novel bio-based resins tend to be more expensive than their petrochemical counterparts. So as to reduce the formulation cost, a lignocellulosic waste product was chosen to replace traditional mineral fillers in a polyester/hydroxyalkyl amide (HAA)



bio-based formulation. For typical thermoset powder coatings, differential scanning calorimetry (DSC) is used for the characterization of cure. However, for polyester/HAA, detection of the enthalpy of reaction using DSC is difficult, therefore another technique is needed to determine the progress of reaction. The present work describes a method using torque rheology to follow the curing behaviour of powder coatings. The thermo-reactivity and the viscosity of the bio-based powder coatings containing renewable and low cost filler are discussed in relation to the quantity of filler in the formulations.

S10-411

Wu Chang-Mou, Lai Wen-You, Cheong Sh-Shen , Chang Teng-Hsiang

Rheological Behaviors of Graphene/Nylon 6 Composites

In this study, effects of graphene content on the rheological behavior and viscous activation energy of graphene/nylon 6 composites were investigated. Twin-screw extruder was used to produce 10wt% graphene/nylon 6 master batch. The banbury mixer was used for dilution process to provide another 3wt% and 5wt%. Differential scanning calorimetry (DSC) and Polar light microscopy (PLM) were used to study the crystalline morphology, graphene dispersion and thermal properties. The rheological properties and viscous activation energy of graphene/nylon 6 composites were studied by rheometer under different temperatures and shear rates. The DSC and PLM results showed that 5°C melting temperature increased by adding graphene and good dispersion of graphene in the nylon 6 matrix. The viscosities of graphene/nylon 6 composites increased with increasing graphene concentration. The interaction between nylon and graphene which results in a strong restriction of movement in nylon 6 molecule was revealed. As the concentration of graphene increased, the flow behavior index (n) decreased from 0.99 to 0.51, indicated the flow behavior changed from newtonian to pusedoplastic flow. The viscosities of graphene/nylon 6 composites were sensitive to temperature. The viscous activation energy of

composites decreases as the concentration of graphene increases.

S10-436

Ratel Olivier, Srour Hassan, Majesté Jean-Charles, Monnereau Cyrille, Carrot Christian

Rheological Investigation of the sol-gel transition of PIL's hydrogels

In the last decade, Lithium ion based batteries have emerged as interesting candidates as high-density energy storage devices. The synthesis of polymer electrolytes and the study of their electrochemical properties is currently a very active topic. Poly(ionic liquids) (PILs), in particular, constitute an increasingly sought-after category of materials, as they are expected to replace flammable, leakageprone organic solvent electrolytes in future energy storage devices. In this work, we have developed (PIL's) ATRP two new polymers from polymerization for energy storage application with two kinds of end groups: phosphonic (PO3H) or ethyl. An imidazolium group is present on each unit of the polymer backbone with a bromide counter ion to allow supramolecular interactions. Moreover, for few formulations, partial crosslinking of the PIL's has been tested in order to investigate its impact on the gelification process. With addition of water, PIL's form hydrogels which present usual yield stress fluid properties and a socalled sol-gel transition. The study shows that galation mechanism is controlled by three main parameters: polymer concentration, cross-linking amount and the nature of the end group. Using rheological measurements, a phase diagram with two main domains (gel like and viscous liquid behavior) has been obtained. From this diagram, we are able to quantify the contribution of each parameter to the gel formation. Moreover, an interesting transition inside the gel domain with respect to the polymer concentration has been observed and can be attributed to different relaxation mechanisms (from friction to elastic interactions of swollen soft particles) in the gel phase. To summarize, it appears clearly that the nature of end groups is a key to control the hydrogel properties and gel formation.



Furthermore, whatever the amount of crosslinking, phosphonic (PO3H) end group enables the formation of a supramolecular network and large variety of hydrogels properties

S10-480

Räntzsch Volker, Özen Mürüvvet Begüm, Ratzsch Karl-Friedrich, Guthausen Gisela, Wilhelm Manfred

Crystallization of Polypropylene Materials Studied by Low-Field RheoNMR

Materials based on semi-crystalline polymers are ubiquitous in today's material science due to their mechanical properties, low densities and affordable prices. A thorough understanding of the influence of temperature, flow and additives on the molecular dynamics of polymer chains with implication on processes such as polymer crystallization is necessary for the determination of structure-property relationships the and development of theories for the prediction of material properties. In order to clarify these relations, model systems based on different isotactic polypropylenes were prepared and characterized using a new low-field RheoNMR technique [1-3] which relies on the implementation of a portable low-field 30 MHz TD-NMR unit in a commercial rheometer. By studying the isothermal crystallization simultaneously with TD-NMR and rheometry, a correlation of microscopic molecular dynamics and the macroscopic mechanical response during polymer crystallization under various conditions was achieved. The systematic investigation of different temperatures, flow profiles and fillers and a comparison with other methods such as benchtop low-field NMR, differential scanning calorimetry (DSC) and microscopy led to new insights in the role of gelation-like solidification processes during the crystallization of polymers. [1] S. Kahle, W. Nussbaum, M. Hehn, H. P. Raich, M. Wilhelm, and P. Blümler, Kaut. Gummi Kunstst. (2008), 61, 92-94. [2] V. Räntzsch, K.-F. Ratzsch, G. Guthausen, S. Schlabach, and M. Wilhelm, Soft Mater. (2014), 12, S4–S13. [3] V. Räntzsch, M. Wilhelm, and G. Guthausen, Magn. Reson. Chem. (2015), in print. doi:10.1002/mrc.4219

S10-561

Zaeferani Erfan, Goharpey Fatemeh

Survey of the Effect of Graphene Nano-sheets on Morphology, Rheology and Electrical Conductivity in PS/PMMA Blend

Polystyrene (PS) and poly(methyl methacrylate) (PMMA) blends filled with surface treated graphene have been fabricated to obtain conductive composites with a lower electrical percolation threshold according to the concept of double percolation. Obviously optimum morphology for this blend is co-continuous that represent the lowest percolation-threshold in compare with other morphologies. In this study co-continuity window of the mentioned blend has calculated theoretically by use of rheological models and then verified with experimental results comprise of microscopic pictures and RMS curves. In addition to determining co-continuity window of this blend, effect of adding surface treated graphene to it is studied and the relation between grephene content and shift in co-continuity window is achieved. Rheological and electrical properties of the blend investigated and electrical percolationwas threshold of it at the top boundary of co-continuity window of immiscible blend is calculated (0.3 wt %) and compared with result of other researchers who disregard the volume fraction of immiscible blend with co-continuous morphology (Mao et al.). Electromagnetic interference shielding effectiveness (EMI-SE) of the blend is also studied and results shows a significant growth in EMI-SE of the blend in compare with similar blends having same electrical conductive filler content. This study represents that change in volume fraction of immiscible constituents of the blend in cocontinuity confine has significant effect on electrical conductive network of particles and percolationthreshold of it. Change in this confinement due to adding surface treated nano-particles is also represented.

S10-570

Özen Mürüvvet Begüm, Ratzsch Karl-Friedrich, Räntzsch Volker, Vittorias Iakovos, Wilhelm Manfred



Correlating Crystallization Kinetics and Rheological Properties of Polyethylene Using a Newly Developed Low-Field Rheo-NMR Combination

During thermoplastic processing, orientation of under polyethylene chains due to flow supercooling causes shear-induced crystallization and affects the final crystallinity of the product, with a strong impact on the mechanical properties of the product. Processing controlling parameters (e.g cooling and deformation rate) and the topology of polymers play an important role in crystallization kinetics. Low-field (time domain) NMR is a useful tool to quantitatively investigate and monitor the molecular dynamics in the phases of a crystallizing polymer [1]. Rheology provides access to the macroscopic mechanical properties of polymer melts [2], making it at promising idea to integrate the NMR measurement into it. Our homebuilt unique low-field Rheo-NMR setup as a combination of a permanent magnet with 0.7 T (30 MHz proton resonance) in a commercial high-end rheometer strain-controlled (Rheometrics/TA ARES) can measure a full rheological shear characterization (G', G'', LAOS, I3/1, FT-Rheology [3]) and the development of crystallinity at once [4]. Additionally, this technique allows for a direct correlation between the changes in the modulus as a function of the degree of crystallinity. Thus, it is possible to evaluate the effect of higher strain amplitudes on the gelation as a function of the crystallinity. The aim of this work is to investigate for the first time the crystallization of polyethylene variating molecular weight, additives and applied shear via low-field Rheo-NMR method. Key words: Rheo-NMR, Crystallization, Polyethylene References: [1] A. Maus, C. Hertlein, K. Saalwächter, Macromol. Chem. Phys. 2006, 207, 1150-1158. [2] T. Dötsch, M. Pollard, M. Wilhelm, J. Phys.: Condens. Matter 2003, 15, 923-931. [3] K. Hyun, C. O. Klein, M. Wilhelm, K. S. Cho, J.G. Nam, K. H. Ahn, J. S. Lee, R. H. Ewoldt, G. H. McKinley, Prog. Polym. Sci. 2011, 36, 1697. [4] V. Räntzsch, M. Wilhelm, G. Guthausen, Magn. Reson. Chem. 2015, DOI 10.1002/mrc.4219.

S10-703

Pircheraghi Gholamreza, Sarafpoor Amirhossein, Hafezi Mohammad Javad, Rashedi Reza, Afzali Seyed Kamal, Sepahi Abdul Hanan

Rheological properties of blacked PE-100 compounds prepared using different carbon black masterbatches

In this work, we have prepared blacked PE-100 compounds containing 2.5 wt. % of carbon black (CB), originated from different commercially available CB masterbatches, using a laboratory corotating twin screw extruder. A control sample with the same CB content was produced using a ptype CB powder in the same condition. Rheological properties of the samples were measured at melt state, 200 °C, and different flow fields including oscillatory shear, rotational shear and capillary shear modes. It was found that, capillary shear flow measurements are not sensitive enough to different microstructures of samples due to observing almost the same flow curve for different blacked samples. This behavior can be explained by the large deformation and hence sever structural changes and orientation encountered during capillary shear flow. On the other hand, distinctive differences between storage modulus, complex viscosity and rotational shear viscosity of blacked samples were observed, helping us to rank different CB masterbatches by comparison of their rheological properties with the control sample, in line with dispersion test results. In other words, oscillatory and rotational shear measurements are clearly sensitive to the microstructure and rheological behavior of blacked samples containing low amount of CB filler, and these rheological measurements can be successfully used to select the proper CB Masterbatch for production of blacked PE-100 compounds.

S10-78

Herrera Valencia Edtson Emilio, Calderas Garcia Fausto, Sanchez Villavicencio Mayra Luz, Perez Camacho Mariano, Medina Torres Luis

Combined Pulsating And Oscillating Flow Of A Non-Newtonian Biological Liquid



Abstract In this work, analytical predictions of the rectilinear flow of a non-Newtonian liquid under a combined pulsating, time-dependent pressure gradient and a random longitudinal vibration flow is analyzed. The fluctuating component of the combined pressure gradient and oscillating flow is assumed to be of small amplitude and can be adequately represented by a weakly stochastic process, for which a quasi-static perturbation solution scheme is suggested, in terms of a small parameter. This flow is analyzed with the Tanner constitutive equation model with the viscosity function represented by the Ellis model. According to the coupled Tanner-Ellis model, the flow enhancement can be separated in two contributions (pulsatile and oscillating mechanisms) and the power requirement is always positive and can be interpreted as the sum of a pulsatile, oscillating and the coupled systems respectively. Both expressions depend on the amplitude of the oscillations, the perturbation parameter, the Reynolds, Deborah and Weissenberg numbers and the exponent of the Ellis model associated to the shear thinning or thickening mechanisms respectively. At small wall stress values, the flow enhancement is dominated by the axial wall oscillations whereas at high wall stress values, the system is governed by the pulsating noise perturbation. The flow transition is obtained for a critical shear stress which is a function of the Reynolds number, dimensionless frequency and the ratio of the two amplitudes associated with the pulsating and oscillating perturbations respectively. Under some considerations, the total flow enhancement due to the coupling flows can be considered as the sum of the pulsating and oscillating flow effects. In addition, the flow enhancement is compared with analytical and numerical predictions of the Reiner-Phillipoff and Carreau models respectively. Finally, flow enhancement and power requirement are predicted using biological rheometric data of blood.

S10-79

Herrera Valencia Edtson Emilio, Calderas Garcia Fausto, Sanchez-Villavicencio Mayra Luz, Perez Camacho Mariano, Medina-Torres Luis

Generalized Darcy Equation of a Complex Fluid Using a Bautista-Manero-Puig Constitutive Equation

ABSTRACT In this work, the case of a worm-like micellar solution of cetyltrimethyl ammonium tosilate (CTAT) at various concentrations flowing through a porous media is analyzed by using a generalized Darcy-Like Equation. The surface velocity is related to the intrinsic permeability, to the apparent viscosity and to the pressure gradient. In order to characterize the complex fluid, the modified Bautista-Manero-Puig constitutive equation (MBMP) has been used. This rheological model couples the Codeformational Maxwell Equation with a kinetic equation that takes into account the structure modification mechanisms induced by flow. According to the BMP model, the apparent viscosity reflects the thixotropy, shearshear thickening and yield stress thinning, mechanisms in the system. The surface velocity is a function of the dimensionless numbers representing the viscoelastic, kinetic and structural mechanisms. Finally, closed expressions are developed to relate the surface flow velocity with the pressure gradient and the macroscopic properties associated to the dimensionless number. The surface velocity and the apparent viscosity are predicted. The system is a model approximation of the complex phenomena that occurs in oil extraction in exhausted wells. Keywords: Bautista-Manero-Puig Equation, Porous Media, Generalized Darcy Equation, Analytical solutions.

S10-793

Fraïsse Frédéric, Rohn Chuck

Using rheology to understand the structureprocessing-property relationships of thermoplastic melts and composites

Measuring and applying rheological material functions which are relevant to polymer fabrication and processing is something everyone should have in mind. We will address the four general categories of requirements for manufacturing the thousands of products produced from plastics. These are Profits. Appearance, Dimensional



Stability and Properties. Two thermoplastic melts will be presented, LDPE and LLDPE. For the composites we will present the rheology of heterogeneous polymer melts, namely ABS and fiber reinforced ABS. Here we will show how data from a stress controlled rheometer and a capillary rheometer increase our understanding of the structure-processing-property relationships of these widely used plastics.



S11- Elastomers and Thermoplastic Elastomers

Keynotes

S11-4

Chatterjee Tuhin, Wiessner Sven, Heinrich Gert, Naskar Kinsuk

Novel Super TPV Based on XNBR Rubber and Polyamide 12

Thermoplastic vulcanisates (TPVs) are a special class of thermoplastic elastomers, produced by simultaneously mixing and cross-linking a rubber with a thermoplastic at elevated temperature. As a result a typical morphology is formed, where the cross-linked rubber particles are generally finely dispersed in a continuous matrix of thermoplastic. High performance TPVs or super TPVs are a new class of TPVs which exhibit high heat resistance as well as excellent oil resistance properties suitable for automotive under-the-hood applications. In the present work, a new super TPV based on carboxylated acrylonitrile butadiene rubber (XNBR) and polyamide (PA12) has been developed. TPVs of three different blend ratios (50:50, 60:40, 70:30) of (XNBR:PA12) have been prepared at an elevated temperature in an internal mixer by using a fixed concentration of Trigonox 311, which is a novel cyclic mono-functional cross-linking peroxide. The final morphology of the TPVs varies from a cocontinuous to a dispersed one depending on the blend ratio. TPV of 50:50 XNBR-PA12 shows the best mechanical properties and the superior thermal stability amongst all TPVs. Detailed thermal characterisation through DSC and DMA rheological characterisation have and been performed. The lowest tand of the TPV with a 50:50 blend ratio of XNBR-PA12 indicates the highest degree of crosslinking and this is also well supported by the overall crosslink density value of that TPV. Heat ageing and oil resistance studies have also been carried out to demonstrate the

performance of these TPVs. Keywords: TPV, XNBR rubber, Polyamide 12, dynamic cross-linking, peroxide, morphology

S11-520

Jana Sadhan C., Raut Prasad, Swanson Nicole, Pugh Coleen

Improved dispersion of carbon black in rubber compounds for manufacturing low rolling resistance tires

The high rolling resistance of tires is blamed among other things on networking of carbon black (CB) particles, although tire tread compounds must contain CB particles for higher toughness and for dissipation of static electricity. In this context, we hypothesize that a reduction of the networking of CB particles via improved dispersion can also reduce the rolling resistance of the tread compounds. In this research, poly(butadiene-graftpentafluorostyrene) (PB-g-PPFS) is used as a coupling agent to promote dispersion of CB particles in styrene-butadiene rubber (SBR) and to subdue the networking. The electron-rich graphitic content of carbon black and electron-deficient π system of the pentafluorostyrene in PB-g-PPFS molecules interact via arene-perfluoroarene interactions to promote dispersion of CB particles. The interactions are analyzed using zeta potential and BET surface area measurements, transmission electron microscopy (TEM), and scanning electron (SEM). The resultant rubber microscopy compounds show 10-20% reduction in loss tangent values measured at 60 °C, an indicator of rolling resistance, while the wet track resistance indicator shows negligible change.



Oral

S11-104

R Padmanabhan, Naskar Kinsuk, Nando Golok

Structure- Property Relationship in Ethylene Octene Copolymer (EOC) - Polydimethyl Siloxane (PDMS) based TPEs for cable insulation applications

The present study focuses on thermoplastic elastomers based on ethylene octene copolymer (EOC) and poly dimethyl siloxane (PDMS) rubber prepared by melt mixing technique nd crosslinked using dicumyl peroxide (DCP). It is found that the addition of peroxide causes crosslinking in both the phases. However, crosslinking without affecting the crystallinity of the EOC polymer leads to tremendous improvement in the mechanical properties including the tensile strength which has improved nearly by 60 % for the 70:30 EOC: PDMS blends. For better understanding about the crosslinking characteristics of thermoplastic vulcanizates (TPVs), significant correlation has been made between the vulcanized network and the physico-mechanical properties. Further, the dynamic mechanical properties and creep behavior of these thermoplastic elastomers (TPEs) and TPVs have also been studied. It is inferred that the TPVs shows a 19 % decrease in the creep compliance, i.e. higher creep resistance compared to uncrosslinked blends. Subsequently, the morphology study of the blends by Atomic force microscopy (AFM) shows that, there is a decrease in the PDMS rubber domains from 0.8 µm to about 0.4 µm after vulcanization. From the thermal studies it was found that, through blending and subsequent crosslinking, the maximum degradation temperature of the EOC was increased from 492.1 °C to 514.8 °C. Ageing and reprocessing studies of the prepared TPVs also show better physicomechanical properties even after reprocessing twice. All the radiation crosslinked blends exhibit lower dielectric constant, lower dielectric loss and higher electrical resistivity as compared to the

virgin blends, which makes them an excellent material for high voltage cable insulating applications.

S11-159

Ebrahimi ali, Katbab Ali Asghar, nazokdast hossein, katbab puya

Fatigue Behavior of Natural Rubber/ OrganoclayNanocompositesunderUniaxialCyclicDeformation:RoleofInterfacialCompatibilization and Strain Amplitude

Fatigue is a typical service failure mode when elastomers are subjected to cyclic loads over a period of time. Deformation gradient plays crucial role in fatigue behavior as elastomers exhibit nonlinear and linear characteristic under large and small deformations respectively. Also, in filled elastomers Mullins effect and hysteresis are another challenges. Natural Rubber (NR)/ Organoclay nanocomposites exhibit enhanced mechanical properties. However, degree of improvement is governed by the state of silicate layers dispersion and their extent of interactions with rubber segments. In the present work, attempts have been made to prepare NR/ Organoclay nanocomposites with intercalated/ and exfoliated nanostructure via melt mixing process. EpoxidizedNR (ENR) was employed as interfacial compatibilizer to modify the interface between NR segments and clay nanolayers. Strain controlled cyclic fatigue test was performed on both interfaciallycompatibilized and uncompatibilizednanocomposites. The alteration of microstructure during cyclic deformation was followed by XRD and hysteresis measurements. Reduced fatigue life was observed for both compatibilizedand uncompatibilized nanocomposites compared with unfilled NR at low strain amplitudes. Whereas, at high strain amplitudes enhanced fatigue resistance was exhibited byboth classes of nanocomposites which was consistent with higher hysteresis and delamination of silicate layers during periodic loading. However, uncompatibilized nanocomposites presented significant enhanced fatigue life compared to the compatibilized samples. Finally results have been modeled using



fatigue crack nucleation model. Keywords: Fatigue behavior, Hysteresis, Microstructure, Compatibilization, Natural rubber, Organoclay, Nanocomposite,

S11-193

Kerschbaumer Roman Christopher, Lechner Bernhard, Friesenbichler Walter

Characterization of the Temperature Profile during Dosing of Different Rubber Compounds under Steady State Conditions by Means of a Specially Designed Screw Test Stand

The distribution of the relative curing degree is one of the dominating structural characteristics in injection molded rubber parts. It influences almost all part properties including tensile strength, hardness, compression set and dynamic properties. In addition, the material temperature distribution significantly influences (1) the reduction of the incubation time during processing and (2) the curing degree homogeneity of the produced part. Thus, it is substantial to know the temperature distribution of the dosed rubber compound prior to injection to be able to ensure the processability of the used material. The apparatus used in this work is a specially designed screw test stand consisting of a plasticizing cylinder and a downstream throttle valve. The design of the plasticizing cylinder and the temperature control is identical in comparison to a vertical Maplan rubber injection-molding machine. In addition, it is equipped with pressure and temperature sensors. Furthermore, the throttle valve offers the ability to measure the temperature distribution of the dosed material as well as to adjust the back pressure. To determine the temperature distribution of the dosed material it is necessary to (1) heat up the plasticizing cylinder to the testing temperature (e.g. T=80°C), adjust (2) the back pressure (e.g. p=50 bar) and (3) screw rotational speed (e.g. n=80 min-1) and (4) perform the measurement under steady state conditions. Therefore, a defined injection cycle with a dosing volume of 150 cm3 was repeated five times to check the steady state conditions prior to the temperature

measurement. Firstly, it could be shown that steady state conditions could be reached after three injection cycles due to a very effective temperature control of the plasticizing cylinder. Secondly, a temperature rise could be observed during dosing.

S11-31

Grady Brian

Secondary Crystallization and Aging in Ethylene-Based Carboxylic Acid Ionomers

Four years ago, this author presented a paper at this same meeting (held in Thailand) that found that for zinc-neutralized ethylene carboxylic acid ionomers, a classic relationship of Flory did not hold true, namely that the fractional crystallinity of a random copolymer depended on the identity of the comonomer. This result did not invalidate the theory, rather Flory did not consider the case of a second phase, namely the ionic aggregate phase, which did not disappear upon melting. Further, the rates of formation of secondary crystals relative to the crystallization amount at infinite time was independent of neutralization level for the phaseseparated ionomers; in other words the Avrami constants n and K were independent of neutralization level for the secondary crystals. Very careful absolute heat capacity measurements were also used to examine the existence of immobilized amorphous phases and it was shown calorimetrically that an immobilized amorphous phase exists above the melting point of the polyethylene segments in the neutralized materials and that the amount of this phase increases with increasing neutralization level. In this presentation, results from other neutralizing cations will be shown and compared to the results of the zincneutralized materials.

S11-310

Damley-Strnad Alexandra, Fittipaldi Mauro, Morales Brigitte, Grace Landon

Control of the surface wrinkling structure on the surface of Polydimethylsiloxane microspheres via a simple low-cost and environmentally friendly route
Mechanical instabilities in soft materials, specifically wrinkling, have led to the formation of unique surface patterns for a wide range of applications that are related to surface topography and its dynamic tuning. However, a continuous, scalable and controllable approach for constructing the wrinkled-structure is scientifically crucial and challenging. Here we introduce a simple low-cost and environmentally friendly route to realize spontaneously wrinkled morphologies on Polydimethylsiloxane (PDMS) spherical surfaces, which have great potentials for the construction of high-performance functional materials. First, the solution of mixed base monomers and the curing agent is mixed with deionized (DI) water with different composition and yielding a uniformlymixed PDMS/DI water suspension, then slowly evaporating water very at room temperature. This slow drying process is very important so that the curvature wrinkles including dimples and labyrinth patterns are successfully induced on the surface of PDMS microspheres. The effects of the experimental parameters, including the stirring speed, evaporation rate, temperature and composition, on these tunable spherical wrinkles have been systematically studied. The control of the amplitude and wavelength of wrinkle structures and the size of PDMS microspheres could be realized by the simply regulation of the composition and string speed. Keywords: Wrinkling; Microsphere; Polydimethylsiloxane Acknowledgments This research was supported by the National Natural Science Foundation of China (Grant No. 51103087, 51421061). College of Polymer Science Engineering, Sichuan University, Chengdu, and 610065, People's Republic of China. Address: Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu, China, 610065. E-mail: xiebangh@tom.com

S11-420

Rüppel Annette, Hartung Michael, Giesen Ralf-Urs, Heim Hans-Peter

The Adhesion of LSR Polycarbonate Composites after Various Secondary Treatment Processes

Owing to their beneficial properties, such as their cold flexibility and temperature resistance, silicones

are applied in many areas today. This material group is used the most in medical technology, because it possesses an excellent mechanical property profile while being a physiologically safe option. Hard-soft composites, which are а subgroup of multi-component elements, are of great interest. They offer the possibility to include various properties into one synergetic component. The adhesion properties of liquid silicone rubber (LSR) and polycarbonate (PC) were examined in this research proposal. In order to guarantee the adhesion of both components, an activation of the surface is usually carried out. The resulting adhesion is dependent on the secondary treatment processes that are common in medical technology. They include tempering, sterilization, and storage. The following secondary treatments were carried out, and the reciprocal effect with the surface activation was subsequently validated using a peeling resistance method modelled after that of VDI 2019. Tempering: Significant differences were not identified for freshly injected, non-tempered, and tempered composites in regards to their exposure times. Sterilization: Sterilization resulted in an increase in the degree of adhesion. Storage / Aging: Artificial aging led to an increase in the degree of adhesion when the dispersion was extensive, but declined again as the exposure time extended. Storage experiments revealed that the exposure time only influenced the adhesion significantly if the samples were stored at higher storage temperatures. Additional results will be introduced in detail.

S11-437

Yrieix Marie, Majesté Jean-Charles, Doméjean Hugo, Valtier Michel

Impact Of Fillers/Matrix Coupling On Rheological Behavior Of Silica/Rubber Nanocomposites

Significant volume defects are observed on rubber/silica nano-filler composites under large deformations such as during extrusion process. To understand the causes of the instabilities, structure and rheological properties of these nanocomposites have been studied especially by NMR spectroscopy

and by relaxation and elongation measurements. The effect of blend composition and mixing conditions on the structure and rheological properties of the rubber/silica composites was investigated. Blends with and without agents such as a polysulfide silane (TESPT) or Octeo were prepared in internal mixer under different experimental conditions (variation of dump temperature or rotation speed). In presence of silane, silica aggregates can be grafted to rubber chains whereas Octeo only react with silica. The grafting of these agents on silica surface induces the improvement of the silica aggregates dispersion thanks to the reduction of filler-filler interactions. In silane blends, NMR spectroscopy allowed the quantification of the silane/rubber grafting and highlighted the presence of unwelcome precrosslinking reactions between rubber chains at high mixing temperature. Therefore different kinds of filler/rubber networks can be noted according to the nature of the agent (silane or Octeo) and to the mixing parameters. Then rheological properties of blends can be linked to the nature of their filler/rubber network. Thereby, elongation measurements and relaxation times showed a strong impact of these networks on the viscoelastic behavior over the whole range of time. Finally, a correlation can be highlighted between the blend structure, its rheology and the emergence of volume defects during extrusion.

S11-447

Mujtaba Anas, Nagaraja Sriharish Malebennur, Beiner Mario

Comparison of filler network related reinforcement contributions in different rubber composites for tire treads

Mechanical properties of different rubber composites like (i) styrene butadiene rubber (SBR) filled with silica nanoparticles and (ii) natural rubber (NR) filled with carbon black (CB) or carbon nanotubes (CNT) are studied. Of special interest are contributions to reinforcement caused by the "filler network" in composites with higher filler contents. Central aim of this work is to quantify and to understand the factors influencing overall

reinforcement and to compare the filler network contributions depending on temperature and frequency in CB and CNT filled NR with those obtained for SBR containing silica. Temperaturedependent shear measurements show that the storage modulus G' in the plateau range decreases significantly with increasing temperature for all composites that contain large filler fractions above the percolation threshold. This decrease of G' is interpreted as a first indication for the existence of a glassy rubber layers located on filler surfaces which soften gradually at higher temperatures than corresponding bulk rubber. Consistent with this observation, low-field NMR studies on SBR composites confirm the existence of a small fraction (a few percent) of immobilized rubber which becomes smaller with increasing temperature. The filler network strength is quantified based on dynamic strain sweeps performed at different temperatures and frequencies which are analyzed using the Kraus model. The results show that the load carrying capacity of the filler network, defined by the difference of the storage moduli obtained at small to large deformations, depends systematically on temperature and frequency. This shows that visco-elastic elements exist in all filler networks significant under investigation despite of differences regarding the filler network topology. A detailed comparison made in this study contributes to a better understanding of the reinforcement mechanisms in composites which is prerequisite for their efficient optimization for tire treads.

S11-469

Riess Gisbert, Berger Katrin, Kern Wolfgang

Novel Silicone Thermoplastic Elastomers With Tailored Permeation Properties

Polysiloxanes such as polydimethylsiloxane (PDMS) combine several unique properties. They exhibit a low glass transition temperature, high thermal and oxidative stability, high UV-resistance, low surface energy and strong hydrophobicity as well as high permeability to many gases. These characteristics are independent over a wide temperature range. Our research deals with the synthesis and properties of thermoplastic silicone

elastomers containing soft segments of dimethylsiloxane and hard urea segments. In order determine structure-property relations, to regarding to permeation properties, the chemical structure was varied. In this study thermoplastic silicone elastomers, based on polydimethylsiloxane oligomers with amino groups and different diisocyanates, were synthesized. The polymers were characterized by nuclear magnetic resonance (NMR) and infrared (FTIR) spectroscopy. The formation of hydrogen bonding of the hard segments was investigated by temperature dependent FTIR-spectroscopy, which demonstrated the thermal stability of the elastomer and defined the processing conditions of such polymers. Thin membranes of thermoplastic main-chain ureasiloxane copolymer were prepared and investigated with respect to the permeation properties of organic solvents. Vials were filled with a mixture of an aromatic (toluene) and an aliphatic hydrocarbon (iso-octane) and were sealed with the polymer films. The concentration of residual solvent mixture was measured by the relation of the peak area of the two solvents. This was investigated by the GC-MS-technique. A separation of the solvent mixture occurred. In conclusion, novel main-chain ureasiloxane thermoplastic elastomers were successfully synthesized with selective barrier properties. These polymers are highly permeable for organic solvents depending on the chemical structure. These siloxane polymers can be used as semipermeable membranes for separation of solvent mixtures in oil field applications.

S11-498

Baumgart Christin, Marl Svenja, Altstädt Volker

Influence of Environmental Conditions on Adhesion of Thermoplastic - Liquid Silicone Rubber – Combinations

Two component parts consisting of soft liquid silicone rubber (LSR) and thermoplastics are predominantly produced via two component injection molding, whereby the hard carrier material (mostly PA or PBT based engineering plastics) is injected first and subsequently, overmolded with the LSR. The adhesion mechanism between the LSR, which contains an adhesion promotor, and the engineering thermoplastics is based on covalent bindings. The durability of the adhesion is not only influenced by the applied polymers and the process parameters, but also by the environmental conditions. Currently there is no report in literature about the influence of temperature on adhesion between engineering plastics and LSR. The adhesion and of course the retention of a minimum level of adhesion has to be guaranteed. Therefore, this study focuses on investigating the stability of thermoplastic-LSRcombinations and also, on examining the adhesion quality including the fracture pattern at different temperatures over a period of one to four month, among them room temperature and 60 °C. For the understanding of the influence of different environmental conditions on the adhesion development the behavior of the single materials has to be evaluated. Thereby the LSR reveals a post cross-linking during the different environmental conditions, which is indicated by an increase of the tear strength (tensile tests) and rise of degree of cross-linking (dynamic mechanical analysis). Besides that, volatile components, e.g. siloxanes or silanes, are diffused during storage. The semicrystalline material (PBT) shows relaxations during storage. These results affect the adhesion between thermoplastic and LSR negative. The peel resistance is reduced at room temperature over four month around 81 % and at higher temperatures over one month around 73 %.

S11-578

BOITEUX Gisele, Salaeh Subhan Salaeh, Nakason Chaeron, Gain Olivier, Cassagnau Philippe

Relationship between Morphology, Mechanical and Electrical Properties in Structured Elastomers

Thermoplastic elastomers (TPEs) (TPO and TPV) based poly(vinylidene fluoride) and epoxidized natural rubber having epoxide group 50 mol% [called ENR-50] blends have been prepared by melt mixing process at different blend ratio. The incorporation of barium titanate (BaTiO3) or BT particles into polymer are widely studied to enhance, in particular, permittivity of materials due

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to their high permittivity and low dielectric loss factor. The dynamic mechanical properties, dielectric analysis and morphological properties of TPEs were investigated. From temperature dependence, the both TPO and TPV showed two relaxations : αa and α relaxations of PVDF and ENR-50, related to segmental motion in amorphous phase of PVDF and ENR-50, respectively. Their evolutions will be studied as function of the composition and morphology of the different materials. In the case of TPO, the phase structure of 80/20 PVDF/ENR-50 exhibited dispersed phase of ENR-50 in PVDF continuous phase while 50/50 PVDF/ENR-50 showed co-continuous phase structure. The incorporation of barium titanate particles into PVDF/ENR-50 blends affected to physical properties and morphological properties. In 80/20 blends, the BT particles were localized at interface between PVDF and ENR-50 while in 50/50 PVDF/ENR-50 blend, BT particles move to ENR-50 phase leading to change the morphology from cocontinuous morphology to dispersed phase/matrix morphology so changing also the properties. Barium titanate particles can be blocked by using dynamic vulcanization process and it will be located at interface of the two phases to act as filler for functionnality or compatibilizer. In general, the filled TPO and TPV at blend ratio 80/20 PVDF/ENR-50 blends showed higher storage modulus and permittivity than that of 50/50 blends due to higher content of polar PVDF.

S11-678

Zhang Ruoyu, Zhang Lisheng, Xu Wei, Liu Wei, Zhu Jin

The Role of Non-planar rings in the hard segments of Polyurethanes: a Multi-scale Investigation

Thermoplastic polyurethanes are frequently used in daily life. However, their endurance of the large strain stretch is poor, just like other thermoplastic polymers. Most of them could only recover to ~88% of its initial length after 500% or larger elongation. We found that the addition of non-planar rings in the hard segment of polyurethanes, which will depress the hydrogen bonding associations, could

surprisingly and largely improve the recovery ratio of polyurethanes, even after their break during stretch. Such phenomenon is closely related to the non-planar ring structure and their multi-scale effect on mechanical properties has been investigated by sing-molecule force spectrum, infrared spectroscopy, X-ray scattering and DMA etc. It is found that the incorporation of non-planar ring could decrease the elastic modulus of the single chain seriously, and the degree of microphase separation is deteriorated too. In contrary to the traditional physical image, the recovery ratio is impressively enhanced from ~85% to 99%.

S11-740

Santos João Paulo Ferreira, Melo Guilherme Henrique França, Nascimento Cassia, Bretas Rosario Elida Suman

A comparison of melt and solution mixing on the dispersion of carbon nanotubes in a styreneisoprene-styrene block copolymer

Multi-walled carbon nanotube (MWCNT)/ styreneisoprene-styrene (SIS) nanocomposites were prepared by two frequently-used approaches, melt and solution mixing. SIS is a thermoplastic elastomer which can self-assembly into welldefined ordered nanostructures. Taking this capability into account, block copolymer materials have long been recognized as scaffolds and used to patter nanoparticles to construct hybrid structures. Therefore, the combination of electrical conductive MWCNTs and SIS in a well-mixed nanocomposite with stable morphology may lead to a material with new and interesting properties for electronic devices. To obtain the equilibrium surface morphology, the SIS film was prepared by solvent casting annealing for 168 h (seven days) at 110 C. The surface morphologies of the SIS specimens were examined by non-contact mode atomic force microscopy (AFM). To produce the nanocomposites by solution the MWCNTs were mixed with SIS using tetrahydroxyfuran (THF) as a solvent and then precipitated in methanol, a non-solvent. Melt mixed nanocomposites were made using an internal mixer (Haake rheometer, model Rheomix 600p) operating at 150°C, 100 rpm for 7 min. The nanocomposites were characterized by impedance



to obtain the AC electrical conductivity, by stress strain tests to obtain the elastic modulus, elongation and tensile at break, and the dispersion of the MWCNT was evaluated by scanning electron microscopy (SEM). The results showed that nanocomposites prepared by casting showed a higher electrical conductivity than the melted. However, the melted samples displayed better mechanical properties than the casting samples. It was found that the dispersion state of MWCNTs was dependent not only on the concentration of MWCNTs but also the mixing method. Solution mixing led to a much better dispersion of MWCNTs than melt mixing at low concentrations of MWCNTs (less than 0.5 wt.%), while the situation was reversed at higher concentrations.

Poster

S11-219

Koca Kayhan, Kodal Mehmet, Özkoç Güralp, Gerengi Hüsnü

The Recent Developments in Tire Uniformity

Tires are highly engineered structural composites whose performance can be designed to meet vehicle manufacturers' ride, handling and traction criteria, plus the quality and performance expectations of the customer. There are several factors and parameters influencing the quality and safety of a tire. One of them is the "uniformity". Uniformity is the performance of tires which should be the same on the circumference direction under static and dynamic conditions. It is very important to determine the tire uniformity after curing process. It is carried out by the specially designed tire uniformity machines. In this study, the factors such as radial and lateral force variation, conicity, bulge and depression that effect the tire uniformity is reviewed. The recent advancements were summarized and the future trends were enlightened. In addition, the methods that can be used to improve the tire uniformity were discussed. Keywords: Tire uniformity, tire quality, tire performance

Honda Shinichiro, Kawamura Takanobu, Tada Toshio

Flow instabilities of silica filled elastomer compounds

Temperature and shear rate dependence of appearances in extruded silica filled styrene butadiene rubber compound have been investigated by capillary rheometer. It was revealed that flow instability spiraling or melt fracture phenomenon took place with increasing shear rate. The shear viscosity with Bagley correction and the extensional viscosity calculated by Cogswell's method were also investigated to look into reveal the relationship between extrudates' appearances and their flowing properties. The shear viscosity with Bagley correction didn't respond to the flow instability occurrence. The extensional viscosity calculated by Cogswell's method, however, responded to increasing extensional rate and then, melt fracture was observed. This phenomenon indicates that melt fracture occurrence for silica filled elastomer is due to strain-hardening by extensional flow in entrance of capillary die.

S11-295

Alonso Ximena, Mantero Carlos, Mosca Daniel, Raimonda Pablo

Synthesis and Characterization of Nanosilica from Rice Husk Ash as a filler of SBR Rubber

Rice husk resulting from the process of obtaining the grain is an environmental problem; the aim of this paper is to study its use as a raw material to produce nanosilica. When rice husk is burnt in a muffle furnace at 590°C for one hour amorphous silica is obtained. Pure silica is extracted using 5N H2SO4 solution with constant stirring at controlled temperature, in a low energetic process, compared with the traditional ones. By refluxing method using HCl, pure nanosilica can be extracted from pure silica trough adjustment of the gelation pH. SEM and TEM results show the particles are in agglomerate form and the dimension cover a range between 10 and 50 nm. XRD powder pattern of nanosilica confirms the amorphous nature of the



substance. FTIR spectrum and EDS analysis add evidence indicating the presence of pure nanosilica. We also made some complementary analysis like BET and TGA in order to compare with the commercial product. The nanosilica obtained is mixed with SBR rubber and its mechanical properties are compared with a commercial product, of US Research Nanomaterials Inc. (Houston - USA).

Zheng Shaodi, Xie Banghu, Liu Zhengying, Yang Mingbo

Control of the surface wrinkling structure on the surface of Polydimethylsiloxane microspheres via a simple low-cost and environmentally friendly route

Mechanical instabilities materials, in soft specifically wrinkling, have led to the formation of unique surface patterns for a wide range of applications that are related to surface topography and its dynamic tuning. However, a continuous, scalable and controllable approach for constructing the wrinkled-structure is scientifically crucial and challenging. Here we introduce a simple low-cost and environmentally friendly route to realize spontaneously wrinkled morphologies on Polydimethylsiloxane (PDMS) spherical surfaces, which have great potentials for the construction of high-performance functional materials. First, the solution of mixed base monomers and the curing agent is mixed with deionized (DI) water with different composition and yielding a uniformly-PDMS/DI water suspension, mixed then very evaporating water slowly at room temperature. This slow drying process is very important so that the curvature wrinkles including dimples and labyrinth patterns are successfully induced on the surface of PDMS microspheres. The effects of the experimental parameters, including the stirring speed, evaporation rate, temperature and composition, on these tunable spherical wrinkles have been systematically studied. The control of the amplitude and wavelength of wrinkle structures and the size of PDMS microspheres could be realized by the simply regulation of the

composition and string speed. Keywords: Polydimethylsiloxane Wrinkling; Microsphere; Acknowledgments This research was supported by the National Natural Science Foundation of China (Grant No. 51103087, 51421061). College of Polymer Science and Engineering, Sichuan University, Chengdu, 610065, People's Republic of China. Address: Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu , China, 610065. E-mail: xiebangh@tom.com

S11-405

Siripornamart Natchaya

Influence of Rubber Latex as an Impact Modifier in Wood Composites

Recently, polypropylene (PP) reinforce with wood flour (WF) or wood composites have gained significant interest for material handling industry due to lightweight materials and low cost. On the other hand, low impact strength is the limitation. Natural rubber latex (NR latex) was introduced to improve the impact properties in wood composites by varying the weight ratio between WF and NR latex (3:1, 1:1, 1:3), and the composition between PP and filler, WF: NR latex (60/40 and 70/30%wt) in twin screw extruder. Moreover, the obtain properties benchmarked with those of commercialized product. The results indicated that the higher amount of NR latex, the better impact properties of composites. Besides, the highest weight ratio of NR latex, 1:3 or W1N3, enhanced impact properties to 59% comparing with the lowest weight ratio of NR latex, 3:1 or W3N1. The W1N3 at 70/30 %wt showed impact properties comparable to commercialized HDPE and lower density, 0.6094 g/cm3, than HDPE, 0.9713g/cm3. Also, this composition was good processability. filler dispersion and strength of However, composites were not satisfied. Dynamic vulcanization with sulfur as vulcanizing agent was interesting technique to improve the properties of composites.

S11-477

Malebennur Nagaraja Sriharish, Mujtaba Anas, Beiner Mario



Influence of viscoelastic filler network on reinforcement and dissipation of natural rubber nanocomposites.

The interrelation between reinforcement and of dissipation phenomena elastomer nanocomposites is of interest to achieve an optimum of mechanical performance in elastomer products. Despite sustained studies. the microscopic origin of both the phenomena is still subject of debate. Results of recent studies suggest that the filler network in SBR filled with silica main contributor nanoparticles as а to reinforcement shows viscoelastic behavior. This is discussed to be arising from glassy bridges acting as viscoelastic elements formed by immobilized rubber in between the filler particles and demonstrated by strain sweeps performed at varied temperature(T) and frequency(ω)[1,2]. In this work, mechanical properties of natural rubber filled with structurally different fillers, carbon black(CB) and carbon nanotubes(CNTs), are investigated by dynamic shear measurements. We show based on the results of isochronal linear response measurements that a gradual decrease of storage modulus (G') in the rubbery plateau region with increasing temperature is a common feature of highly filled rubbers. The interpretation is that immobilized rubber interacting with the filler surfaces is softening. Also, a significant increase in the loss modulus (G'') in the same region occurs with increasing the filler fraction(Φ). This can be understood within the same physical picture. Further, the existence of viscoelastic elements in filler network is confirmed by comparing the Kraus fitting Parameters from an analysis of strain sweeps for rubbers with a Φ above the percolation threshold Φc at varied T and ω . An interesting observation is that the viscoelastic behavior of filler network is relying on filler network topology, fillermatrix interaction and geometry of the glassy bridges(3). Taking the analysis to the next step, possible interrelations between reinforcement and considered. dissipation will be Possible contributions to dissipation will be discussed and quantified based on strain Amplitude

S11-75

Bex Gert-Jan, De Keyzer Jozefien, Desplentere Frederik, Van Bael Albert

Two-Component Injection Moulding of Thermoplastics with Thermoset Rubbers: Process Development

injection moulding Two-component is а manufacturing process for combining polymers with different properties in a single injection moulding process. The process is typically used to combine thermoplastics with another thermoplastic or with a thermoplastic elastomer to create colour differences or hard and soft areas respectively. The present study aims at the development of a twocomponent injection moulding process for the combination of a thermoset rubber and a thermoplastic. Currently products that consist of those two materials (e.g. wheels, syringes and other products with gaskets) are made by assembling separate components. Implementing the twocomponent injection moulding technique for these products will result in better interphase properties, savings on rubber and avoiding costs related to the assembly process. A technological challenge is posed by the fact that injection moulding of rubbers and thermoplastics is fundamentally different. The injection moulding of a rubber requires a heated mould (140°C-180°C) whereas thermoplastics need a relatively cold mould (20°C-100°C) for the polymer to solidify. In this study a versatile twocomponent mould is proposed in which the mould cavities for the rubber and the thermoplastic are thermally separated and equipped with facilities to temperature of both control the cavities individually. The design of the mould also makes it possible to vary the sequence of injection. In this way it is possible to test several processes variations. Preliminary test results will be presented for specific rubber-thermoplastic combinations.

S11-769

Manteghi Amin, Ahmadi Shervin , Arabi Hassan

Polyolefin Elastomer grafted Unsaturated Hindered Phenol Esters: Synthesis and Antioxidant Behavior



This paper discusses synthesis of novel antioxidant group from esterification of 3,5-di-tert-butyl-4hydroxybenzoic acid and 3-(3,5-di-tert-butyl-4hydroxyphenyl)propionic acid with unsaturated fatty alcohols. Esters were effectively synthesized and characterized using FTIR and NMR antioxidant activity spectroscopy. The was evaluated both in blending and radical grafting of Esters 3-(3,5-di-tert-butyl-4processes. hydroxyphenyl)propionic acid showed significantly longer oxidation induction time than polymer samples stabilized with commercial antioxidant. Further, the effect of chain length and phenolic group were investigated on efficiency of antioxidants. The results of radical grafting reaction revealed that synthesized antioxidants were successfully grafted onto polymer chains and the phenolic moiety was functional after extraction process, while pure and commercially stabilized samples were degraded instantaneously. Also, different initiator systems were utilized to enhance the extent of grafting. Among MEK, DCP and DHBP peroxides, DHBP could be more effective in increasing the antioxidant grafted onto polymer. In addition, possibility of rising in graft content was investigated in presence of redox initiator. Findings suggest that these stabilizers could be used in radical grafting process to prolong the thermal stability of polymers. Keywords: unsaturated ester, sterically hindered phenol, antioxidant, radical grafting, polyolefin elastomer.



S12- Fibers, Films, and Membranes

Keynotes

S12-148

Ko Junghyuk, Ashani Vahid, Yao Selina X., Jun Martin B.G., Lee Patrick C.

A Novel Fiber Processing Technology Based on Fused Deposition 3D Printing Combined with Melt Electrospinning

Melt electrospinning is an effective processing technique to fabricate microfibers for many applications such as tissue scaffold engineering, catalysts, fabrics, and filters. Compared to solution electrospinning, melt electrospinning does not involve a solvent and thus it is beneficial for biomedical applications such as the tissue engineering of cell constructs where solvent toxicity or accumulation is a major concern. Two limitations of melt electrospinning are: (i) a larger fiber size (approximately 100µm) compared to that of solution electrospinning, and (ii) unsatisfactory fiber deposition control which prevents creating a well-defined 3D geometry. In this study, we developed a novel fiber processing technology which combines fused deposition modeling (FDM) based 3D printing and melt electrospinning using Polycaprolactone (PCL). The objectives of this study are two folds; (i) to investigate and optimize the significant parameters associated with the melt electrospinning process that influence fiber diameter, including applied voltages, distances between nozzle and counter electrode, and processing temperatures in order to produce microfibers with less than 100 um diameters, and (ii) to develop 3D structures with two different microfiber morphologies which consist of electrospun fiber mats surrounded by well-defined 3D boundary structures by FDM 3D printing. Scanning electron microscopy (SEM) was used to image the 3D structures with bi-modal microfiber distributions and the fiber diameters were

measured using Quartz-PCI Image Management Systems in SEM.

S12-15

Silverwood Richard James, Ballen Claudia Yaneth, Tabatabaei Seyed Hesamoddin, Ajji Abdellah

PVOH Based Barrier Coatings: A Matter of Interface

Various materials allow the implementation of barrier properties to multilayer structures. This study explores the versatility and limitations of coating as a means to an industrial implementation of high barrier properties based on polymer/nanoparticles solutions. This is done thru comparison of the performance of various substrate films in the lab scale as well as the effect of processing parameters for waterborne coatings applied with a flexographic printing press designed for solvent borne inks. Process parameters studied included the effect of moisture, line speed, application of an ink layer and lamination with a solvent-less adhesive. Our study stresses the importance of surface compatibility of the multiple layers involved. All the coatings were done with a layer of modified polyethylenimine (PEI) primer, followed by one or more polyvinyl alcohol (PVOH) layers. In the lab scale, corona treated films were found to perform the best with the selected chemistry. Also, polyethylene terephthalate (PET) and Nylon provided excellent oxygen transmission rates of 0.068 cc/(100in2*day)and 0.079 cc/(100in2*day) respectively. These low values compete with PVDC coated films that were analysed and used as references. This combination of coating and application process proved to perform adequately in attaining high barrier properties.

S12-751

Macosko Chris

Surface Modified Filter Media from Melt Blown Nanofibers

Melt blowing is the major process for making nonwoven products. We have developed a lab scale



melt blowing line for preparing filter media with new polymers. We have used it to demonstrate surface modification of polybutylene terephthalate fibers by hydrolysis and fluorination. Nanofiber mats have been prepared by melt blowing blends of immiscible polymers followed by removal of a water soluble matrix. Tan, D. H.; Zhou, C.; Ellison, C. J.; Kumar, S.; Macosko, C. W.; Bates, F. S., Meltblown Fibers: Influence of Viscosity and Elasticity on Diameter Distribution. J. Non-Newtonian Fluid Mech. 2010, 165, 892-900. Wang, Z.; Macosko, C. W.; Bates, F. S., Tuning Surface Properties of Poly(butylene terephthalate) Melt Blown Fibers by Alkaline Hydrolysis and Fluorination. ACS Appl. Mater. Interfaces 2014, 6, 11640-11648. Zuo, F.; Tan, D. H.; Wang, Z.; Jeung, S.; Macosko, C. W.; Bates, F. S., Nanofibers from Melt Blown Fiber-in-Fiber Polymer Blends. ACS Macro Lett. 2013, 2, 301-305.



Oral

S12-14

Silverwood Richard James, Tabatabaei Seyed Hesamoddin, Ajji Abdellah

Development of Improved Ultra Violet Light Resistance Multilayer Films

Packaged product lifetime improvement is one of the main features and objectives of food packaging. With high interest in transparent flexible packaging as an attractive alternative to other types of packaging solutions, the need to impart ultraviolet light (UV) blocking properties to the multilayered films constituting the flexible package has become obvious. This study overviews some solutions to impart UV resistance properties to clear films and an evaluation of the performance of various additives. At additives contents of 0.3%, LLDPE films with a thickness of 55 microns provided a significant barrier to ultraviolet light with total transmissions in the UVB range of 1.6% for Chiguard 1064[®]. Other additives showed total transmissions of 5.5%, 9.7% and 39.7%. Finally, we present some of our work to reconcile UV blocking additives and food safety through tailoring of a multilayer structure to prevent additive migration. To achieve this objective, an experimental array including the influence of the matrix and adjacent layer composition as well as its encapsulation in a multilayer structure was performed. The most efficient additive's migration was tracked using high precision liquid chromatography (HPLC).

S12-200

Ishikawa Tatsuya, Kim KyoungHou, Ohkoshi Yutaka

Visualization of pillar-shaped fiber bundle in model needle-punched nonwoven fabric by X-ray micro computed tomography

In the needle-punching process, barbs of needle catch the fibers and orient it along the thickness direction of fabric. The oriented fibers form a pillarshaped fiber bundle, which act as a bonding point of fabric. Therefore, the structure of pillar-shaped fiber bundle governs the mechanical properties of needle-punched nonwoven fabric, both of which largely influenced by needle-punching are conditions. However, the three-dimensional (3D) structure of pillar-shaped fiber bundles and its development due to needle-punching the conditions have not been revealed. In this research, we used X-ray micro computed tomography (XCT) and visualized the pillar-shaped fiber bundles by using PET and PE fibers, between which there is a large difference in X-ray absorption rate, then we investigated the 3D structure of pillar-shaped fiber bundles and its development as a function of penetration depth of needle. In the 3D images obtained by XCT, we could clearly observe the 3D structure of pillar-shaped PET fiber bundles by erasing the PE bulk fibers, and the pillar structure developed with the increase of penetration depth of needle. Especially, at the penetration depth of 19.0 mm, the pillars protruded from the bottom surface of fabric and the fibers constituting the pillar were interlocked with the fibers of following pillar with the large increase of the number of fibers constituting a pillar.

S12-243

Shibata Seiji, Takarada Wataru, Kikutani Takeshi

Analysis on crystallization behavior of oriented poly(ethylene terephthalate) fibers and films

To investigate the effect of orientation and orientation mode on crystallization rate, crystallization and melting behaviors of oriented amorphous poly(ethylene terephthalate) (PET) fibers and films were analyzed using the fast scanning chip calorimetry (FSC) and the conventional differential scanning calorimetry (DSC). Uni-axially oriented fibers with various degrees of molecular orientation were prepared through the melt-spinning with various take-up velocities and bi-axially oriented films were prepared through the simultaneous equi-biaxial stretching of amorphous and isotropic PET films to various draw ratios at 90 degrees C. In the FSC measurement, significant data fluctuation caused



by the thermal shrinkage of the oriented sample was observed at around the glass transition temperature (Tg). We found that this fluctuation could be suppressed without a considerable effect on crystallization behavior by applying preliminary shrinkage process which contains heating up to 120 degrees C and immediately cooling down to a temperature blow Tg at high heating and cooling rates. Based on this technique, measurement of the cold crystallization behaviors was conducted at various heating rates applying the timetemperature profiles including the pre-thermal treatment. The models for crystallization kinetics proposed by Ozawa1) and Nakamura2) were to calculate the non-isothermal combined crystallization rate of oriented PET fibers and films. Even after applying the thermal shrinkage, the highly oriented fibers or films showed much faster crystallization rate than that for the barely oriented fibers or isotropic films. 1) T. Ozawa, Polymer, 12, 150 (1971) 2) K. Nakamura, K. Katayama, T. Amano, J. Appl. Polym. Sci., 17, 1031 (1973)

S12-26

Hufenus Rudolf, Quandt Brit Maike, Leal A. Andrés, Hegemann Dirk

Synthetic fibers tailored for medical textiles

Aiming at innovative medical textile applications, product enhancements on the fiber level are very effective, and multicomponent synthetic fibers are among the most promising developments. To combine functionalities in a single fiber, we develop bi- and tri-component fibers with various crosssections and material combinations. As example, we developed a novel category of bi-component polymeric fibers with a liquid core. Spinning trials resulted in the continuous production of liquid filled fibers with 50 µm diameters, which are expected to open a new field of multilumen microcatheter applications. Using bicomponent meltspinning technology we developed highly flexible prototype polymer optical fibers (POFs) that fulfill the requirements of textile processes and that provide comfort during wear. One sensor principle uses embroidered fabrics of these novel POFs to build a wearable pulse oximeter, where two

different wavelengths are used to determine the ratio of oxygenated and deoxygenated hemoglobin. Another sensor principle is based on urethane/siloxane block copolymer POFs integrated into a textile structure. Due to the elasticity of these POFs, the fiber cross-section changes under pressure, out-coupling light, and resulting in a location-dependent, pressure-sensitive fabric. Our low-pressure plasma sputtering process yields metal coated fibers for the development of smart medical textiles that behave and perform like conventional textiles in terms of robustness, flexibility and haptics. Thin insulating polyurethane coatings have successfully been applied to qualify the fibers to be used as an interconnection platform for technology-driven medical clothing. Additional conductive PEDOT:PSS polymer coatings proved to be sensitive to external conditions, making the respective fibers ideal candidates for combined pressure and humidity sensors.

S12-281

STA MARWA, Aguiar Graziele De Jesus , Medeiros Simone De Fátima , Dos Santos Amilton , Demarquette Nicole

Electrospinning of Poly(Nvinylcaprolactam)/polycaprolactone blend for Drug Delivery Applications

Electrospinning is a technique used to produce micro to nano-sized polymer fibers. This method is based on electrostatic forces; the application of electric field on the polymer solution leads to the projection of a jet and the creation of polymeric fiber. Many polymer solutions have been electrospun for different biomedical applications such as drug delivery applications. Thanks to its large surface area, the fiber structure can retain the biological fluid. In this study, a blend of Poly (Nvinylcaprolactam) (PNVCL), a thermoresponsive, biocompatible and hydrophilic polymer and polycaprolactone (PCL), а biodegradable, biocompatible and hydrophobic polymer was electrospun to create thermosensitive, biocompatible and biodegradable nanofibers. The electrospinning of PNVCL/PCL blend polymer



solution was optimized to obtain continuous and smooth nanofibers; the morphology of PNVCL/PCL nanofibers was evaluated by Scanning Electron Microscopy (SEM). In addition to the process parameters, the solution concentration and the type of solvent were also optimized. Different morphologies of PNVCL/PCL fibers were obtained according to the solvent used. The biodegradation of the PCL particles created pores in the fiber which should facilitate drugs release. The particle size of PCL in PNVCL/PCL blend solution was evaluated by Dynamic Light Scattering(DLS). Keywords: Electrospinning, PNVCL, PCL, Nanofibers.

S12-282

Kurusu Rafael, Demarquette Nicole

Hydrophilization of electrospun mats by blending with amphiphilic PEO-PPO-PEO copolymers

Nonwoven mats produced by electrospinning present high surface area so that understanding and controlling surface properties like wetting is crucial to obtain a desired performance. Many polymers produce hydrophobic electrospun mats due to a combination of surface chemistry and an increase in surface roughness. However, hydrophilization is needed for many biomedical and environmental applications where there is interaction with aqueous fluids. This can be achieved by a post-treatment of hydrophobic membranes, but with an increase in time and cost. Polymer blending is an attractive alternative to control the surface properties of the mats in a onestep process. In this work, hydrophobic polymers were blended with amphiphilic PEO-PPO-PEO copolymers aiming to control the segregation of this component to the surface. The PPO block tends to segregate to the surface and drag the PEO chain ends. Once in contact with aqueous medium, the PEO segment will extend and hydrophilize the fiber. Also, hydrophilic electrospun mats cannot be seen only as a rough surface, but also as a porous membrane subject to wicking. The mats were characterized by water contact angle and wicking measurements, scanning electron microscopy and image analysis. The effect of chemical composition,

mat and fiber surface morphology on the wetting behavior was evaluated.

S12-297

Sato Takeshi, Taniguchi Takashi

Multi-scale simulation for melt spinning process -Analysis of entanglement and orientation –

In the polymer melt spinning process used to create polymer fibers the macroscopic dynamics is tightly connected to the microscopic state of the polymer chains through the stress and strain-rate fields. To probe the different time- and length-scales in the system, it is necessary to use a combined micromacro simulation method. In this study, we apply such a multi-scale simulation to study the polymer spinning process. In our multi-scale simulations, we a microscopic model to describe use the entanglement polymer dynamics and а macroscopic model to track the deformation rate imposed at a material point. For the former, we use a slip-link model, for the latter a particle-based Lagrangian model. With this approach, we are able to successfully take into account the memory effects, as well as provide a quantitative evaluation of the polymer dynamics, including the effects of entanglement. We performed extensive simulations to study the relationship between the macroscopic spinning conditions and the microscopic properties of the melt, such as the orientation and level of entanglement of the polymer chains.

S12-306

Sekiguchi Yuta, Takarada Wataru, Kikutani Takeshi

Structure and properties of melt-spun fibers of polyethylene blended with cellulose fibers

Melt spinning of polyehtylene blended with cellulose fibers was carried out with the aim of evaluating maximum mechanical properties of the compound. Some chemical modifications were applied for polyethylene to improve interaction with cellulose fibers. When the fibers prepared at the same take-up velocities were compared, tensile properties of polyethylene fibers blended with only 1 wt% of cellulose fibers showed higher tensile



modulus and strength in comparison with those for neat polyethylene fibers. Structure analysis of the fibers through the wide-angle X-ray diffraction and birefringence measurement revealed that the improvement of the mechanical properties was caused through the enhancement of molecular orientation of polyetylene rather than the reinforcement by the cellulose fibers.

S12-502

Al Rahhal Samer, Brünig Harald, Gohs Uwe, Heinrich Gert

Melt spinning of modified PP and PP/EOC blends prepared by continuous electron induced reactive processing

Polypropylen (PP) is known as a thermoplastic material with lot of advantages as low cost, low density, chemical resistance, well processability, etc. The simultaneously melt spinning of PP and glass filaments (Online Hybrid Fiber Spinning) opens the possibility to produce hybrid yarns for glass fiber reinforced composites using textile processes. However, the applications of PP in electrical and automotive industries as matrix material for endless fiber reinforced composites are limited because of its low stiffness, low tensile strength, insufficient impact strength. Improving the poor mechanical properties of PP to get at least a low cost high performance material that benefits the requirements of modern reinforced light weight constructions seems to be a challenge of our time. In the presented work, PP and blends of PP and maleic anhydride functionalized PP and/or ethylene-octene copolymer (EOC) were prepared by electron induced reactive processing (EIReP) using various blend ratios at low electron doses (up to 18 kGy) and fixed electron energy of 1.5 MeV. Melt spinning trials of the modified PP and PP/blend materials were carried out by means of an industrial near extruder spinning equipment to investigate the spinnability and to get optimum spinning parameters as well as the effects of blend components and electron beam irradiation to the mechanical properties of as-spun fibers. It is well known, that blending PP with 2.5mass-% EOC increase the Charpy impact strength but has no or

lowering effect to E-modulus. The treatment with electron beam allows further improvements. The presentation shows, that under well balanced conditions, significant improvement of adhesion and impact strength as well as modulus for the modified PP-matrix material can be reached. As example, the figure below shows the increase of tensile modulus in dependence on electron dose for low oriented melt spun PP/EOC blend fibers.

S12-507

Kawai Kouya, Takarada Wataru, Kikutani Takeshi

Effect of Blending High and Low Stereoregularity Components on Crystallization and Melting Behaviors in the Polypropylene Fibers

Crystallization and melting behaviors of blend fibers of two types of polypropylene (PP), i.e. high stereo-regularity/high molecular weight PP (HPP) and low stereo-regularity/low molecular weight PP (LPP), was investigated. Blend fibers consisting of various HPP/LPP compositions were prepared through the melt spinning process. Differential scanning calorimetry (DSC), temperature modulated DSC (TMDSC) and wide-angle X-ray diffraction (WAXD) analysis were applied during heating process for clarifying the crystallization and melting behaviors of individual components. In the DSC measurement of blend fibers with high LPP composition, continuous endothermic heat was detected between the melting peaks of LPP at around 40 °C and that of HPP at around 160 °C. Such endothermic heat was more distinct for the blend fibers with higher LPP composition indicating that the melting of LPP in the heating process was hindered because of the presence of HPP crystals. On the other hand, heat of crystallization was detected at around 90 °C in the case of blend fibers with LPP content of 30 to 70 wt%, indicating that the crystallization of HPP component was taking place during the heating of as-spun blend fibers in the DSC measurement. Through the TMDSC analysis, re-organization of the crystalline structure through the simultaneous melting and re-crystallization was detected in the cases of HPP and blend fibers, whereas recrystallization was not detected during the melting



of LPP fibers. In the WAXD analysis during the heating of fibers, amount of alpha-form crystal was almost constant up to the melting in the case of single component HPP fibers, whereas there was a distinct increase of the intensity of crystalline reflections from around 100 °C, right after the melting of LPP in the case of blend fibers. These results suggested that the crystallization of HPP in the spinning process as well as during the conditioning process after spinning was hindered by the presence of LPP.

S12-510

Jana Sadhan C., Kim Sung Jun C., Gu Senlong C., Rajgarhia Stuti C.

Design of nanoscale polymeric building blocks for high efficiency separation processes

Airborne nanoparticles in the size range 15-150 nm present severe health hazards while micrometer size water droplets suspended in diesel fuels reduce fuel economy and promote corrosion of metallic components. Current technologies cannot adequately address both these issues. Glass fiberbased air filters cannot efficiently remove airborne nanoparticles of size below 300 nm. Also, improper tuning of hydrophobicity and hydrophilicity in glass fiber mats limits their performance in separating water droplets from diesel fuels. Our research focuses on the fundamentals of design of polymeric building blocks to address both these problems. First, we exploit reaction-induced phase separation or thermo-reversible gelation for designing polymer aerogel monoliths with appropriate balance of meso- and macro-porosity. The characteristic features of polymer networks spheres of typical dimension 20 nm or cylindrical strands of typical diameter 50 nm - show strong dependence on temperature, solid concentration, and the nature of the solvent and uniquely determine a balance of meso- and macroporosity. The resultant macropores handle bulk of the air flow while the mesopores remove the nanoparticles with efficiency approaching 99.998%. Second, we exploit evaporation-induced phase separation of immiscible polymer designing pairs in interpenetrating network morphology in polymer

nanofibers of diameter 100-300 nm. These nanofibers, coated onto glass fiber mats, provide separating droplets functionality in water suspended in diesel fuel with much higher efficiency than is possible in current technology. This paper discusses the principles of size and shape selection of polymeric building blocks in aerogel monoliths and bi-component polymer nanofibers using several processing variables. In addition, the paper discusses quantitative data on airborne nanoparticle filtration and water droplet separation from diesel fuels and relates them to polymer morphology.

S12-559

Cosas Fernandes Joao Paulo, Gonon Laurent, Mareau Vincent, Mendil-Jakani Hakima

A new process to convert proton exchange membranes into high performances and reliable hybrid membranes for fuel cell

Proton exchange membrane for fuel cell (FC) is a promising environmentally friendly and oil-free technology. One of its key components is the polymer electrolyte membrane acting as separator and proton conductor. Improving both the performances and durability of the membrane is a crucial issue. Different strategies have been explored to improve the mechanical properties of the membrane and to reduce the ageing impact. Despite a lot of progress, their functional properties (conductivity, water sorption, thermomechanical chemical stability...) stay below properties, expectation when operated above 100°C whereas higher operating temperature (150°C). Therefore, there is currently an increasing interest in using reliable alternative membranes that are capable of operating at higher temperatures, low relative humidity to ensure long term performances. Popular candidates are polyaromatic polymers like sPEEK which present good mechanical properties at high temperatures but poor functional properties (proton conductivity and durability in FC). We will demonstrate that the sPEEK performances can be significantly improved using а suitable hydrothermal treatment up to becoming equivalent to that of Nafion the benchmark material. SAXS



analyses performed on hydrothermally treated sPEEK show that the increase in molecular mobility induced by the pretreatment (water, temperature) allows a gradual nano-structuration of the membrane and a sharp increase of its proton conductivity. To improve the membrane durability, we have developed an original strategy based on the insertion of a chemical stabilizing network by a sol-gel process. These hybrid membranes will combine excellent proton conductivity at high temperature and low relative humidity and will be stable under hard operating conditions. The process involved should be universal allowing to improve the membrane properties of common ionomer membrane

S12-632

Almeida Ronaldo José, Sene Tarcisio Sanson, Pessan Luiz Antonio

Foaming of PC/PMMA membranes with CO2 and ethanol as co-solvent

It was studied the effect of using ethanol as cosolvent in the CO2 foaming process of polymeric membranes for microfiltration applications. Flat membranes of partially miscible blends of PC/PMMA were prepared through a one-step foaming method. The interaction and miscibility between the phases in the polymer blend was characterized by DSC, whilst the morphologies of the flat membranes were analyzed by scanning electron microscopy (SEM). The permeability of nitrogen and water through the membranes were evaluated by appropriated techniques. This study showed that foaming homopolymers solely with CO2 generates closed cell foams with a dense skin layer whereas foaming the PC/PMMA blend solely with CO2 still formed closed pore walls with dense skin layer. On the other hand, the polymer blend foamed with the ethanol/CO2 mixture showed a very interesting morphology where the ethanol/CO2 mixture led not only to the openness of the pore walls in the polymer blend, but also inhibited the formation of the dense skin layer. Bubble point tests were performed for the PC/PMMA sample foamed with ethanol/CO2 mixture and the results displayed a pore size

distribution suitable for microfiltration applications.

S12-634

Sugimoto Masataka

Electrospinning of PVAaq solutions with ZnO nanoparticles and antibacterial properties of the electrospun mats

In order to obtain nano fiber mats which posesses antibacterial properties, we studied the electrospinnability of PVA solutions. Due to less toxiccity of ZnO to humans than silver, they are attractive as antibacterial agents in biomedical applications. First the effect of the nanoparticles on the solution viscosity of PVA solutions, especially we focused on the effect of the particle size and the nanoparticle volume fraction on the viscosity of the suspension. We found that the unusual increase of the solution viscosity of the suspensions as increasing the volume fraction of the nanoparticles and decreasing the size of the particles despite of very low volume fraction of 0.02%. The measured viscosities at the volume fraction of the nanoparticles are significantly higher than those predicted by the Einstein's equation. The increased viscosities affected the electrospinability of PVA/ZnO suspensions. We will also present the influence of the size of ZnO nanoparticles on their antibacterial action against strains of three bacteria: one Gram-negative, Escherichia coli and two Grampositive, Bacillus subtilis and Staphylococcus aureus.

S12-69

Tanimura Aya, Horinouchi Kazuhito, Inagaki Jun, Funaki Kenichi, Shimizu Toshiyuki, Numata Yukihiro, Ito Katsuya

Structural Characterization By X-ray Scattering Of PET Film By Near Melting Point Stretching

Biaxially oriented Poly (ethylene terephthalate) film is excellent in heat-resistance and transparency, which is utilized in technical and packaging application. Heat resistance, mechanical strength, or dimensional stability is achieved by the use of



biaxial orientation method, which is characterized in machine-directional and transverse-directional stretching under specific temperature. It is well known that difference of the amount of heat, temperature profile, draw ratio and strain rate in stretching process improve the film properties. Generally, the temperature of stretching process is set on a little higher than glass transition point, in order to avoid the deterioration of thickness homogeneity caused by overheating. In this work, the authors studied the new biaxial stretching process at high-temperature condition near melting point of PET. Generally it is difficult to stretch PET film at high-temperature near melting point, because tensile stress decreases during stretching process. However, PET film stretched at such high temperature can be obtained by undergoing heatcrystallization of pre-stretching film. The PET film by near melting point stretching exhibited specifically thermal dimensional stability. The result of property and structural characterization by X-ray scattering of our new film was discussed. Moreover, we studied structural change during stretching by in-situ characterization. It clarified that there is a specific crystal construction process at near melting point that affects the thermal dimensional stability.

S12-7

Lee Demei, Huang Tzu-Wei, Liu Shih-Jung

Co-axial electrospinning of sheath-core structured chitosan/polylactide nanofibers for the filtration of metal ions

Biodegradable sheath-core structured nanofibers, with chitosan as the sheath material and polylactide (PLA) at the core, were developed for the removal of metal ions. For the electrospinning of sheath-core nanofibers, predetermined weight percentages of chitosan were first dissolved in trifluoroacetic acid (TFA) with sonication for 30 minutes, and then mixed by a magnetic stirrer for 12 hours. The same procedure was conducted with polylactide (PLA). The chitosan and polylactide solutions were then fed into two different capillary tubes with needles of small diameter, respectively, for co-axial electrospinning. The delivery rates of the solutions

were controlled by two independent pumps for the sheath chitosan solutions and the core PLA solution. The morphology of the electrospun nanofibers was examined by a scanning electron microscope (SEM). The average diameter of the electrospun nanofibers was found to range from 234 nm to 562 nm. The influence of various process conditions on the metal removal was also investigated. The removal efficiency of the sheathcore chitosan/PLA nanofibers was measured and compared with the efficiency of blended chitosan/PLA nanofibers. The experimental results the electrospun suggested that sheath-core nanofibers exhibited superior metal ion removal efficiency compared to the blended nanofibers. The removal efficiency of the nanofibrous membranes increased with the initial metal ion concentrations and the pH value and decreased with the temperature of the solutions.

S12-722

Tran Nguyen Hoai An, Brünig Harald, Auf der Landwehr Maria, Heinrich Gert

Fibrillation mechanism of PLA/PVA blend along the spinline

The effects of spinning conditions on the fibrillation process of polymer blends, on the example of poly(lactic acid) (PLA) and poly(vinyl alcohol) (PVA) blend systems, in an elongational flow within fiber formation zone are systematically and thoroughly investigated for the first time. By considering the relationship between the changes in filament parameters with the focus on the maximum axial strain rate (ASR) and tensile stress at maximum ASR and the morphological evolution of the dispersed PLA phase along the spinline, the fibrillation process from rod-like to nanofibrillar structures of the dispersed PLA phase in a binary blend with PVA matrix is elucidated. The final morphology of the dispersed PLA phase in PLA/PVA blends is controlled by the changes in the spinning conditions. The lengths and diameters of the PLA fibrils are caused not only by only the deformation of their initial sizes but by the combination of the deformation, coalescence, and break-up process.



Paiva Maria C., Cunha Eunice P., Fernandes Bruna M., Duarte Fernando M.

Aqueous suspensions of graphite nanoplates and polyurethane for films and coatings

Nanocomposite films based on polymer and carbon nanoparticles are expected to have excellent properties. However, the production of these nanocomposites requires good dispersion/exfoliation of the nanofillers that tend to form stable agglomerates through Van der Waals interactions. In addition, they are hydrophobic in nature, which hinders their dispersion in water and in aqueous polymer suspensions. The present work aims at the study of the dispersion of exfoliated graphite in water through non-covalent functionalization with modified pyrenes, the production of composites in aqueous suspensions of polyurethane, and the characterization of the composites produced in terms of nanoparticle dispersion, thermal, mechanical and electrical properties. Three types of exfoliated graphite, with different particle sizes, were used, as well as the oxide of one graphite type. In addition, the influence of the dispersion parameters was studied, such as time of ultrasound application, the concentration and type of surfactant and the concentration of graphite, in order to find the best dispersion conditions. The exfoliated graphite suspensions were characterized by UV-visible spectroscopy, and were characterized by optical and electron microscopies and Raman spectroscopy. Polyurethane films were produced using these suspensions by solvent evaporation and by automatic doctor blade technique. The mechanical, thermal and electrical properties of the films were measured, and the morphology was characterized by optical and electron microscopies. The sonication time was relevant for the dispersion level achieved, and the larger nanoparticles (lower surface area) required longer dispersion time to reach a significant dispersion. The dispersion level was observed to have a significant influence on the final mechanical properties of the composites.

Gahleitner Markus, Mileva Daniela, Gloger Dietrich, Tranchida Davide, Androsch René

Polymer Structure Effects on Crystallization and Properties in Polypropylene Film Casting

Recently more attention has been paid to the mesomorphic phase of isotactic polypropylene (iPP), not the least because better calorimetric techniques and instruments had become available, enabling studies at high cooling rate. In addition to the scientific interest sparked by the availability of novel differential scanning calorimetry (DSC) equipment enabling cooling rates up to 3.000 K/s (FSC, fast scanning chip calorimetry), the mesomorphic phase also plays an important role in high-speed conversion processes for iPP like castfilm extrusion, metal coating and cable insulation. The presence of this phase can be either positive, e.g. for transparency and toughness in case of films, or negative in terms of long-term stability and postcrystallization. Recent investigations have shown that the reduction of crystallization rate by increasing chain disturbance (stereodefects or comonomers) shifts the growth transitions from the á-crystalline to the mesmorphic phase to lower cooling rates. An extensive cast film study was performed with several iPP homopolymers of different isotacticity and an ethylene-propylene (EP) random copolymer at two different film thickness levels (50 and 200 µm). Melt and chill roll temperature were varied systematically together with the processing speed. The produced films were characterized by standard tests and wideangle X-ray scattering (WAXS). The parameter variation resulted in a significant difference of crystallinity, mechanical and optical properties together with the behavior on subsequent annealing and further processing. At higher effective cooling rates the mesomorphic phase dominated the leading to higher films, transparency and lower modulus. In parallel, the polymers were studied by FSC technique at 0,1 to 1.000 K/s, seeking to use the results for a better understanding of iPP film casting. It must however be concluded that the competition between flow induced crystallization and quenching effects defines the film properties.

S12-76

PPS[®]32

S12-22

Huang Sz-Chieh Melody Melody, Lue Shingjiang Jessie Jessie

Multi-layer polyelectrolyte on polymer surface for direct methanol fuel cell

The objective of this research was to prepare polybenzimidazole-

polydiallyldimethylammoniumchloride- graphene oxide (PBI-PDDA-GO) composite membranes by layer-by-layer assembly for direct methanol fuel cell. The pure PBI, 5-layered PDDA-GO and 10layered PDDA-GO composites on PBI were prepared and tested for conductivity, methanol and direct methanol fuel permeability, cell performance. The purposes are to decrease permeability by using GO and to increase ionic conductivity using PDDA to attain enhanced cell performance. The ionic conductivity of the 5layered membrane exhibited a value of 1.46×10-2 S/cm at 30oC, much higher than those of the pure PBI membrane (1.12×10-2 S/cm) and 10-layered composite membrane (0.84×10-2 S/cm). The 5layered composite resulted in the highest opencircuit voltage in fuel cell test. The cell voltage drop in the ohmic loss region of the polarization curve was the least among three membranes. Therefore, this 5-layered composite performed the highest peak power density of 230 mW cm-2. On contrary, 10-layered composite had the the lowest conductivity and resulted in higher voltage drop. Despite of its higher open-circuit voltage than the PBI film, the 10-layered composite demonstrated the lowest power density. Keywords: graphene nanocomposite, layer-by-layer assembly, alcohol fuel cells, ionic conductivity.

S12-25

Wang Yi-Chun, Shih Chao-Ming , Lue Shingjiang Jessie

Polyelectrolyte Complex Containing Graphehe Oxide Nanofillers as Desalination Membranes

In this work, graphene oxide (GO) nano-additive was incorporated into polyelectrolyte complex (PEC) to prepare PEC-GO water selective membrane for water desalination process. The synthesized thin film composites consisted of a PEC-GO separation layer, а microporous poly(vinylidene fluoride) layer and a non-woven substrate. Glutaraldehyde was used as a crosslinker to enhance mechanical strength of the composite membranes. The resulting membranes were investigated on nanofiltration systems to examine the water permeability and salt rejection efficiency. The results showed that 100 ppm GO in the PEC exhibited a high desalination efficiency on 1000 ppm NaCl solution. This composite rendered permeance values in the range of 69.3-88.9 kg/m2hMPa for various salt solutions. The Na2SO4 solution resulted in the highest rejection ratio of 62.1%, followed by the NaCl rejection (45%). The MgCl2 and MgSO4 solutions had lower rejections of 12.2 and 22.0%. It seems that the PEC-GO composite was more efficient in removing monovalent cation while maintaining high filtration flux.



Poster

S12-114

Chin Chih-Ping, Cheng Kou-Bin, Liu Jenyung, Chang Jing-Tang, HUANG FU-LIANG

Influences of Deposition Time of Arc Ion Plated Diamond-liked Carbon Films on the Polyamide 66 fabric

An Arc Ion Plating (AIP) system was used to deposit diamond like carbon coatings onto polyamide 66 fabrics. Coatings with different thickness were obtained by controlling deposition time. The tensile strength, wear resistance, water contact angle, heat conductive coefficient, fastness to laundering and stiffness of different coated fabrics were measured and compared. The results show that, depositing DLC coatings enhances the stiffness, hydrophobic property and heat conductive coefficient of polyamide 66 fabrics. The stiffness and thermal conductivity of fabric increased with increasing the coating thickness. The tensile strength of coated sample initially increases with deposition time. The sample of 30 minute deposition exhibits a maximum tensile stress of 50.39 N/mm2. The wear resistance of the sample of 10 minute deposition is 212.2% higher than uncoated polyamide fabrics. The DLC coatings effectively change the hydrophilic polyamide 66 into hydrophobic. The stiffness of sample with 40 minutes deposition shows a 17.21% in warp and 45.45% in weft improvement and better than uncoated fabric. It also shows a 25.51% higher thermal conductivity and better than uncoated fabric. However, the accumulated heat during deposition may cause deterioration of polyamide 66 fiber. The coated polyamide 66 fabrics with optimized tensile strength and wear resistance are obtained between 10 to 30 min depositions. These results evidence the feasibility of applying DLC on polyamide 66 fabrics and the other polymeric fiber products for several potential applications.

S12-155

Can Buse Nur, Kuman Aylin, Gozutok Cansu, Ozkoc Guralp

Corn-Bran as an Alternative Cellulosic Filler in Polypropylene Matrix

bio-renewable Recently natural fibers from resources have attracted considerable interest from research community owing to their unique intrinsic properties such as biodegradability, availability, friendliness, easy environmental flexibility, processing and very high mechanical properties. Natural fibers have been frequently used as the reinforcement component in polymers to add the specific properties in the final product. Natural fiber-based materials are finding their applications in a number of fields ranging from automotive to biomedical devices. Corn bran (CB), the hard outer shell of corn that protects the grain from the elements, is a source of natural cellulosic fibers. In this study, the applicability of corn-bran fibers as a reinforcing filler in polypropylene (PP) matrix was investigated. The properties of CB/PP composites were compared with wood fiber reinforced PP composites. In order to enhance the interfacial adhesion, maleated-PP (PP-g-MAH) was used. The composites were prepared in an Xplore laboratory compounder. The standard samples were obtained via injection molding. The mechanical and thermal properties were obtained via tensile tests and differential scanning calorimeter (DSC), respectively; and the morphology was investigated by means of scanning electron microscopy (SEM). It was found that at lower concentrations, CB was competitive to WF in terms of tensile properties. The response of the fiber in the presence of compatibilizer was dominate in the case of WF with aspect to CB. It was shown that CB is an alternative candidate to be used as reinforcing natural fiber source for thermoplastic composites. Keywords: Natural fibers, corn-bran, polypropylene, wood fiber, mechanical properties

S12-238

Shimada Hikaru, Nobukawa Shogo, Yamaguchi Masayuki



Anisotropic Structure and Birefringence Control of Polymeric Films

Precise control of both orientation and form birefringences is carried out using a single material. Hot-stretched cellulose triacetate (CTA) films containing diisodecyl adipate (DIDA) show negative orientation birefringence with ordinary wavelength dispersion, as similar to that of the pure CTA film; the absolute value of the birefringence increases with wavelength. However, after extracting DIDA from the stretched films by immersion into organic solvent, the an birefringence of the film dramatically changes from negative to positive with extraordinary wavelength dispersion; the magnitude of the birefringence increases with the wavelength. This is an inevitable property for a multi-band quarter-wave plate which is used for optical devices. Numerous ellipsoidal pores are detected by SEM observation in the film after extraction, indicating that DIDA is segregated and formed ellipsoidal domains in the CTA matrix during annealing and stretching. These results indicate the great contribution of form birefringence originated from anisotropic pores, and the combinations of orientation birefringence from CTA molecules and form birefringence from pores give extraordinary wavelength dispersion. Furthermore, the amount of an additive, annealing time and stretching condition affect the number, size, and aspect ratio of pores. Total birefringence values of CTA films after extraction increase with increasing the DIDA amount and the strain rate at the stretching process. Transmittance of CTA/DIDA decreases with the annealing time, suggesting that DIDA is segregated from CTA and forms domains during heating. Therefore, the annealing time should be minimized to keep high transparency.

S12-239

Kunimitsu Tatsuma, Toyoda Kai, Ikaga Toshihumi , Kim KyoungHou , Ohkoshi Yutaka, Koike Katsuhiko

Effects of molecular weight distribution and stereoregularityon mechanical properties and structure of Isotactic Polypropylene (iPP) fiber

Isotactic Polypropylene (iPP) fibers are used in a wide range and required higher performance. In this study, we aimed to improve the strength of iPP fibers and examined for the effects of molecular weight distribution and stereoregularity.

S12-300

Yamaguchi Masayuki, Nobukawa Shogo, Kiyama Ayumi

Precise Control of Three Dimensional Refractive Index by Incorporation of Additives

It is required to adjust the three dimensional refractive index for an optical compensator film used in a liquid crystal display with wide visual angle. Although there have been various techniques proposed, such as biaxial stretching, doping a second component, and laminating, it is not easy to enhance the refractive index in the thickness direction of a film. Furthermore, the refractive index control has to be performed in the wide range of wavelength for color display. In this study, a cellulose triacetate film containing a specific additive having strong polarizability anisotropy is used to control the refractive index. Since the additive has an anisotropy also in its shape, it shows the orientation accompanying with the orientation of polymer chains. Consequently, the refractive index in three dimension is modified.

S12-389

Lei Jun, Yang Shu-Gui

Flow-Induced Fibrillation of Isotactic Polypropylene under Pressure

We systematically researched flow-induced fibrillation at pressure (50 MPa) by using the custom-designed pressurizing and shearing device (PSD) equipped with well-designed dynamic sealing structure, which successfully solved the problem of melt leaking. Polarized Fourier transform infrared spectroscopy, small angle x-ray scatter and scanning electron microscope were employed to reveal the orientation of molecules and crystalline structure. The results clearly show that specific work of shear flow (extended to the case in the presence of pressure, which is closer to



the industrial melt spinning) determines the degree of orientation (fc) or the formation of flow-induced fibrillation in isotactic polypropylene (iPP). Specific work of shear flow displays a critical value for the shear-induced fibrillation, suggesting a minimal energy needed for fiber formation in iPP melt, that is, melt cannot be induced to form fibers when the practical flow work imposed on melt is lower than the critical value. Additionally, even though higher pressure is beneficial for products to gain better performance, engineers should keep in mind that selecting a suitable processing pressure is crucial because the enhancement of pressure will make the situation tougher for flow-induced fibrillation and increase energy cost as well. These interesting and significant results shape a clear understanding in flow-induced fibrillation under pressure and provide the chance to lower the energy cost by optimizing processing conditions in synthetic fiber industry.

S12-392

Wang Yue, Yang Mingbo

The study of microporous membranes obtained from polyethylene by blown film process

The research of microporous membranes used in Lithium batteries has a major significance all over the world. In this field, the study of microporous membranes obtained from polyolefin by blown film process is highly concerned by many scholars. In this paper, high-density polyethylene (HDPE) was used to study the evolution of the pre-film morphology and its influence on the postsecondary stretching condition through blown film process. Scanning electron microscope (SEM) and Small angle X-ray scattering (SAXS) were used to characterize the orientation of lamellar structure. The molecular chain configuration of HDPE precursor film was characterized by Differential scanning calorimetry (DSC) tests. It was found that through adjusting the blow up ratio and draw up ratio in blown film process, the crystalline structure in precursor film changed from spherulite to lamellae and the lamellar stucture oriented along the machine direction (MD). When the traction speed is too large, the oriented lamellar structure

will be destroyed. Key words: Orientation; secondary stretching; high-density polyethylene; microporous membrane College of Polymer Science and Engineering, Sichuan University, Chengdu, 610065, People's Republic of China. Address: Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu , China, 610065. E-mail: yangmb@scu.edu.cn

S12-531

Chen Jieng-Chiang, Wu Chang-Mou, Teng Yi-An, Wang Jie-Mao

Interfacial Strength of Twaron Fiber/PCL Composite Materials

Twaron fibers were treated with H3PO4 solution to rough the surface of Twaron fibers. Three H3PO4 solution concentrations (1%, 10% and 30%) and treating time (1 min, 2 min and 3 min) were chosen to rough the fibers. Both treated and untreated Twaron fibers are reinforced polycaprolactone (PCL) matrix. Interfacial shear strength and tensile strength of treated and untreated were carried on a material testing machine (MTS 810) The results that the increasing H3PO4 solution show concentrations and treating time decreased the tensile strength of the treated fibers. However, increasing H3PO4 solution concentrations and treating time increased the interfacial shear strength of the Twaron fibers/PCL materials. The optimal treatment for Twaron fiber with H3PO4 was 30% for 3 minutes. We also found that appropriate coating light-cured HV3 resin on the treated fibers enhanced the interfacial shear strength of Tawron/PCL materials.

S12-534

Chen Jieng-Chiang, Wu Chang-Mou, Yang Chin-Chih

Tensile Characteristics of Cotton Fabrics/PLA Composites

Cotton plain fabrics were used to reinforce polylactic acid (PLA) resin to make green composite materials. The PLA has been modified with PPgMA to improve the interface properties between cotton and the PLA. Various contents (2%,



4%, 6%, 8%, 10% and 12%)of PPgMA were added into the PLA to improve the adhesion and toughness of the PLA. TGA was applied to analysis the thermal stability of the modified PLA. In addition, the tensile characteristics of the modified PLA and the cotton plain fabrics reinforced composites are discussed in current study. Furthermore, the failure modes for the PLA and composites after the test were observed by SEM. The results show that the tensile strength and modulus increased with increasing the amount of PPgMA. The PPgMA enhanced the cohesion and compatibility between cotton fiber and PLA resin. The optimal amount of PPgMA was 6%.

S12-562

Cosas Fernandes Joao Paulo, Gonon Laurent, Mareau Vincent

AFM-Raman Co-localization setup: Advanced characterization technique for polymers

The comprehension of the process-structureproperties relationship is an imperative achievement in order to develop high performances materials. The complexity of this understanding demands multiple characterization techniques. We have developed an innovative setup of characterization that couples Atomic Force Microscopy (AFM) with Raman spectroscopy, making possible the successive analysis of the same sample area providing multiple information at multiscale. The AFM is able to give quantitative mechanical properties of the sample at the nanoscale (force-distance curves). Confocal Raman micro-spectroscopy is a complementary technique to access chemical and structural information at a micro-scale, which can be correlated to AFM measurements. In order to optimize the access to the multiple information provided by both AFM and Raman analysis, one should be interested on a well-designed sample preparation technique. We will present our strategy for sample preparation using cryo-ultramicrotomy (CUM), which is suitable for the co-localization of AFM-Raman analyses and for complementary analysis with electron microscopy (ultrathin cross-sections). This approach allows optimization of the manufacturing

process and the investigation of polymer materials during all their life-cycle. In addition, we have developed an original methodology allowing to properly open a thin membrane (20-300µm) and to collect the sections without any epoxy embedding and therefore no chemical contamination. We will display the developed AFM-Raman setup as well as the sample preparation method with CUM, highlighting the challenges that had to be overcome to apply this technique. Through the study of a variety of heterogeneous or multiphase polymer systems we will present the high information content that can be obtained through this method. In particular, this powerful technique will be by the of illustrated study the sol-gel manufacturing conditions on the physical properties of hybrid membranes.

S12-607

Al Aiti Muhannad, Bruenig Harald, Leuteritz Andreas, Gohs Uwe, Wagenknecht Udo, Heinrich Gert

Key attributes for lignin-based high modulus carbon fibers

The potential of the formation of carbon fibers from sustainable, carbon rich resources such as Lignin has attracted both academic and industrial interests in the recent decades. Lignin is the second most abundant natural polymer after cellulose and the most occurring aromatic natural polymer, which is gained as a byproduct of the pulping industry. The high aromatic carbon content enhances theoretically the assumption of the possible formation of a turbostratic or even graphitic-like carbon crystal structure upon the thermal treatment. The literature demonstrates that lignin cannot be processed into carbon fibers with adequate mechanical properties due to its infusibility, poor thermal stability, the heterogeneity of the chemical structure, the wide molecular weight distribution, the etherified chemical structure and the high impurities content. In this research work we demonstrate what the key attributes are needed in order to produce high modulus carbon fibers based on lignin. Three different low sulfur-low ash lignin types: Sofwood lignin (BioChoiceTM); Hardwood lignin (AlcellTM) and annual plant lignin (Soda-Process) were used



for this research work. The three lignin types were fully characterized using a range of analytical methods (TGA, DSC, Py-GC-MS, FT-IR, Raman-Spectroscopy and wide angel x-ray diffraction). The carbonization process of the three lignin types has been investigated. The temperature induced carbon structure formation from lignin has been fully investigated using the Raman-Spectroscopy, FT-IR, Py-GC-MS and WAXs. The heat treatment-induced structural changes of lignin and lignin-like compounds have been compared with that of PAN and MP. Different conclusions regarding the carbon crystal structure formation mechanism have been drawn and the key attributes of the formation of lignin based high modulus carbon fibers have been formulated. Keywords: lignin, carbon fibers, thermal stability, turbostratic and graphitic-like carbon crystal structure

S12-688

Liao Shen-Kung , Lee Chia-Chun, Wu Chung-Tse, Liao Yu-Chen

Study of Dyeing Polylactic Acid Fiber with High Molecular Dyestuffs

Polylactic acid (PLA) fibers have properties that are high crystallization, good flexibility, heat-resistant and very durable. This product has superior performance and may replace polyester fibers in daily use. The main advantage is that PLA is biodegradable and eco-friendly. On disposal a will be released to allow microorganism fermentation and breakdown the high polymer chain within the fiber. It will decompose causing non-crystallization of the fiber that then becomes a low molecular compound. It will crack the fiber and the surface will corrode and wrinkle. Although it is similar to PET in various aspects, dyestuffs which give good dyeing results on PET do not necessarily result in good color yield and fastness properties on PLA. Finally, it will turn into water and carbon dioxide. Therefore, it will not cause more pollution in the environment. In this thesis, we will try to synthesis high molecular disperse dyes (as shown photo), so we can make dyestuffs products that have a strong Van der waals force with the fiber to increase the combination of dyestuffs and PLA. In

order to determine that the dyestuffs have synthesis correctly we used spectrometric identification of organic compounds, utilizing K/S value to compare the dyeing of the fabric under every condition. Finally, we checked degradation of the fabric under temperature, using observation through an electronic microscope, and then using an atomic force microscope to set up a dyeing model for polylactic acid fibers. Keywords: Polylactic acid, crystallization, dyeing model, disperse dye, fastness

S12-689

Liao Shen-Kung, Lin Wan-Li, Lai Yan-Rong

Vinylsulphone Reactive Dye to Dyeing three kinds of fiber with Supercritical Fluid Carbon dioxide

This research of using cationic surfactant KC-3A(Quaternary ammonium salt) modify C.I. Reactive Blue 19 (RB19) to the water dyeing process and dyeing polyester, nylon 6.6 and Tencel (a kind of cellulose) fibers with supercritical fluid dyeing method. The modify dye (MRB19) structure determined by FT-IR. RB 19 and MRB 19 were dyed polyester, nylon 6.6 and Tencel fiber in exhausting dyeing process. The results were found it maybe dye these fibers with good fastness properties and to acceptable color depth. The positive effect of long alkyl of Quaternary ammonium salt modify dye is due to an effect of increased molecular weight and due to an effect of reactive groups on the reactivity of the dye-fiber system to diminish where the alkyl chain increases the hydrophobicity of the dye. The experimental result showed the dyeing with MRB 19 dye of nylon 6.6 and polyester fibers are satisfactory by dyeing in supercritical carbon dioxide with good fastness properties and accept color depth. Besides, Tencel was dyed by supercritical carbon dioxide with pre-treatment of the fiber the color depth was higher than the other on water dyeing process. For Tencel fiber, optimum dyeing results are obtained at 140 °C (300 bar) ; nylon6.6 fiber, optimum dyeing results are obtained at 120 °C (300 bar) ; polyester fiber, optimum dyeing results are obtained at 120 °C (250 bar). The wash and rub fastness of all dyed fibers were rated at between 3-4 and 5. Keywork : Cationic,



Vinylsulphone, Supercritical Fluid, Reactive Dyes, Hydrophobic.

S12-694

Khalifi Taghzouti Othman, El Mabrouk Khalil

Biocomposites materials based on carboxymethyl cellulose/polyethylene glycol/hydroxyapatite for bone regeneration

Novel carboxymethyl cellulose/polyethylene glycol/hydroxyapatite (CMC/PEG/HAP) biocomposites based-scaffolds were studied for their ability to nucleate bioactive calcium phosphate crystals for future bone healing applications. Biocomposites were realised via solution casting. The surface morphology and properties of the scaffold were investigated by infrared absorption spectra (IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), mechanical testing and soaking in simulated body fluids (SBF). The results showed a good interaction between three phases. Moreover, the comparison of SEM images of both the scaffolds indicated that the incorporation of PEG influenced the surface morphology while a better in-vitro bioactivity has been recorded in three phases. Also, the higher CMC/PEG/HAP showed mechanical strength compared to CMC-HAP supportive of bone tissue ingrowths.

S12-709

Wang Shan, Xiong Chuanxi, Guo Shaoyun, Ajji Abdellah

Hydrophilic modification of polypropylene microporous membrane via molecular migration and self-assembly of DMDBS under elongational flow

Polypropylene (PP) is one of the most used polymers for microporous membrane fabrication due to its good thermal stability, chemical resistance, mechanical strength, and low cost. However, the hydrophobic nature of PP membrane greatly limits its application, e.g., being susceptible to fouling when applied in an aqueous application, and suffering from wetting when used as battery

separator or membrane contactor. To address these issues, numerous efforts have been devoted to the hydrophilic modification of PP membrane. In this work, a novel amphiphilic molecule, 1,3:2,4-Di(3,4dimethylbenzylidene) sorbitol (DMDBS), was added into PP during extrusion of the cast films. By regulating the processing conditions, DMDBS can migrate onto the film surface and assemble into the nanofibers network as observed by SEM. The precursor films were fabricated into the microporous membranes according to the common dry stretching strategy same as that of the pristine PP film. Water vapor transmission rate (WVTR) measurements show the WVTR value gets improved as the polarity of DMDBS facilitates the adhesion of the water vapor molecules with the membrane. Consistently, reduced water contact angle can be observed for the PP/DMDBS membrane, compared to that of the neat PP membrane.

S12-725

Fernández Ronco María Pilar, Hufenus Rudolf, Heuberger Manfred

Sub- and Supercritical CO2 assisted melt spinning of biopolymers

Thermoplastic polymers are quite often sensitive to thermal degradation. As a result of conventional melt polymer processing technologies, molecular weight is considerably reduced with respect to the neat polymer, and the mechanical properties of the final material suffer from this reduction in molecular weight. This, however, is the best case scenario allowed for certain polymers, such as PET, P3HB[1], while others are not even able to be processed due to their higher melting point in comparison to the degradation temperature. In recent years, several publications were focused on the use of CO2 as an assisted fluid to carry out polymer melt extrusion[2]. CO2 can be dissolved into the polymer, promoting higher mobility of polymer segments and therefore acting as a plasticizer. The extent of the plasticizing effect will then depend on the amount of CO2 introduced to the system, which should be finely selected according to the thermodynamics of the polymer-



CO2 system. In this work, we extend the applicability of assisted melt extrusion processing to melt spinning of polylactic acid (PLA). A new design of a conventional melt spinning plant to allow a continuous assisted CO2 processing has been evaluated, and different CO2 concentrations have been tested regarding morphological properties of the final fibers. Increasing amounts of CO2 lead to the production of porous fibers with pore sizes in the range of few micrometers, contrary to what has been observed at low CO2 concentrations, where the obtained pores are bigger. However, even these low amounts of CO2 are able to reduce the processing temperature, enabling in that way to preserve PLA from further degradation. References: [1] R. Hufenus, F. Reifler, M.P. Fernández-Ronco, M. Heuberger. Eur. Poly. J. 71 (2015) 12-26. [2] M. Sauceau, J. Fages, A. Common, C. Nikitine, E. Rodier. Prog. Polym. Sci. 36 (2011) 749-766.

S12-95

Lien Wei , Cheng Liao-Ping, Lee Chia-Fen , Don Trong-Ming

Preparation and properties of PCL hollow fiber and its guidance on the proliferation of Schwann cells

Asymmetric polycaprolactone (PCL) hollow fiber was prepared by wet spinning method for the guidance on the proliferation of Schwann cells. The PCL was dissolved in DMAc as solvent incorporated with tween20 as a pore former to modify the structure and the isopropanol solution was used as a soft coagulant. The dope solution with 18wt.% tween20 and 18wt.% PCL was extruded simultaneously with 15% (v/v)isopropanol solution as bore solution from the annulus-shape nozzle. After passing through 10-cm residence air gap, the fiber was immersed in the 25% (v/v) isopropanol solution bath where coagulation occurred. Scanning electron microscope was used to observe the morphologies of the prepared hollow fibers. The results indicated that the hollow fiber inner surface had pore sizes ranging from 10 to 15 micron. On the other hand, the outer surface was smooth and dense.

Furthermore, tensile mechanical properties and thermal properties of the PCL hollow fiber were measured. The culture of Schwann cells inside the hollow fiber was also evaluated.

S12-567

KIM Do-Kun, LEE Joo-Hyung, LIM Ki-Sub, NAM In-Woo, HAHM Wan-Gyu

Structure Control of Poly(Ethylene Terephthalate) Fibers using Capillary Diameter of Spinneret in Melt Spinning Process

In this study, to investigate the effect of capillary diameter of spinneret on fiber structure in melt spinning process, melt spinning of PET of I.V. 1.21 dl/g was conducted by using spinnerets with diameter. different capillary Characteristic relationship between the thermo-mechanical properties of obtained as-spun PET fibers and the spinning conditions such as shear rate and draft influenced by capillary diameter was studied focusing on the control of melt structure of polymer in detail. As expected, fiber orientation and development increased with structure draft influenced by capillary diameter and spinning velocity. However, in the case of as-spun fibers obtained at low spinning velocity; low draft, toughness showed a tendency to increase as capillary diameter decrease. These results indicate that melt structure of polymer can be controlled by the capillary conditions.

S13- Injection Molding and Mold

Keynotes

S13-250

Six Wim, Appermont Raf, Desplentere Frederik, De Keyzer Jozefien, Van Bael Albert

Design And Simulation Of Conformal Cooling Channels In SLM Produced Injection Molds: Effects On Process And Product Quality

In the injection molding process, the cooling step is the most inefficient and time consuming phase. Moreover, the cooling of the product often leads to defects such as unexpected warp due to unevenly distributed cooling in the mold. These conditions can be attributed to the classical manufacturing techniques for injection molds as drilling, milling and EDM. The major drawback of these techniques is their inability to produce 3D curved cooling channels, preferably parallel to the product wall. In the present study, the Selective Laser Melting (SLM) 3D printing technique is used to overcome these limitations. Moreover, SLM printed materials have superior material properties compared to Selective Laser Sintered (SLS) molds . Via numerical simulations and experimental measurements on existing molds, the original situation is characterized. Important parameters average like mold (surface) temperature, temperature gradients, cycle time, time to reach steady state condition, etc... are determined. Conformal cooling and SLM printing both have important constraints which are described in literature. In this study, different than in most other studies, constraints of both techniques as shape, max. diameter, overhangs,... are taken into account to develop mold inserts in order to obtain a conformal cooled core and cavity insert. Thermal and Moldflow simulations are combined to

optimize the design of the conformal cooling channels in the core and cavity inserts. Also CFD simulations were used to optimize the flow distribution and pressure drop in the cooling channel itself. With these simulations, improvements on the process (times and temperatures) and on the product (warp) were obtained. The conformal cooled inserts were printed in maraging steel and extensively tested including in-mold temperatures measurements. Simulations and measurements showed a good agreement. Finally an economical study was made to determine the profits resulting from the conformal mold.

S13-448

Tuinea-Bobe Cristina Luminita, Xia Hesheng, Liu Yan, Whiteside Ben R, Coates Phil D, Fei Guoxia

PEEK crystallisation phases analysis in microinjection moulding

The crystalline state of PEEK is very similar with the one of other polymers containing parasubstituted aromatic moieties in the main chain. Its crystalline structure and morphology is similar to those of such polymers with para-aromatic linear chain structure as polyphenylene sulfide and polyphenylene oxide. What makes PEEK special is its unusually high plasticity and its toughness, and its ability to experience cold drawing at temperatures considerably below its Tg. Not only amorphous, but also semi-crystalline PEEK samples are capable of undergoing sufficiently large plastic deformation even at 100°C. Cold drawing of semicrystalline PEEK results in loss of crystallinity. In order to control the mechanical properties of PEEK and to refine the general knowledge about orientation processes in polymers further investigation is required especial for the case of microinjection moulding. This paper presents data on the change in crystallinity upon micro-injection moulding of PEEK at various mould temperatures, injection speeds and hold pressures. The samples were analysed using X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), and Small-angle X-ray scattering (SAXS).



S13-625

Smit Tim M, Hulsen Martien A, Anderson Patrick D

Predicting the fountain flow instability

Instabilities in polymer processing limit production rates and may influence to some degree the optical or mechanical properties of the final product. One prominent example is the fountain flow instability, which takes place during the mold filling stage of an injection molding process. It has been shown experimentally that these instabilities manifest themselves in the form of a periodic oscillation of the flow front stagnation point between the two walls of the mold channels. The onset of instability is determined by a critical Weissenberg number, at which perturbations to the steady flow are amplified rather than damped. Different values have been predicted numerically in previous work, and . We use the finite element method (FEM) and a number of stabilization techniques for flows of convective (SUPG) and viscoelastic (DEVSS-G) nature to do a full non-linear, transient simulation of a branched polymer melt (XPP constitutive model) in a channel. We investigate both the onset and behavior of the fountain flow instability, with the focus on distinguishing the mechanisms that the instability, drive and their physical interpretation. Several numerical difficulties had to be overcome, like the treatment of the contact point where the polymer is deposited on the mold wall. A perturbation is applied to the symmetric steady state flow field. We analyze the stability of the system by observing the perturbation norm (how much the flow deviates from the steady state flow field). We can also predict for which Weissenberg number a perturbation grows, and for which it is damped. For high Weissenberg numbers, we observe a clear oscillating behavior of the flow field, as seen in experiments.

S13-677

Shaayegan Vahid , Park Chul B., Costa Franco, Han Sejin

Experimental Studies and Numerical Simulation of the Foam Injection Molding Process using Gascounter Pressure

The mechanism of cell nucleation and growth in foam injection molding with gas-counter pressure is investigated through molding experiments and numerical simulation. The molding data includes the visualization of cell nucleation and growth during foam injection molding as well as cavity pressure data. A numerical simulation is developed in this study to model the foam injection molding process with gas-counter pressure. The model is then validated using the experimental results. The effect of process conditions such as filling time, packing pressure and gas counter pressure are examined. The cell nucleation process is modeled using both the fitted nucleation model and the modified heterogeneous nucleation model and the effectiveness of each model is discussed. The importance of material properties such as surface tension, solubility and diffusivity on the bubble nucleation and growth models is also studied.

S13-421

Hartung Michael, Heim Hans-Peter, Giesen Ralf-Urs

The Influence of the Process Parameters in Multi-Component Injection Molding on the Composite Adhesion of the Material Combination PA6 with Self-Adhesive Liquid Silicone Rubber (LSR)

The development of types of LSR with modified adhesive properties enabled the injection molding of thermoplasts to be performed without surface activation. This made it possible for complex components that consist of hard-soft components to be manufactured with low production costs. The adhesion mechanisms induced in the marginal layer during overmolding are meant to lead to a firmly bonded connection of the components so as to obtain a durable composite. However, there are numerous influencing factors and reciprocal effects that affect the quality of the composite strength. the material compatibility, These are the construction of the molded component, the types of stress, and the manufacturing conditions. The injection molding process parameters represent a significant challenge in practice for processing parties in regards to guaranteeing a consistent level of adhesion of the self-adhesive LSR on the thermoplast. An analysis that employed statistic experiment planning was performed to determine the process parameters that are of significance for composite adhesion. It became clear that the temperatures of the tool wall, the holding pressure, and the vulcanization time decisively influence the adhesive strength of the material combination PA6 and self-adhesive LSR. These substantial factors were examined in depth in the further course of events, and a regression equation was created that enables the theoretical composite adhesion to be calculated. The VDI guideline 2019, which defines a standard sample geometry and the execution of peel tests, was used to determine the adhesive strengths.

S13-105

Moritzer Elmar, Martin Yannick

Experimental Investigations on the Fibre Length Degradation in Injection Moulds

The sustainable use of natural resources such as raw materials and fuels, and the carbon footprint of products are becoming increasingly important in many industrial sectors. Due to the substitution of materials such as steel and aluminium, the use of fibre-reinforced thermoplastic materials has increased dramatically in recent years. The properties of injection moulding products are considerably dependent on the resulting fibre length in the components. Increased fibre length results in a significant improvement concerning tensile strength, stiffness and impact strength of the moulded parts. The fibre length reduction occurring in the injection unit is already the subject of current research, while the decrease inside of injection moulds has hardly been investigated. By the use of a special design and arrangement of the cavities, a modification of the runner system, as well as a gate adjustment a reduction in the shortening of the reinforcing fibres in the injection mould can be achieved. Thus, the material potential can be utilized better by these optimizations. In the presented study different injection moulds were examined by determining the length of fibre at different locations along the flow path. From these results, the most important factors influencing the fibre damage can already be identified. To create a methodological description for the prediction of fibre length reduction, approaches to mathematical description of the fibre fracture mechanisms are created. Afterwards a comparison of the functional interrelations and the experimentally determined results is shown.

S13-119

Schneider Dorothea, Schüpbach Kurt, Reichert Volker

Modular Technological Inserts for Injection Molding Machines

Injection molding process yields many possibilities to create innovative plastic part solutions. Multi



component injection molding evolved as one of those technologies, injecting two or more plastic melts next to or within each other within one cycle. The broadening of the field of application of injection molding machines is made possible by the use of intermediate plates with individually suitable "modular technological inserts". The intermediate plate is then mounted to the platen of the injection molding machine between mold and machine. Thereby it is possible that all kinds of platens include the intermediate plates, that is the fixed and the lose platen as well as so called middle platens used in turning plate technology or cube technology. One group of modular inserts make those hot runners which include shut off and control functions to separate or join melt flows from different injection units into one cavity. So these make for the sequential or modules the simultaneous injection of melts necessary to for example produce parts yielding a skin/core structure. Ongoing research aims at modules which allow for the storage of melts while maintaining the pressure within the melt as well as the merging with additional material or even to apply additional energy like for example ultrasound. In conclusion the discourse will point out the possibilities given by this technology concerning cost savings in terms of giving an alternative for the purchase of costly special machinery as well as material savings. In that account projects which already were realized will be shown ranging from production facilities to equipment for research laboratories. The potential flexibility those components are able to add to standard injection molding machinery will be pointed out using a newly developed technology assessment method which bundles and focuses technology aspects by the use of modeling techniques to conquer the full potential of the given technological resources.

S13-125

Holzer Clemens H., Lucyshyn Thomas, Des Enffans d'Avernas Lara-Vanessa

Simulation of the Influence of Thermal Properties of the Mould Steel on the Injection Moulding Process The thermal properties of the mould steel influence the cooling situation in the injection moulding process. There are some experimental studies investigating the influence of special mould materials like copper alloys, but these studies are limited to a few polymers. In the present work, an extensive parameter study with the commercial injection moulding simulation software Autodesk Moldflow Insight was performed to further analyse the influence of the mould steel on the injection moulding process, specifically the cycle time and warpage behaviour. The investigated part was a square box with two thickness variations (1 mm and 3 mm) to see also the influence of the part thickness. A conventional mould steel (W300 from Böhler, Austria) was compared with a newly developed steel grader (W620), featuring approximately double the thermal conductivity compared to the conventional grade. In a systematic parameter study more than 150 simulations were performed with 18 different polymers covering the most common material families including amorphous, semi-crystalline, unfilled as well as glass fibre reinforced polymer grades. The whole mould including the cooling system was modelled with a 3D-mesh and a transient cooling simulation was used. As expected, the higher thermal conductivity reduced the cycle time - surprising was the range of this effect, though (< 5 % up to 25 % of cycle time reduction), which strongly depends on the used polymers and the related processing conditions, but also the part thickness. For the extent of the cycle time reduction a correlation was found with the ratio of the difference between melt and mould temperature to the difference between ejection and mould temperature. With this correlation it was possible to predict the range of cycle time reduction for other polymers based on those three temperatures. Furthermore, the simulations showed that the higher thermal conductivity of the mould steel resulted in a reduced warpage of the part.

S13-158

Aris-Brosou Margaux, Agassant Jean-François, Billon Noëlle, Vincent Michel, Hoffmann Philippe, Popineau Sylvain



Characterization of the Welding of Thermoplastic Sheathing of Offshore Pipelines

One of the challenges in the offshore exploitation of ultra-deep oil resources is to keep the oil at a temperature sufficiently high so that it flows, despite the low water temperature. For that, metallic pipes are thermally insulated by a thick multilayered coating (70 mm) based on polypropylene with hollow glass microsphere (GSPP). The coating extremities of the 12 meter long pipe sections are removed to permit the welding of the metallic tubes. A polypropylene-polyethylene blend is injected to ensure the continuity of the coating in the welding area and thus the thermal insulation. A perfect weld between the two thermoplastic polymers is necessary. Cracks may be observed especially between the coating and the weld and this will damage thermal insulation but also induce corrosion of the metallic tube. To evaluate and characterize the industrial welding, a laboratory scale test has been established. A thick block of GSPP (70×50×25 mm) is placed in a mold. One surface is heated by contact with a hot plate. The polypropylene-polyethylene blend is then injected to form the welding. The samples are instrumented with thermocouples to determine the thermally affected zone which depends of the temperature and time of the heating phase and of the injected polymer. Computational simulation is used with Abaqus[©] software to establish the experimental protocol and predict the evolution of the thermally affected zone. The mechanical properties of the welding are analyzed by tensile performed at different temperatures tests corresponding to different locations in the thickness of the pipe coating. The morphology of the thermally affected zone is studied by scanning electron microscopy, X-ray diffraction and differential scanning calorimetry. The optimal welding conditions between these two thermoplastic are investigated and will be adapted to the industrial process. Keywords: Welding, Injection molding, Thermally affected zone, Thermoplastic.

S13-178

Koch Michael, Schneidmadel Stefan, Qin Xiang

Molecular Orientation and Residual Stresses Impact on Optical Properties of Plastic Lenses

The substitution of glass for plastics progresses with functionalized plastic parts. Especially for optical applications as lenses and visual indicators high quality requirements are desired. Shrinkage and warpage impact on optical properties due to inaccuracies of surface shape consistency. The physical effects of shrinkage and warpage can be traced back to the order and distribution of molecular chains in the plastic material. These effects influence refractivity as well as transmission. Additionally, a gradient in the number of molecular chains correlates with different density values which cause residual stresses in the part. Negative impacts can be deflection and diffusion of light rays which have to be transmitted through the part. This research examines the processing, which effect mechanical and thermal stresses on molecular chains. This leads to a shortening or orientation pattern of molecular chains. To identify the main influences, i.e. injection velocity, melt and mold temperature, a parameter study has been carried out on an injection molding machine and compared with calculated properties such as shear strain in a FEM flow simulation. Correlating the transmittance of the test specimen with calculated stresses, a proposition for optical behavior of plastic parts can be determined. PMMA, PC and cyclical olefin types are compared. The temperature regime during cooling of these lenses show major influence on achievable optical properties. Higher melt temperature leads to higher transmittance through the material. This finding can be confirmed by subsequent heat treatment leading to lower residual stresses and better transmittance. Reduced injection speed also improves transmittance. A prediction of residual stresses in optical lenses is possible using FEM flow simulation, although variant cooling conditions lead to a difference of measured residual stresses and calculated shear stresses. Comparisons between calculated and measured results are presented.

S13-240

Bakharev Alexander, Ray Shishir, Costa Franco, Astbury David, Speight Russell



Taking into account normal stresses during simulation of thermoplastic injection molding

The article deals with the effect of the first and the second normal stress difference on the predicted flow front and pressure distribution during the filling stage of the thermoplastic injection molding. The normal stresses are predicted using the nonlinear Criminale-Ericksen-Filbey model incorporated into a comprehensive 3D simulation software for moldfilling analysis. The model parameters are estimated from the viscosity curves using the Abnormal Cox-Mertz rule. The additional term improves the prediction of the so called ear-flow effect (melt racing on the edge of the cavity) as well as pressure predictions at high injection rates.

S13-248

Sorgato Marco, Masato Davide, Lucchetta Giovanni

Effects of different mould coatings on polymer filling flow in thin-wall injection moulding

Injection moulding of parts having small flow length/thickness ratio is a challenging task for both micro and packaging applications. In the filling phase, high-speed injection can cause a raise of cavity pressure, which prevents the complete replication of the mould geometry. Therefore, in this paper, the effects of mould coatings, e.g. diamond-like carbon, chromium nitride and silicon oxide, were investigated. In particular, the filling of a representative micro-part was studied as a function of mould coating, injected polymer and different process parameters, in order to identify the best processing conditions in terms of cavity pressure and part quality.

S13-259

Zaccone Marta, Armentano Ilaria, Cesano Federico, Scarano Domenica, Cravanzola Sara, Frache Alberto, Monti Marco

Morphology and electrical properties of injectionmolded PP carbon-based nanocomposites

CNTs are well known to be electrically conductive nanofillers that can considerably modify the

electrical properties of insulating polymers [1, 2]. properties However, final of polymer nanocomposites based on CNTs, are strongly affected by the processing technologies [3]. In most of the techniques for obtaining a final polymerbased item, the morphology and the final properties of CNT-polymer nanocomposites are strongly influenced by what occurs during the shaping phase, when the polymer is in the molten state [4, 5]. In this work, PP/MWCNT nanocomposites were developed with special care to the processing condition. The MWCNT dispersion was performed in a co-rotating twinscrew extruder and the obtained nanocomposites were injection molded to obtain the desired shape of the testing specimen. Electrical characterization was then performed in the produced materials in the three main directions, i.e. the one longitudinal to the flux of the material while filling the mold and the two transversals. Due to the fact that injection molding is one of the most important processing technique to convert polymers into objects, the aim of this work is to investigate the of the injection molding process influence conditions, on the non-conductive (or lessconductive) skin layer which is formed on the sample and its effect on the electrical properties of PP/MWCNT nanocomposites. As a results of the electrical characterization, it was obtained that the tuning of process conditions influences the electrical properties of the produced sample. This has explained by the multilayered been morphology skin-core-skin, which was studied by SEM and validated by a theoretical also mathematical model. Keywords: nanocomposites; carbon nanotubes; polypropylene; injection molding; skin effect Bibliography [1] P.C. Ma, Composites: Part A, vol. 41, pag. 1345 – 1367 (2010) [2] S. K. H. Gulrez, Polym. Compos., vol. 35, pag. 900 - 914, (2014) [3] S. Versavaud, Polymer, vol. 55, pag. 6811 - 6818, (2014) [4] S. Pegel, Polymer, vol. 49, pag. 974 – 984, (2008) [5] J. Tiusanen, Composites Science and Technology, vol. 72, pag. 1741 - 1752 (2012)

S13-417

Lin Gwo-Geng, Chao-Tsai Huang , Chiu Hsien-Sen



The Influence of Polymer Viscoelasticity on the Optical Features during an Optical Lens Development

In modern life, polymeric optical lens has been utilized in many electronic devices, such as camera, mobile phone, tablet, and so on. Although hundred million lenses are produced annually for those devices, the quality is the key to the main suppliers. Indeed, the optical quality is affected by both the geometric features and the optical birefringence. However, how the material's viscoelasticity influences the optical features is still not fully understood yet. In this study, we have systematically investigated the viscoelastic effects on the optical property of a lens made of Zeonex COP 480R material by the traditional injection molding, simulated with n = 0.4 and τ^* = 217,000 Pa in the Cross model. We assumed that the rheological parameters can be modified artificially based on the White-Metzner model of viscoelasticity, in which the viscosity was of the Cross-type model. Results show that if the powerlaw index (n) was changed from 0.1 to 0.6, the total fringed order has no significant difference, but the fringed patterns was varying dominantly in the perpendicular direction, instead of the flow direction. This situation was matched with the distribution of the flow-induced residual stresses. Moreover, if the τ^* in the Cross model was varied from 100,000 Pa to 300,000 Pa, the total fringed patterns were apparently changing from being dominated in the flow direction to being in the direction perpendicular to the flow. The influenced width of the fringed patterns was almost linearly increased with the increasing τ^* . The results can be applied as some guideline for either the further material modifications or the new material developments.

S13-424

Siepmann Jens Peter, Wortberg Johannes, Heinzler Felix Alexander

Investigation of the two-dimensional shape of caverns viewed in the context of electroplating quality demands using image analysis By processing technical polymers like acrylonitrile butadiene styrene or polycarbonate/ acrylonitrile butadiene styrene blends with injection molding machines for a following electroplating coating there is, next to the electroplating parameters, the surface of the injection molded part which is responsible for the conjunction of the polymer and the metal and influenced by processing parameters. The influences of injection molding parameters on the resulting caverns in polymer surfaces are investigated. For this purpose relevant processing parameters influencing polymer surfaces are examined. Further, a developed objective image analysis method to quantify the two-dimensional shape of caverns is used to investigate part surfaces. The analysis is based on scanning electron microscope (SEM) images of chemical etched polymer part surfaces (ABS, PC/ABS). For quantifying the surface, meaningful key figures, such as roundness, degree of orientation, caverns/µm² and area of caverns are emerged. Different ABS and PC/ABS Materials are tested, compared and coherences between shape of the caverns, processing parameters, material properties and geometry influences are elaborated. Therefore, a factorial design of experiment with varying the screw advance speed, mold temperature and melt temperature is conducted. Two different spots on the part, which differ by shear stress and strain are selected by the support of 3D computational injection molding simulation. The effects of processing parameters and geometry to the surface are elaborated and compared to the state of the art.

S13-457

Liparoti Sara, Calaon Matteo, Speranza Vito, Tosello Guido, Pantani Roberto, Hansen N. H., Titomanlio Giuseppe

Effects of Fast Mold Temperature Evolution on Micro Features Replication Quality during Injection Molding

The growing demand to manufacture, with high accuracy, functional structures in the micro and sub-micrometer range polymer based microsystem products calls for reliable mass production processes. Being injection moulding (IM) the



preferential technology employed for polymer mass fabrication and mould temperature one of the most influential process parameter to enhance polymer replication at the micro meter scale the present study investigates effects of fast mould temperature evolution on final replication quality of produced injection moulded parts. Micro features master geometries were produce by UV lithography and subsequent nickel electroplating. The mould temperature was controlled by a thin heating device, composed by polyimide as insulating layer and polyimide loaded carbon black as electrical conductive layer, that is able to increase temperature on mould surface in few seconds (70°C/s) by joule effect and cool down soon after. This heating device allowed to maintain mould temperature at a constant value for a time that could be equal to the filling time or longer. A fully characterized isotactic polypropylene was used as the polymer substrate material during experimental injection moulding. The experiments revealed that the replication was mostly sensitive to the cavity pressure and mould temperature. In particular holding pressure and mould temperature increase enhanced the replication. Also the heating time increased the replication quality. The replication ability was also correlated to the morphology of the samples.

S13-468

Theriault Matthew, Yoeuth Suzanne, Matar Jessica, Martin John, Bello Dhimiter, Barry Carol

Investigation of Nanoparticles Emitted When Injection Molding Neat and Additive-filled Polypropylene and Polycarbonate

Injection molding of thermoplastic resins is well known to produce volatile organic compounds which can adversely affect operator health, but there is little understanding of particulate emissions. Recent molding of nanocomposites produced no emission of carbon nanotubes, but emission of organic nanoparticulates of unknown composition. This work is an investigation of those particulates with the gaseous phase emissions of airborne nanoparticles collected during injection molding of neat and additive-filled polypropylene

polycarbonate compounds. The starting and materials, collected nanoparticles, and molded parts were analyzed using thermogravimetric analysis, thermogravimetric analysis coupled with Fourier-transform infrared spectroscopy, differential scanning calorimetry, and gas chromatography-mass spectrometry. The results were analyzed to determine the composition of the nanoparticulates and compounds lost from the polypropylene and polycarbonate during injection molding. Characterizing these emissions will allow for a better understanding of the precautions and safety equipment needed during melt processing.

S13-473

De Jesus Vega Marisely, Mead Joey, Barry Carol

Injection Molding of Micro and Nanostructured Surfaces From Liquid Silicone Rubber

Although liquid silicone rubber has very low viscosity, cures rapidly, is biologically inert, and has high temperature resistance, there is limited research on injection molding of microstructures from liquid silicone rubber. This work was an indepth investigation on the effects of feature dimensions and processing conditions on liquid injection molding of liquid silicone rubber. Tooling contained feature sizes of 100 to 0.1 um with aspect ratios and spacing ratios of 1:1, whereas processing conditions included mold temperature and vulcanization time. Replication (feature definition and depth ratio) was measured using a scanning electron microscopy and was then correlated with processing conditions and tooling feature sizes.

S13-483

Kietzmann Clinton, Rigoni Guillaume , Chen Lu, QUILLIET Stéphane

Induction Heating Simulation And Validation For The Plastic Injection Molding Process

In mold induction heating is proving to be an efficient method of producing high quality low cost injection molded parts. Autodesk Moldflow is the world leader in plastic injection molding simulation products. RocTool is the foremost technology

provider of induction heating equipment for plastic injection and compression molding. Autodesk Moldflow and RocTool have collaborated to develop a three dimensional finite element simulation of the Maxwell equations for the induction heating process in plastic injection molding. This paper describes the key features of this electromagnetic solver together with validation results from tests conducted on existing molds. In order to simulate induction heating a true three dimensional finite element solution of both the real and imaginary components of the Maxwell obtained, equations was without any simplifications or assumptions. The derivation and the numerical techniques used in implementing this unique solution of the Maxwell equations on the injection mold domain are presented. Simulation of induction heating offers the mold designer an insight into the mechanisms of induction heating. Induction heating creates a very hot non-uniform temperature distribution concentrated in the surface skin of the mold body very quickly. Ideally the surface skin layer touching the part is at the material's melt temperature during the filling phase of the injection molding cycle. With most of the heat concentrated in the very thin skin region of the mold touching the part, the mold can be cooled down to ejection temperature very quickly thereby, ensuring a desired short cycle time. In the paper, induction heating simulation is demonstrated on a real world model. The simulated results are compared to results provided by RocTool that were measured in their test facility. Any discrepancies between the simulated results and the experimental results are discussed in detail.

S13-485

Meyer Tino, Sherratt Paul , Haworth Barry, Harland Andy, Holmes Chris , Lucas Tim

Complex Injection Moulded Components -Bridging the Knowledge Gap

The specification of new or enhanced materials is often based on results from simplified injection moulded test specimens produced by idealised melt flow conditions. Design data obtained is then used to predict the mechanical behaviour of a final part, using practical or computational techniques, often without sufficient attention to the change in performance due to differences in flow behaviour when injecting more sophisticated geometries. To overcome this problem without being dependent on a time-consuming prototyping phase, the aim of this investigation is to evaluate a new mould concept which allows controlled modification of the material flow by adding specific mould tool design features which lead to flow hesitation, creation of weld-lines and combinations of each of these irregular flow phenomena. Verification of these effects from practical research based upon polyamides was evaluated by thermal analysis (DSC), whilst optical microscopy was used to highlight microstructural differences of injection moulded test components produced with the concept mould and in more complex products. In parallel, the influence on the mechanical performance was investigated by testing specimens obtained from regions of the concept tool with varying microstructural features, with particular focus on high-velocity impact, tensile and dynamic fatigue properties. Results showed significant changes in impact energy, tensile toughness and fatigue behaviour for the new mould specimens produced at certain locations within the concept mould where flow modifications were evident; similar behaviour is anticipated for finished parts with similar microstructural features. Therefore, this approach narrows the existing knowledge gap by delivering results with a higher practical relevance while still allowing consistent sample preparation to comply with industrial standards. KEYWORDS: Injection moulding / concept mould /

S13-494

Nguyen Thi Thanh Binh, Yokoyama Atsushi, Hamanaka Senji, Yamashita Katsuhisa, Nonomura Chisato

microstructure flow hesitation / weld lines

Advanced Fiber Orientation Prediction for High Filler Content Short-fiber/Thermoplastic Composites

Properties of fiber-reinforced composite are dominated by the microstructure of the fabricated part rather than the properties of constituent



materials. As the microstructure of composite is related to the flow-processing route of the fiberreinforced suspensions and the geometry of the mold, the microstructure of composite can be tailored in order to achieving high-performance composites by exercising control over the flow processing. Thus, numerical methods are used to model the resin flow, the fiber orientation, and mold design, and they become important challenges during molding process. In our previous research, a theoretical fiber-fiber interaction model with a global fiber interaction coefficient was developed. In this study, the three-dimensional (3D) fiber orientation distribution is predicted by combining our developed fiber interaction model and improved Anisotropic Rotary Diffusion -Retarding Principle Rate (iARD-RPR) model. The fiber orientation calculation started from the gate, and from a random orientation to alignment orientation is investigated at that location as the inlet boundary condition. Moreover, simplified deformation behavior of fountain flow was employed for fiber orientation in the flow front region. In experimental, short-glass fiber-reinforced polyamide 6 specimens produced using plateshaped cavity having three different thicknesses ranging from 2 mm to 4 mm and with the fiber contents ranging from 30 wt% to 65 wt% are carried out using injection molding. The 3D fiber orientation observation and measuring are exactly and automatically examined by Micro-computed Comparisons tomography system. with experimental results, it is showed that this prediction advanced methodology can be effectively used for the 3D fiber orientation prediction in complex parts.

S13-495

PPS[®]32

Pacher Gernot Alois, Hutterer Thomas, Berger Gerald Roman, Friesenbichler Walter

Influence of Processing Conditions and Filler Type and on the Crystallinity of PLA Compounds

It is well known that neat PLA is not inclined to crystallization, which results in inferior mechanical properties compared to commodity plastics like polyethylene. To empower PLA for commercial

32nd PPS International Conference 2016, Lyon, France

applications, the overall degree of crystallinity has to be increased. In this study, the crystallinity of PLA-compounds was influenced via (a) processing conditions and (b) addition of fillers. Mold temperatures for conventional injection molding on PLA are generally set in the range of 10 °C to 25 °C while the crystallization temperature lies well over 100 °C. In general, this leads to amorphous parts. Due to this fact, tempering is often used as a second manufacturing step in order to generate crystallinity. Another well-known approach to promote crystallization in PLA is the addition of fillers as nuclei. In this work, an in-mold-tempering approach via Rapid-Heat-Cycle-Molding was designed and conducted to enable single-step manufacturing of crystalline PLA parts. To enable crystallization, the mold temperature was elevated above the crystallization temperature before start of injection, held for prolonged times (time for inmold-tempering) and rapidly cooled down to conventional mold temperatures again. In order to evaluate the effectiveness of the in-mold-tempering approach, different PLA compounds (with varied amounts of silica and talcum) were tested in addition to neat PLA, followed by measurements of the degree of crystallinity via differential scanning calorimetry.

S13-515

Fischer Matthieu, Kuehnert Ines

Micro Injection Molding: Investigation of Interfacial Fracture Behavior

In relation to standard injection molding the challenges of testing methods, increasing complexity as well as the process and equipment requirements of micro injection molding will be discussed. The mechanical behavior of micro injection molded specimens was investigated. Therefore, a new tensile test specimen was developed to evaluate systematically the impact of interfaces (e.g. weld lines/ multi material interfaces) on small scale applications. A failure observation of micro injection molded specimen was carried out under a light microscope. The processing effects on spherulitic structure were linked to bonding
strength, material properties and injection molding simulation.

S13-518

Kuehnert Ines, Zimmermann Martin

Assembly injection molding of hard-soft material composites: Processing and adhesive strength test

Assembly injection molding (AIM) provides excellent possibilities for the economical bonding of polymer materials either among themselves or with other materials. Local functionalities can be placed in the product without any restrictions. Typically, different mechanical properties are required, so that the so-called hard-soft material composites that are made from thermoplastics (hard component) and thermoplastic elastomers (soft component) are already established on the market for many decades. Their functionality is focused on damping and sealing properties and comfortable haptic perception as well. Due to the still increasing relevance of these plastic-material composites for new products, it is necessary to further extend the understanding of fundamentals of material bonding mechanisms and knowledge about applications with regard to their adhesive strength and failure behavior. In order to give an up-to-date overview, this work covers therefore the following topics: interfacial effects and compatibility principles, specifics of processing, testing methods for soft-rigid plastic and metal-soft plastic composites as well as test standards, including a discussion of the adhesive strength test results.

S13-52

Huang Chao-Tsai, Tseng Huan-Chang, Chang Rong-Yeu, Hwang Sheng-Jye

Study on the Fiber Breakage History through a Barrier Structure Screw in Injection Molding

In recent years, using short and long fiberreinforced thermoplastics (LFRT) to replace some metal components has become one of the most attractive lightweight technologies. However, the microstructures of fiber inside plastic matrix are too complicated to manage and control during the injection molding through the screw, the runner, the gate, and then into the cavity. On the other hand, to enhance the plastification for better melt quality, the barrier type screw is very popular. But how the barrier design will influence the long fiber breakage is still not clear yet. In this study, we have integrated the screw plastification, to injection molding for fiber microstructures investigation. Specifically, we have focused on fiber breakage history through a barrier structure screw in injection molding. Results show that when 13 mm carbon fibers go through the barrier screw, the length of fibers is down to 1.75 mm (the number average) at the exit of screw. It is 10% shorter than that when fibers go through the regular type screw system. Moreover, the fiber breakage phenomena for two types of fibers (glass fiber and carbon fiber) are also investigated. At the exit of the barrier screw, the number average of glass fibers is 2.21 mm. Clearly, the carbon fiber is easier to be broken. Furthermore, the carbon fiber length distribution has higher peak at the exit of the screw. This discovery is consistent with the experimental results of some current literature.

S13-556

Nair Karthik Jayan, Whiteside Benjamin, Babenko Maksims , Grant Collin, Coates Philip

Comparison of mechanical and dimensional properties of polymeric microneedle arrays manufactured by micro-Injection moulding and ultrasound moulding.

Abstract The emergence of microneedle (MN) technologies offers a route for a pain free, straightforward and efficient way of transdermal drug delivery, but technological barriers still exist which pose significant challenges for manufacture of MN systems with high volume outputs at low cost. Our aim here is to develop new routes for MN manufacture using micro-injection and ultrasound moulding processes with high performance engineering thermoplastics (Poly ether ether ketone and Polycarbonate). For such small polymeric components, subjected to the extreme stress, strain rate and temperature gradients encountered in the micro-moulding process, detailed material



characterisation combined with process monitoring is desirable to highlight variations in moulding conditions and this will assist in creating a viable manufacturing process with acceptable quality products. Polymeric MNs should have good mechanical strength to sustain the insertion force to pierce the human skin and delivery the drugs. Therefore it is of paramount importance to check the mechanical properties of the moulded microneedles. A depth-sensing nanoindentation devices allow the amount of penetration of an indenter into a material to be measured as a function of applied load. In this study a nanoindentation technique was employed to study the material hardness, contact depth and modulus of the moulded MN samples. The MNs manufactured from both the moulding processes were also dimensionally assessed were then geometrically using a range assessed of characterisation techniques such as atomic force microscopy, confocal microscopy and scanning electron microscopy. The output from these studies will be able to measure the responses of microscopic regions which can be a key to understanding mechanical behaviour of the polymeric microneedles. Keywords: Micro-injection moulding, microneedles, poly ether ether ketone, moulding, polycarbonate ultrasound and nanoindentation.

S13-572

Gilson Millan-John, Caton-Rose Phillip , Whiteside Ben, Kelly Adrian

Fibre Dispersion and Fibre Length Distribution in Long Glass Fibre Reinforced PP Injection Mouldings

Fibre reinforcement of commodity polymers, such as polypropylene, is an established method for the manufacture of components with significantly increased mechanical properties compared to their unfilled counterparts. Glass fibre polymer composites incorporate short glass fibres, 250 μ m, or long fibres, up to 12 mm in length, within a polymer matrix. The mechanical performance of any moulded component is highly dependent on the final fibre orientation, in the case of short fibres, alongside fibre length distribution and overall fibre dispersion, long fibres. In this paper a 40 wt% long glass fibre filled PP has been used to investigate the effects of processing parameters, including nozzle geometry, on fibre degradation and dispersion during the injection moulding process. Results show that over 50% of 12 mm long fibres have reduced in length to between 0.25 and 1.25 mm by the time they enter the mould. Additionally, micro-CT images show a complex flow field within the nozzle section prior to the mould, which in some cases continues down the sprue.

S13-588

Pohl Markus, Stommel Markus

Designing and producing joining partners for a multi-material design by injection molding

The development of weight-optimized structures uses increasingly a multi material design. This approach uses the concept that the right material is used in the right place. Based on this idea the connection between different materials gains in importance. Depending on the joining partners and the processing chain different approaches can be applied. This contribution focuses on direct (adhesive-free) adhesions between thermoplastic polymers and thermosetting polymers. The polymer-to-polymer connection is realized by mechanical interlocking which consists of different scales - a micro-scale such as the surface roughness and a macro-scale like structural elements on the surface. The thermoplastic join partner is produced by injection molding. This large scale production process is suitable for this application because the surface structure is casted directly onto the part. There is no need for a subsequent processing step mechanical interlocking. to form the The thermosetting join partner is a fibre reinforced plastic which is produced by an injection process, the resin transfer molding. This process is also used for a high-volume production. It uses a liquid resin that is inserted into a mold where the reinforcing fibres and the before-mentioned thermoplastic join partner are located. The resin forms the adhesion between the polymers by interlocking on the surface structure of the thermoplastic part. This



contribution treats the production and the design of different surface structures on thermoplastic parts and their ability to transmit forces on the interface to other materials. Thus a way to produce costeffective multi-material components without additional adhesives is presented.

S13-620

Larochette Mathieu, Brulez Anne-Catherine, Benayoun Stéphane, Vera Julie

Replication of hierarchical textured surfaces by injection molding: Global approach for the optimization of the replication quality

Previous works allowed the to improve understanding of the influence of the process parameters, as example like the mold temperature or the injection velocity on the efficiency of the filling of cavities and texturations [1-3]. However, few studies quantifies the effect of each of these parameters alone on the quality of the replication. In this work, we develop an original method which allows to understand the phenomena taking place during all the injection molding steps, the real physical response of the material to the injection molding process and the measured replication rate for the polymer parts is performed. In an industrial context just as much scientific, it is essential to understand the process of filling and the interaction between polymers and multiscale texturation. We developed an instrumented mold with standard components to handle all the key parameters of the molding machine injection (pressures and temperatures of the polymer during the filling, (volume and air trapped into cavity) and the in-situ response of the material. Multi-scale topographical analysis were carried out comprising a detailed analysis of the surface roughness in terms of statistics and replication rate. This original method allows us to obtain input datas for the numerical simulations [4] and to understand the influence of textures on each of the injection molding process steps. Optimal conditions of injection have been determined in order to get optimal qualities of replication on various industrial injection molding machines. [1] N. Zhang et al; "Characterization of Micro injection molding process for the replication

of micro/nano features using bulk metallic glass insert", Int. J. of Engin. & Tech., 5(2), 2013 [2] J.C. Vasco; "Thermo-rheological behavior of polymer melts in microinjection moulding", J. Micromech. Microeng. 19, 2009 [3] J. Vera et al; "Influence of the polypropylene structure on the replication of nanostructures by injection molding", J. of Micromech. & Microengin., 25 (11), 2015 [4] Rebecca Nakhoul et al; "Modeling the injection of textured molds", CFM 2015 Lyon Keywords: Injection molding, hierarchical structures, replication, industrial conditions

S13-655

Khatavkar Vinayak, Seitz Michelle, Bulters Markus

Adhesion In Overmolding Applications

Overmolding is a process where one material is molded over an already solidified part. To save labor costs, reduce cycle times, and achieve improved part quality two-shot injection molding is growing in popularity [1]. Adhesion between the overmolded materials is a critical requirement. In order to achieve adequate adhesion, the polymer chains in the overmolded surface must achieve sufficient mobility to allow interdiffusion or chemical reactions to occur. For high performance polyamides, this is often challenging due to their high melting points. For a symmetric flat interface, the contact temperature estimated as the average between the temperature of the first shot surface and the second shot melt temperature is well below the melting points of polyamides of interest. Trivially the contact temperature can be increased by either raising the mold and or melt temperatures. Practically, however, increasing the mold temperature leads to unacceptable cycle times or poor part integrity while concerns about degradation limit melt temperatures. Our idea to overcome the above problem which is explored in this work is to use InterFacial Geometries(IFGs). IFGs are protruding ribs with a favorable area-tovolume ratio which are able to accept heat from a larger volume of melt than a flat interface. By making first shot with IFGs, local melting can be adhesion achieved promoted and without detrimentally impacting cycle times or melt



degradation. This study illustrates by a combination of modeling and experiment how IFGs work and can be optimized to give good adhesion in overmolding applications.

S13-698

Porsch Alexander, Andrae René, Wortberg Johannes, Koehler Peter

Knowledge based approach for an automatic rheological optimization of injection molded parts

The motivation for the presented approach results from the absence of an integrated method of supporting the designing of injection molded parts. Thereby, the focus lies on the rheological optimization, which is ensured by knowledge transfer from the production engineer to the designer. I. e. the mentioned aim is achieved by creating a knowledge base including the expert knowledge. This method is based on an integrated product simulation containing the interconnection of CAD and CAE-systems. The first step in the process is a filling simulation done by a standard injection molding process simulation software. The gate location is considered as fixed and optimal. Nevertheless, it is still possible that a uniform mold filling is not reached. To determine an uneven mold filling the results of the simulation are exported as scalar values to a post processing software tool. Thus, a knowledge based analysis of the results using user defined parameters based on flow length, pressure distribution, etc. is enabled. To enhance the filling the original part design is modified by adding flow aids or barriers. Their positioning is calculated by the post processing software tool and this result is returned to the CAD-system. There the preliminary design is done by an analytical approach. By iterations of the mentioned method the geometry of the flow aids or barriers and thus the mold filling are improved. The presented approach is illustrated exemplarily by an injection molded part. As a result the designer is supported methodically in designing injection molded parts by implementing and using expert knowledge. So the number of iterations and the development time (costs) are reduced.

S13-726

Hamanaka Senji, Yamashita Katsuhisa, Nonomura Chisato, Nguyen Thi Thanh Binh, Yokoyama Atsushi

Measurement of Fiber Orientation Distribution in Injection-molded Composites with High Filler Content

Short-fiber-reinforced composites are widely used in a number of industries and applications, including in the transportation industry, and in business machine, durable consumer items, and sporting goods. Properties of fiber-reinforced composite depends on its fiber orientation distribution. Thus, knowing the fiber orientation is of great importance, and a number of researchers have been interested in developing useful and accurate techniques for determining the fiber orientation in injection-molded parts formed from short-fiber composite. However, out-of-plane orientation was preformed manually and difficulties arise when employing the technique in the case of composites with high fiber contents, over 50 wt%. In this research, short-glass fiberreinforced polyamide 6 specimens produced using two different plate-shaped cavities having three different thicknesses ranging from 2 mm to 4 mm and with the fiber contents ranging from 30 wt% to 65 wt% are carried out using injection molding. The three-dimenstional (3D) fiber orientation observation and measuring are examined by Microcomputed tomography system Y.Cheetah µHD which cooperated with a calculation software using a calculation model (ex. Monte-Carlo Model). Herein, detailed 3D fiber orientation distribution from skin to core at different locations in high filler content composite specimens is automatically, and fast clarified. This novel measurement methodology may enable us to evaluate the ability of new model theory, the effective of implementation procedure for fiber orientation and mechanical property prediction in injection-molded composite.

S13-743

Wang Shiwei, Li Qian, Shen Changyu, HU Guohua



Morphology and mechanical properties of microinjection molded polymer products

Novel multi layer and stripe morphology were investigated in micro-injection molded isotactic polypropylene gear. The annealing treatment was performed on the gear tooth under different temperature and time to control its morphology evolution. The effects of the mold temperature of micro-injection molding on the microstructures and mechanical properties of isotactic polypropylene gears were studied. The micro-injection molded gears present a skin-core type of morphology. The core layer is much thicker than the core and shear layers. Nanoindentation tests show that the modulus decreases along the flow direction and increases with increasing mold temperature. The highly oriented shear layer has the highest nanoindentation modulus compared with the skin and core layers.

S13-765

Lin Chung-Chih , Lee Bean-Yin, Chen Jenn-Yih, Lee Guo-How

Design and Fabrication of Injection Mold Using Gypsum

Rapid tooling (RT) technology has been recognized as a good approach for the initial trial during the product development process. Lots of RT methods are revealed for making tools with different pilot Gypsum (calcium sulphate run requests. dehydrate) is a well-known mineral obtained from natural resources and burned to calcium sulfate hemihydrates or anhydrite to be used as plaster of Paris in different applications such as buildings, art or ceramics. The inherent property of gypsum is weak and porous so that the mold made from gypsum can only be used for low pressure molding process, i.e., casting. In an attempt to provide a rapid and economical alternative for making mold with low volume production, the potential of gypsum as a mold insert used in injection mold is developed. The design and fabrication process of the mold insert was implemented, starting with the gypsum powder, mixing the powder with water and binder to form plaster. Before the plaster

solidified, an additional compression was introduced to enhance its strength. Then the plaster was machined into a mold insert and validated by optimal injection test. The combination of ingredient, 58wt%/37wt%/5wt% of gypsum/water/binder, was found to work best. A coin pattern was selected to build the gypsum insert for checking the replication accuracy of the molded part. In addition, the life cycle of the gypsum insert for injection molding was also evaluated in this study. Keywords: rapid tooling, gypsum, injection molding,



Poster

S13-432

Jeong Euichul, Kim Jongsun, Yoon Kyunghwan, Lee Sangyong, Son Jungeon, Lee Sunghee

A Study on manufacturing thermoplastic CFRP products using Injection/Compression molding process

Recently, subdivided and sophisticated industry causes energy depletion and environmental issues. That problem causes fuel efficiency and exhaustion of carbon dioxide regulation. So many company need to develop lightweight and environmental materials. CFRP(Carbon Fiber Reinforced Plastic), plastic combined with carbon fiber composite materials, was had the limelight by substitute materials because it has high specific strength and stiffness. In this paper, thermoplastic CFRP manufactured by using a composite was injection/compression molding process. Previously to manufacture using a injection/compression molding process, an experiment of thermoplastic CFRP was progressed by using a hydraulic press forming process. It was for judgment of impregnation and getting a basic properties of thermoplastic CFRP. The results of hydraulic press forming process, as the volume fraction of carbon fibers increases the tensile strength of the composite is increased. On the basis of the result of press forming results, mold for injection/compression molding process was designed. The injection/compression molding process was to make it easier to impregnate matrix to carbon fiber. The impregnation rate of thermoplastic CFRP product by used injection/compression process was not good because of frozen layer of resin. So, in order to improve this, the molded product was reproduced by insert and overmold process. It has a faster production cycle time to make thermoplastic CFRP by using a injection/compression molding process.

S13-737

Wang Shiwei, Li Qian, Hu Guo-Hua

Morphology and mechanical properties of microinjection molded polymer products

Novel multi layer and stripe morphology of a micro-injection molded isotactic polypropylene gear are investigated. The gear tooth is treated thermally at different temperatures and periods of time to control its morphology. The effects of the mold temperature of the micro-injection molding on the microstructures and mechanical properties of the gear are studied. The micro-injection molded gear presents a skin-core type of morphology. The core layer is much thicker than the core and shear layers. Nanoindentation tests show that the modulus decreases along the flow direction and increases with increasing mold temperature. The highly oriented shear layer has the highest nanoindentation modulus compared with the skin and core layers.

S13-86

Hopmann Christian, Theunissen Matthias, Ochotta Philipp, Katmer Sukran, Bobzin Kirsten, Öte Mehmet, Linke Thomas Frederik, Liao Xifang

Production of plastics parts with partially or fully metallic surfaces using the In-Mould-Metal-Spraying (IMMS)

Although various technologies are capable of producing plastics/metal hybrid parts for electrical applications, they all have disadvantages in common due to several manufacturing steps and limitations in productivity or the level of achievable geometrical part complexity. In addition, the material groups are often regarded separately, particularly when it comes to the materials-related forming processes. One approach to overcome these disadvantages, which is currently examined at the Institute of Plastics Processing (IKV) and the Surface Engineering Institute (IOT) at RWTH Aachen University within the scope of the Cluster of Excellence "Integrative Production Technology for High-Wage Countries", is to combine the plastics injection moulding and the thermal spraying of metals to create a new multi-integrated process with regard to the production of



plastics/metal hybrid parts. The In-Mould-Metal-Spraying (IMMS) is intended to enable the integration of metallic areas on plastics parts. In the first step a metallic layer is applied to specific areas of the mould's surface using the thermal spraying, which is immediately followed by the plastics injection. During this second step the metallic layer is transferred onto the plastics part. The plastics part including the transferred partially metallic surface is then removed from the mould. A strong, permanent connection between the plastics and the metallic layer and an exact outline replication of the metallic layer in the pre-assigned areas are to be realised. To develop and improve the new technology the influence of different plastics types on the transferability of the metal layer onto the plastics part has been investigated systematically. Additional evaluations relating to the component design are to be made with the help of a more complex test part which possesses a structured surface. The results provide valuable information on the favourable process configuration and plastics/metal combination.

S13-99

Hopmann Christian, Theunissen Matthias, Schmitz Mauritius, Nikoleizig Philipp

Development of a highly segmented temperature control in injection moulding for reduced warpage and increased process stability

In the plastics processing industry a growing demand for precision moulded parts can be identified, especially regarding avoidance warpage as well as achieving high process stability. To meet these requirements, an approach based on local material properties within the injection mould during the moulding process is pursued, utilising the so-called pvT-optimisation. The goal of the pvToptimised process is the optimisation of the shrinkage by establishing a constant specific volume (v) of the melt and part during the injection moulding process. This is pursued by controlling the holding pressure according to the in-mould pressure (p) and part temperature (T). Due to the nature of flow dynamics and material characteristics the pressure within the mould is

inhomogeneous. Especially in injection and compression phase, pressure varies from ambient pressure at the flow front to a high injection pressure caused by the pressure loss. In packing phase the local specific volume varies due to pressure and temperature differences. To establish a local control of the specific volume, in addition to the injection pressure the temperature is added as a controlled variable for this new concept. To achieve an accurate and dynamic temperature control, tempering concepts including fluid-based tempering, CO2-tempering, resistance heating as well heating by laser radiation as and electromagnetic induction are evaluated regarding reaction time and performance. In usability, addition, local temperature and pressure measurements are needed to accurately adapt the temperature in the mould. Therefore, available measurement techniques for injection moulding are evaluated regarding reaction time and efficiency. A mould concept is developed to meet the requirements needed for an inline, online as well as a self-optimising temperature control, based on a model-based measurement correction, predictive temperature control and system-wide а optimisation function.

S14- Mixing and Compounding

Keynotes

S14-611

Maia Joao, Carson Sidney, Covas Jose

Extensional Mixing Elements for Twin-Screw Extrusion: Computational and Experimental Validation For Liquid-Liquid and Liquid-Solid Systems

A new type of mixing element for twin screw extrusion, dubbed the Extensional Mixing Element (EME), was developed for the purposes of imparting extension dominated stresses on polymer melts during processing. Even though extensional forces are much more efficient in dispersion during polymer compounding or processes most mixing action in standard blending, processing equipment is shear dominated. The EME was built as a static mixer for the inside of the barrel of a twin-screw extruder, the unit riding along bearings and stays stationary while the rest of the extruder screw spins, forcing flowing material through hyperbolic converging and diverging channels designed to impart extension-dominated stresses at a specific extension rate. Previously, we demonstrated the improved dispersive mixing capabilities of the EME when compared to a standard shear kneading block (KB) by compounding liquid-liquid blends (immiscible polypropylene/polystyrene blends at 80/20 wt.% ratio) and comparing the resulting morphologies under SEM. Expanding on these studies, the efficiency of the EME in the compounding of liquidsolid filler systems was investigated in a similar manner. Carbon fillers of different morphologies (spherical, high aspect ratio, 2D sheets) were compounded with polypropylene using both KB and EME configurations based on previously implemented screw designs. The initial results of this study indicate that the EME will show similar

improvements vs. the KB based on the process characteristics recorded during compounding. Optical microscopy images of the bulk filler dispersion and distribution levels further validate the enhanced mixing capabilities of the EME. Further computational studies of different contraction geometries and their effect on the physics of the mixing taking place in the EME were conducted and were intended to provide design guidelines for different types of materials (high vs. low shear thinning, strain hardening vs. non-strain hardening).

S14-66

Andersen Paul

The Zsk At60: A Retrospective Of Technology Development With A View To The Future And Growth Of Non-Traditional Applications

The ZSK co-rotating, fully intermeshing was invented by Erdmenger while working for IG Farben in the 1940's and subsequently licensed, developed and commercialized by Werner and Pfleiderer in the 1950's. During the intervening years it has become the primary production unit for compounding of polymer based materials. It also has had a long term presence in processing material in the chemical and food industry and more recently in pharmaceuticals. While this equipment might be considered a "mature" technology and reached market saturation, it has not experienced a decline in new process development opportunities as might be expected, but rather a significant number of advancements continue to evolve. This paper will trace the early development of twinscrew devices from units designed for producing ceramic bricks through and beyond the development of the ZSK. It will also highlight some of the more atypical applications such as animal feed, candy, snack food, ethanol, energetics and more.



Oral

S14-191

Stratiychuk-Dear Dmytro, Looney Kieran, Oliver Paul, Blackburn Stuart, Simmons Mark

Investigating the Impact of Operating Conditions on the Extent of Additive Mixing in Thermoplastic Polymer Systems

The use of additives in thermoplastic polymer films allows for the film properties to be tailored to a specific application; such photovoltaic as backsheets or flame retardant films. The properties of the film are highly dependent on the extent of mixing achieved as well as the degree of polymer degradation during twin screw extrusion processing. The work aims to establish the effect of operating conditions such as screw speed, throughput and torque on the extent of dispersive mixing observed. More importantly, it attempts to relate the 'calculated' parameters which are directly dependent on the operating conditions such as specific mechanical energy input, specific output and residence time to the degree of mixing achieved. The impact of polymer viscosity is assessed through the use of higher molecular weight polymers as well as the changes associated with temperature differences induced as a result of changes to the barrel temperatures. The extent of polymer degradation is monitored though the analysis of intrinsic viscosity in order to understand the nature of the compromise between achieving adequate mixing and maintaining the polymer matrix properties. The work identifies key parameters required for effective scale up of twin screw extrusion mixing processes.

S14-245

Mostafa Abdelhamid, Pacher Gernot , Lucyshyn Thomas, Holzer Clemens, Flachberger Helmut , Krischey Elke, Fritz Bertram, Laske Stephan

Effect of Compounding Method on Rheological, Thermal and Mechanical Behavior of Blast Furnace Slag Filled Polystyrene Compounds

The influence of melt-compounding technique on blast furnace slags (BFS) filled polystyrene (PS) compounds is almost lacking in literature. BFS are by-products of iron industry, and are formed during the production of iron via thermo-chemical reduction in blast furnaces. BFS are mineral structured materials composed principally of different oxides such as silicon oxide (SiO2), calcium oxide (CaO), magnesium oxide (MgO) and alumina (Al2O3) as well as other minor oxides and elements. Such combination of oxides might be of technical advantage if BFS is properly prepared and tailored for use as a functional filler for PS. In BFS outstandingly inexpensive addition, is compared to common mineral fillers used in polymer industry such as calcium carbonate and talc, giving BFS an economic significance. In current study, compounds were produced via meltcompounding approach, where two different processing equipment were used: (1) simple laboratory internal mixer (IM) and (2) co-rotating twin-screw compounding extruder (TSC). Three PS formulations filled with two types of BFS, granulated (G-type) and air-cooled (A-type) were produced. Fillers were incorporated into PS matrix at 20 wt.-% loading and 0-71 and 0-40 µm ranges. Compounds processed via each equipment were compression molded and investigated for rheological, thermal and mechanical performance. It was found that compounding process did not have a strong influence on either rheological or mechanical behavior. However, an influence on thermal behavior was noticed, where transition temperatures (Tg) of TSC compounds shifted to lower values compared to corresponding IM-ones.

S14-367

Castro Landinez Juan Felipe, Medina Jorge Alberto

Thermal Diffusivity Behaviour Of The High Density Polyethylene With The Addition Of Pigmentation Masterbatches



The thermo-physical properties are useful in designing manufacture processes for polymers, as they supply relevant information about the performance of the material during the different manufacturing stages. The thermal diffusivity is one of the most important of these properties because it contains information about other properties such as the heat capacity, the density and the thermal conductivity. Therefore, the analysis of the thermal diffusivity is paramount, especially when fillers are added to the polymer mixture, an example of those are the pigmentation masterbatches. Moreover, several methods and techniques have been developed to characterize the thermal diffusivity, such as the xenon-laser method. Using this method, the aim of this research is to determine the effects in the thermal diffusivity of a high density polyethylene after supplementing it with different kind of pigmentation masterbatches at a variable concentration (red, blue and gray). The results of the experimentation show the dependence of the diffusivity with temperature changes, which are affected by alterations in the composition and concentration of the added low density polyethylene (matrix of the masterbatch) and the inorganic material (pigment). These alterations are more evident in a domain of high temperatures, near to the melting temperature, in which case the competence between amorphous and crystalline phases is taking place [1]. The experimental data was compared with the results from a theoretical model found in the literature that predicts the behavior of the thermal diffusivity in a compound polymer [2]. These results are relevant in the manufacture process in polymers because it can explain the difference in the processing times by adding different kind of pigments, that are influenced by the concentration of the masterbatch instead the nature of the inorganic components.

S14-38

Roca-Blay Luis, Galindo-Galiana Begoña

Scale up of Polypropylene/Carbon Nanotubes Nanocomposites: Dispersion Improvement by Means of Simulation Software In this work Co-rotating twin screw extruder (Co-TSE) simulation software was employed to optimize the dispersion of carbon nanotubes (CNT) in the polypropylene (PP) nanocomposites scale-up from 25 mm diameter (Co-TSE) to 50 mm for multifilament melt spinning production. To do so different processing conditions and screw configurations were simulated employing the Corotating Twin Screw simulation software from SCC Consultants Ludovic[®]. In order to assess the degree of dispersion optical microscopy was done following the standard ISO 18553:2002 "Method for the assessment of the degree of pigment or carbon black dispersion in polyolefin pipes, fittings and compounds", the degree of dispersion achieved was determined from the values given by a particle treatment software, the main values to analyze were agglomerates density and average size of agglomerates. Once a good dispersion was obtained running at certain conditions in the 25 mm Co-TSE (PP CNT compound was successfully melt spun) these conditions where simulated in the 50 mm Co-TSE. The main processing data to match with Ludovic software in both extruders were Specific mechanical Energy (SME) and residence time directly linked with the mixing energy and hence with dispersion. After different simulations for 50 mm extruder modifying screw profile, similar values of residence time and specific mechanical energy were obtained, compounds were made and Dispersion was measured by optical microscopy. Particle counting software showed an important reduction of average particle size and agglomerates density which allowed the multifilament extrusion at industrial scale without blocking the die orifices.

S14-387

SANO Yukinori, TANAKA Tatsuya, BETSUDAN Midori

Compression properties of the inorganic fillerthermoplastic composites

In earthquake-prone country Japan, in order to ensure the earthquake resistance and breathability of housing, the ventilator window have been provided on the concrete foundation. However, at the time of the earthquake, the foundation for house was collapsed due to stress concentration occurring in the ventilator window.Recent year in Japan, instead for this ventilator window, a packing for house which is used the inorganic fillerthermoplastic composites have been attracted. By separating the foundation for house and the ventilator window, to prevent the collapse of foundation for house. For the further growing demand for packing, there is a need to clarify the between the inorganic relationship fillerthermoplastic composites and compression strength. However, there has not been studies which focused on this relationship. In this study, we prepared a different particle diameter of the inorganic filler for composites. We compared for disparsion of the filler within the molded specimens which was measured from X-ray images and compressive strength. From the above, we investigated what kind of influence a different particle diameter of the inorganic filler is to compression properties of the inorganic fillerthermoplastic composites.

S14-415

Bruchmueller Matthias, Koch Michael, Geis Julius, Schneidmadel Stefan

Modelling Mechanical Properties of Glass and Basalt Fiber Filled Thermoplastics

Filaments and short fibers as fillers are one of the most common ingredients to thermoplastics modification in order to impact on mechanical properties of injection molded parts and maintain cost efficiency at minimum part weight. In this study, glass and basalt fibers are processed into a thermoplastic matrix to compare achievable mechanical property improvements as a result of fiber type, content, length and orientation in various plastic matrix materials. Fibers are processed into the thermoplastics matrix by a twin screw extruder, regranulated and then injection molded into components. Mechanical properties of these components are measured. Results of experimental studies are compared and correlated in order to derive quantitative relationships to be able to predict properties for different material combinations of glass and basalt fibers and a

variety of thermoplastics. Major parameters of the model are fiber content, length and orientation as a result of processing conditions. Comparable to the CHAMIS laws, a relationship is established to predict achievable Young's modulus and tensile strength for both types of fibers used. Based on the material model, a determination of required fiber content, length and orientation is feasible. The desired configuration of the compounded fiber filled material and its alteration in the injection molding process needs to be taken into account to assert the desired property enhancement in the injection molded part. The steps of the process are analyzed and methods to predict fiber length during processing and reduction resulting orientation are comprehended. The study will introduce ways to predict properties of fiber filled thermoplastics more accurately and thus allow comparing glass and basalt fiber effectiveness.

S14-500

Tomczynska Magdalena M., Choong Gabriel Y. H., Ward Michael, Canciani Alessia, Walton Kirsty, De Focatiis Davide S. A., Grant David M., Irvine Derek J., Parsons Andrew J.

Processing and properties of PLA-HA nanocomposites: the effect of particle morphology and dispersants

The load bearing capacity of biodegradable polymeric medical devices remains limited; an improvement in mechanical properties is desirable to widen the range of applications. Incorporation of nanoparticles is explored to increase the mechanical properties of the base matrix whilst maintaining desirable polymeric processing routes. Various nanomaterials have been investigated for polylactic reinforcement acid (PLA) for orthopaedic applications; hydroxyapatite (HA), the main inorganic constituent of bone, is one of the most promising bioresorbable nanofillers. However, uncoated nanoparticles agglomerate easily during compounding; tailored coatings can offer new opportunities to improve dispersion. This study investigates the effectiveness of novel tailored dispersants on particle dispersion, rheological on macroscopic properties and mechanical



properties, when coated onto HA nanoparticles (HANP). The dispersants consist of short-chain PLA with isosorbide head groups (isPLA), or neat dodecenylsuccinic anhydride (DDSA). HANP were synthesised via a hydrothermal counter-flow process with dispersant coatings added in-situ. Neat DDSA was purchased whilst isPLA was polymerised via a standard ring-opening route involving lactide, a tin catalyst and isosorbide initiator. Nanocomposites were compounded in a twin-screw recirculating extruder and assessed by TEM, rheology and mechanical measurements. Preliminary findings show that the addition of 2.5 wt% uncoated HANP to PLA increases flexural strength by 20 % and modulus by 26 % relative to neat PLA. Introducing different coatings onto the HANP enhanced different mechanical properties: flexural strength increased by 22 % with DDSA, while modulus increased by 36 % with isPLA. This suggests that different mechanical properties can be influenced by the choice of HANP coating. Improved dispersions with coating were also observed in TEMs, and are reflected in the rheological responses of the melts during isothermal frequency sweeps.

S14-506

Grosso Giovanna, Hulsen Martien A., Fard Arash Sarhangi, Overend Andrew, Anderson Patrick D.

Modelling and Optimization of the Cavity Transfer Mixer

The blending of different materials is an important process in polymer industry, where a good mixing is essential to guarantee adequate performances of the finished product. In the 80s a new device called the Cavity Transfer Mixer (CTM) was invented and patented by Gale at Rapra Technology Limited, as an add-on to be mounted downstream of existing extruders. The CTM consists of two concentric cylinders, the rotor and the stator, both provided with staggered rows of hemispherical cavities. The inner cylinder rotates, while the outer remains still, whereas the pressure load imposed upstream, pushes the fluid through the mixer. The result of the interaction between the moving geometry, the pressure load and the rheology of the fluid is the complex flow field driving the mixing mechanisms inside the device. Because of the variety of the phenomena involved, a clear understanding of the CTM mixing processes is still missing and the system development encounters noticeable difficulties. In this context, the present work proposes a full three dimensional model of the CTM, able to accurately simulate the device operations. A finite element solver provides the transient velocity field, which is used in the mapping method implementation in order to compute the concentration field evolution. A broad range of simulations is run assessing the impact on mixing of several geometrical and functioning parameters, such as the number of cavities per row, the number of rows, the size of the mixer, the rheology of the fluid and the ratio between the rotation speed and the fluid throughput. Results are used to develop some design and operation guidelines for the CTM.

S14-517

Matsumoto Koki, Nakade Yoji, Sugimoto Keita, Tanaka Tatsuya

An Investigation on Dispersion State of Graphene in Polypropylene/Graphite Nanocomposite with Extensional Flow Mixing

Graphene nanoplatelets (GNP) have attracted considerable attention because of their excellent mechanical, thermal and electrical properties. Many researchers have tried to exfoliate GNP directly from graphite (Gr) in polymer by shear flow mixing process with twin-screw extruder, internal mixer and so on. The reason is that the processing is very easy and the process cost is very cheaper than producing the GNP directly. By usual shear mixing, however, exfoliation of GNP is very difficult and the processing is very inefficiency. Hence, chemical treatment pretreatments (e.g. and mechanical treatment) have been applied to Gr before compounding these materials usually. In this study, we focused on the extensional flow for exfoliating the GNP from Gr without pretreatment. Theoretically, shear flow is energetically inefficient for dispersion and the droplets can be broken up more efficiency in extensional flow from Grace



Curve. From our past results, the dispersion of CNTs in polypropylene (PP) was improved in dominant extensional flow with Blister Disk (BD) for twin-screw extruder. The geometry of BD is similar to seal segment and has small throughholes. It can be generated the more dominant extensional flow. This study was carried out to clarify the dispersion effect of extensional flow for PP/Gr nanocomposites. Primary, PP/Gr pellets were obtained by twin-screw extruder and these pellets were filled to self-designed extrusion machine that several type of BD can be equipped. These pellets were extruded by plunger under certain conditions. Then, the dispersion state was investigated by TEM observation, XRD, rheological and electrical properties for PP/Gr nanocomposites after passed to BD. From this results, some few-layer graphenes (about 4µm wide and 2 or 3 GNP sheets) could be observed.

S14-563

Scharr Kim Jacqueline, Westhues Tobias, Schöppner Volker

A New Sample Preparation Method to Investigate Melting Phenomena within a Partly Filled Melting Zone Of Co-Rotating Twin Screw Extruders

Polymer melting in co-rotating twin-screw processing equipment is an active field of research. Especially melting mechanisms such as plastic energy dissipation due to compression in the kneading blocks or disperse melting in fully and partly filled screw areas have been explored extensively in the recent past. Though melting in these machines has already been described and examined, it is still very complicated to generate experimental quantifiable values for the partial melting of polymer samples and to examine the melting length along the screw. The process design for economic, material protecting melting and the consequent scale-up is only possible, if co-rotating twin screw extruders apprehend thermo mechanic processes in the melting zone correctly. In this paper we present a method to generate experimental quantifiable values for the partial melting of polymer samples out of different melting

zones. Furthermore, we introduce the results from the melting study within partly filled and fully filled twin screw zones. These insights offer a lot of important information about the melting behavior of tightly intermeshing co-rotating twin screw extruders. Within the evaluation an alternative concept, which uses only partly filled twin screw channels, is introduced. The advantages are discussed.

S14-423

Leuteritz Andreas, Spörer Yvonne, Wang De-Yi, Kuehnert Ines

Influence of metal composition in Zn/Mg LDH flame retardant polypropylene nanocomposites

Layered Double Hydroxides are a promising sort of materials in several applications reaching from drug delivery, catalyst systems, energy application to many others. LDH have turned out to be effective synergists in flame retardancy, when to nanoscale. In dispersed the presented investigation the special focus is on the metal composition of Zn and Mg based LDH in use for synergist preparation. Composites based on polypropylene, intumescent flame retardant and LDH were prepared on a twin screw extruder and flammability test including LOI and cone calorimetry was performed. The results show a significant influence of the burning behavior from the metal composition to be discussed in the presentation.



Poster

S14-319

Li Miao, Wang Xianbin, Wu Yongxin, Liang Yaodong, Li Kanshe

The Study of Preparation and Heat Stabilization of Complexes of Calcium,Zinc,Lanthanum (Ⅲ)With N-(2-amino ethyl) Maleamic Acid Radical on PVC

The Study of Preparation and Heat Stabilization of Complexes of Calcium,Zinc,Lanthanum (Ⅲ)With N-(2-amino ethyl) Maleamic Acid Radical on PVC* Miao Li, Xiao-bin Wang, Yongxin Wu, Yao-dong Liang, Kan-she Li** Polymer Research Institute, College of Chemistry and Chemical Engineering of Xi'an University of Science and Technology, Xi'an China, 710054 Abstract: Due to the limitation of thermal degradation of PVC, thermal stabilizer must be added when processing, it makes thermal stabilizer becoming a rapidly growing field. However, The rare earth stabilizer have a unique electronic structure, so they can form complexes with such many organic compounds including the coordinated atoms: N and O which used as PVC thermal stabilizer. Amide type open chain of rare earth ions have a strong ability of coordination and high selectivity, we can obtain with new structure complexes at the same time, which has received the widespread attention. In this paper, maleic anhydride, ethylene diamine, sodium hydroxide, lanthanum chloride, zinc chloride and calcium chloride as the raw material, adopts the direct legal system had not reported three kinds of complexes, the N-amino ethyl maleamic acid lanthanum(LaL3), ZnL2,CaL2.And through their recombination to study the synergistic effect between them and the impact on the thermal stability of PVC. By melting point determination, element analysis, infrared spectrum, such as the composition, structure and properties were studied. Congo red test and TG analysis shows that the three kinds of complexes have good thermal stability of PVC. By these three composite heat stabilizers, suggests LaL3/ZnL2 and

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CaL2/ZnL2 composite heat stabilizer on PVC thermal stability increased significantly, and could effectively suspend "zinc burning". Key words : complexes of lanthanum(III) ; N-(2-amino ethyl) maleamic acid radical (L-) Lanthanum (III) ; Polyvinyl chloride (PVC) ; Heat stabilizer

S14-505

Mostafaiyan Mehdi, Wiessner Sven, Heinrich Gert

An Insight Toward the Distributive and Dispersive Mixing in a Pressure Flow

To investigate the effect of the rheological and geometrical parameters on the mixing quality in a laminar pressure flow, the dispersive and the distributive mixing are studied in a converging pipe. For, this purpose the mean strain function and Manas-Zloczower mixing index are calculated using an in-house finite element code to explain the effect of the rheological and geometrical parameters on the distributive and dispersive mixing, respectively. Keywords: Particle tracking, Finite element, residence time, dispersive mixing, distributive mixing

S14-82

Hopmann Christian, Adamy Maximilian, Windeck Christian, Yesildag Nafi

Properties of Polyamide 6-Graphene-Composites Produced and Processed on Industrial Scale

Graphene's remarkable properties make it interesting as functional filler for plastic composites to enhance the mechanical, electrical and thermal properties of various plastic products, even at low filler contents. Thus, the potential of enhancing the mechanical, electrical and thermal properties of plastics by adding graphene is highlighted in numerous scientific publications. But the preparation of graphene composites is performed on lab scale, which is not scalable to industrial scale. Especially the mixing conditions influence the exfoliation and dispersion of the graphene in plastics and this plays a key role in order to exploit



the extraordinary properties of graphene in graphene composites. To unlock the potential of graphene for plastic applications, the properties of graphene composites made on industrial scale have to be investigated. Therefore, polyamide 6graphene-composites are produced on a twinscrew-extruder with a throughput of 10 kg/h. Afterwards the compounds are further processed in injection moulding to produce specimens for tensile testing and analysis of thermal and electrical properties. The results show, that the production and further processing of polyamide 6-graphenecomposites on industrial scale is possible. The adding of graphene type N006-P polar Graphene powder of the company Angstron Materials, Dayton, USA, into Polyamide 6 (PA6) causes in higher Young's Modulus and higher tensile strength in comparison to non-reinforced PA6. Due to the adding of 1 wt.-% graphene the Young's Modulus increases from 3085 MPa to 3715 MPa and the tensile strength is enhanced from 72 MPa to 78 MPa. A further increase of the graphene content produces no significant further improvement. Otherwise the elongation at break is reduced substantial from > 100 % (non-reinforced PA6) to 4 % (graphene content 1 wt.-%).

S15- Morphology and Structure Development (With a scheduled session for honoring J-M. Haudin)

Keynotes

S15-454

Speranza Vito, Liparoti Sara, Pantani Roberto, Titomanlio Giuseppe

Morphology and Structure Development during Injection molding with fast mold temperature evolution

The effect of temperature, pressure and flow on relaxation time, nucleation density, crystallites growth rate, the interrelation among these quantities and the distributions of deformation rate and cooling time during the process determine the morphology distribution in the final injection molded object. A simple model linking all these quantities was developed to describe morphology evolution during the process. The effect of flow on nucleation density and growth rate was described on the basis of a molecular stretch parameter; the molecular stretch evolution being described by a simple nonlinear Maxwell model whose relaxation time, in its turn, is determined by the molecular stretch and, obviously, by temperature, pressure and crystallinity. The transition between spherulitic and fibrillar morphology was related to the local viscous work, which in its turn is related to the evolution of rheology during crystallization. The predictions of the model are compared with the morphology distributions of samples obtained by injection molding with fast mold temperature evolution during the process of a very accurately studied iPP as far as rheology, quiescent crystallization, effect of flow on nucleation and spherulitic growth rates and spherulitic/fibrillar transition. The model predictions reproduce main characteristics of the experimental results for both

pressure and temperature evolution and final morphologies distributions.

S15-482

Cardinaels Ruth, Bharati Avanish, Seo Jin Won, Wübbenhorst Michael, Moldenaers Paula

Enhancing the conductivity of carbon nanotube filled blends by tuning their phase separated morphology with a random or block copolymer

Nowadays, there is a large demand for deformable conductive materials in applications such as flexible electronics, EMI shielding or soft robotics. Immiscible blends containing conductive nanoparticles form a versatile class of materials with excellent possibilities to tune electrical functionality by means of tailoring their morphology and particle localisation. In the present conductivity of two-phasic blends work, the poly-alpha-methyl-styrene-coconsisting of polymethylmethacrylate acrylonitrile and (PAMSAN/PMMA) containing multiwalled carbon nanotubes (MWNTs) was optimized by tailoring the blend morphology with a polystyrenepolymethylmethacrylate(PS-PMMA) copolymer. The PAMSAN/PMMA blend has a lower critical solution temperature (LCST) and undergoes spinodal decomposition upon heating above the LCST during which the MWNTs selectively localize in the PAMSAN phase. The effects of the molecular weight, architecture (block or random) and concentration of the copolymer on blend conductivity, linear viscoelastic moduli and morphology were systematically investigated. The copolymer induces a huge conductivity increase, whereby blends with only 0.5 wt% MWNTs and 0.25 wt% copolymer exhibit the same conductivity as blends with 2 wt% percolated MWNTs [1]. The increase in conductivity is caused by a morphology refinement and increased degree of cocontinuity with copolymer, leading to double percolated networks. At low molecular weight a block copolymer has a more pronounced effect whereas at high molecular weight the difference between random and block copolymers vanishes. Finally, the dielectric spectra of the blends show an interfacial relaxation peak whose dielectric strength



and relaxation time reflect the contact resistance and interfacial capacitance of PAMSAN entrapped between neighbouring MWNTs. From this microcapacitor behaviour, an estimate of the gap spacing between MWNTs was obtained for the different systems. [1] Bharati et al., Polymer 79, 271-282 (2015

S15-608

Ren Weijie, Jayaraman Krishnamurthy

Orientation of nanolayers and crystalline lamellae in blown films of PP-clay nanocomposites

This paper follows up on recent results from our laboratory pertaining to the use of silane coupling agents in polypropylene-clay nanocomposites. The object of the present work was to locate the silane coupling agent at both faces and edges of the nanolayers and prepare nanocomposites of a polypropylene copolymer with the resulting nanoclay (at 5 wt% and 8 wt%) for film blowing. A 2:1 ratio of maleated PP copolymer as compatibilizer to organoclay was effective in producing very good dispersion of the nanolayers as seen from transmission electron micrographs of the compound before film blowing. 1 mil thick films of the nanocomposite --with coupling at both faces and edges-- and the unfilled polypropylene were prepared with a blow-up ratio of 3.2 and characterized for mechanical properties and morphology. The nanolayer orientation distribution in the blown film as well as the lamellar orientation were examined with SEM and FESEM respectively. Refractive index measurements and mechanical testing revealed that blown films of the nanocomposite were more isotropic in the plane of the film than films of the neat PP. These trends may understood in terms of the orientation be distributions of the crystalline lamellae in the films. FESEM images revealed that cross-hatching of lamellae was absent from the blown film of unfilled PP but pervasive in the blown film of nanocomposite. The rectangular nanolayers were seen to be oriented in the plane of the film with the longer dimension largely along MD. The lower extent of lamellar orientation around nanolayers

may be attributed to the strong reduction in mobility of the chains attached to the nanolayers.

S15-97

Peters Gerrit W.M., Roozemond Peter

Measuring and Modelling Multiple Phases & Multiple Morphologies in Isotactic Polypropylene Depending on the processing conditions, isotactic Polypropylene (iPP) can form different crystalline phases, Injection molding samples show а distribution of four different phases (α , β , γ , meso) over the thickness of the sample. However, a key issue in studying the crystallization process of semi-crystalline polymers is the need for controlled boundary and initial conditions; injection molding does not meet these requirements. Here, the results of extended dilatometry are used to reveal the crystallization kinetics and the resulting morphology of an isotactic polypropylene homopolymer resulting from a combination of nonisothermal cooling at elevated (isobaric) pressures and shear flow. Based on the flow strength, defined in terms of the Weissenberg number, the crystallization kinetics can be classified in three regimes; quiescent crystallization, flow enhanced point nucleation and flow-induced creation of oriented structures. Using ex-situ WAXD and SAXS the details of the (oriented) crystalline structures for the different regimes, including the different phases (α, β, γ) , are revealed. Some unique oriented structures of combined α - and γ -phase were found. We developed a model in terms of a set of rate equations for the different phases, which are partially coupled. The most important ingredients of the model are: - Flow creates nuclei and shishkebabs - Fixed portion of flow-induced nuclei is assigned to the β -phase (~0.2%), the rest is assigned to α/γ according to their momentary crystal growth rate - Shish form parents and daughters -Parameters for crystal growth rates for all phases are taken from literature. - There are two limiting cases for the γ -phase; daughters grow on α -kebab only or - γ -phase can grow on shish as parents as well as daughters on α -kebab Combining a known nucleation model with a known multi-phase model gives qualitative agreement with experiments. To our knowledge, this is the first time that such an extended modeling is presented.



Oral

S15-660

Edmonds Neil, Plimmer Peter N, McKee John

Commercial Plastics: Tertiary Level Education Requirements

The Postgraduate Certificate in Engineering in Plastics is a joint initiative between The University Auckland of and Plastics New Zealand (www.plastics.org.nz) and was introduced to meet demand from industry for a high level programme focussed on and the chemistry, design and processing of plastics materials. This need arose from industries employing both engineering and science graduates who generally had little formal education in polymer science or knowledge of the commercial world of plastics. Four courses are delivered over a two year period with lectures delivered by both academic staff and industry experts. The programme started in 2010 at the Plastics Centre of Excellence at the University of Auckland (www.pcoe.org.nz) and is run as weeklong block courses to best accommodate the parttime study requirements of employers and their staff. In addition to the block course, students also complete course and work-based assignments over each semester plus complete a final three hour exam. While full-time students can attend courses the highly commercial nature of the content means that some industry experience is required to fully benefit from the programme. Graduates have reported a very high level of satisfaction with the value of the programme to their employment.

S15-212

Houichi Hikmet, Maazouz A, Elleuch Boubaker

Study of poly (lactic) acid casting film process: structure-process relationship

A novel way using a polarized optical microscopy and statistical image analysis techniques for direct investigation of the crystallization kinetics and spherulitic morphology of poly (lactic) acid induced by casting film process has been proposed. DSC analyses were carried out to explore the effect of drawing in thermal properties of PLA. We found that the rate of cold crystallization was sharply increased with draw ratio. Isothermal calorimetric results reveal that thin films crystallize slowly compared to sheets. Moreover, thin films don't fit the Avrami model demonstrating that more stretching may modify the crystallization kinetics of films. POM experiments showed the existence of two different spherulitic populations in thin films and two nucleation mechanisms was identified. Accordingly, the growth rate was found to be not linear with time. Furthermore, the X-Ray diffraction analyses showed the presence of α and α' crystal form in thin films contrarily to sheets with α form. Afterwards, poly (ethylene glycol) was used to improve process ability, flexibility and ductility of PLA casting films. Rheological analysis showed an improvement of viscoelestic properties of PLA films and a decrease of thermal degradation in the extruder with addition of different amount of PEG. The presence of PEG as plasticizer was found to reduce major extrusion defects even at high shearing rate and improve the PLA casting films process. In addition, POM experiments revealed that the presence of PEG greatly controls the crystalline morphology of PLA. Obviously, PEG addition led to the development of finite spherulites nucleating close together which influences greatly the germination rate and the growth rate; but preserves the same nucleation mechanism of PLA. Finally, we have shown that the addition of PEG and optimized processing conditions lead to the development of new materials with controlled structures and good mechanical properties.

S15-278

Schawe Jürgen E.K.

SECA: A novel method to use the crystallization behavior for investigation of the thermal short time stability of semicrystalline polymers

The thermal short time stability is relevant for fast heating processing techniques like fused filament



fabrication, selective laser sintering or polymer welding. Also the application of polymeric materials with temporary stress high at temperatures requires knowledge of the short term stability at high temperatures. Thermogravimetric analysis (TGA) is a standard technique to measure the thermal stability. This technique has two drawbacks: • The decomposition at high temperatures does not necessarily contain the same reaction steps as measured by TGA. • TGA is not sensitive for degradation steps which are not related to mass loss. However, such reactions can significantly influence the properties of polymeric materials. It is shown on differently stressed polymers that the crystallization behavior changes sensitively with molecular modifications due to the stresses. The modification in the crystallization behavior due to thermal stress can be studied by DSC. However, for investigation of fast technical processes the heating and cooling rates are not sufficient. We introduce a novel analytical method called SECA (stability estimate by crystallization analysis) for short time stability based on fast scanning calorimetry (FSC). This method analyses the change in the crystallization kinetics due to thermal stress. FSC enables the extrapolation to fast heating rates because the time constants of the instruments are in the millisecond range. The measurements can be performed at heating and cooling rates in the order of several thousand K/s. At such scanning rates the degradation can be prevented. SECA is used for analyzing polyamides, poly(ether etherketone) (PEEK) and polymer materials developed for selective laser sintering (SLS). The results show a remarkable discrepancy to the TGA results and the high sensitivity of the change of the crystallization behavior for the early steps of decomposition reaction.

S15-304

Zhang Xiaomeng, Zhang Jiajia, Wu Hong, Guo Shaoyun

Enhanced thermal conductivity of oriented boron nitride/polymer composites prepared through multistage stretching extrusion In-plane thermal conductivity of h-BN platelets is more than 300W/(m×k), so how to control the orientation of h-BN in the polymer matrix is critically important for optimizing the performance of its composites. Therefore, in this paper we report a new method to prepare thermally conductive polyethylene matrix composites with highly oriented boron nitrde simply through multistage stretching extrusion. Based on the characterization of SEM and XRD, it was proved that h-BN flakes are well oriented along the flow direction. Then, the effect of filler orientation on the the thermal conductivity of resulting composites was also investigated, and the results indicate that the thermal conductivity along the alignment direction increases remarkably, compared to the isotropic samples. The mechanism of processing and the evolution of fillers morphology were also analysed in depth.

S15-335

Ghiassinejad Sina, Ranjbar Behnaz, Katbab Ali Asghar, Hosseinpour Ali, Nazockdast Hossein

Structural recovery mechanism of multi-walled carbon nanotube in a simple shear flow

In this work the flow induced orientation and the mechanism governing for structural recovery of multi-walled carbon nanotube filled polypropylene nanocomposites were investigated. A series of melt linear and nonlinear rheological measurements including start-up flow test and time sweep experiments were performed in order to study the structural breakdown and/or nanoparticles orientation and subsequent structural recovery at different temperatures and MWCNT loadings. The results showed that the structural recovery occurs in two stages. The first quick recovery which was independent of temperature could be explained in terms of interparticle van der Waals interaction. This stage which was named as "initial aggregation" and had major role in increasing storage modulus. The second stage of recovery (secondary aggregation) that was much slower, was found to be highly dependent on temperature and therefore was attributed to rotary diffusion of nanoparticles. These result were in good agreement



with those calculated using van der Waals and diffusion concepts.

S15-357

Rabie El Otmani, R. Kamal Musa , Derdouri Salim, Boutaous Mhamed

Numerical And Morphological Studies Of Polymer Micro Gear In Micro Injection Molding Process.

Interest in the micro-injection molding (µIM) process has grown as the demand for micro parts increased for various electronics, transportation, communications, biomedical and other applications. Recently, we have conducted an intensive research program to understand the details of this process and the material-processproperty relationships for various polymers. In the present study, a micro-gear micro part was presented, in order to investigate the effects of conditions on microstructure, processing mechanical properties, and thermal properties, microtomed and examined using polarized light microscopy, and differential scanning calorimetry morphology. for investigation of Various microstructural features, such as morphological layer thickness and crystalline polymorphs, were analyzed in light observed and of the thermomechanical history. A skin-core region was observed, with spherulites predominating the core region, and highly oriented lamellae appeared in the skin layer. Numerical simulation of filling phase of micro gear gives us a detailed description of the thermal history and flow, in which contribute to better understanding on the origins differences in the morphologies among the layers across the part thicknesses in view of the prevailing process Keywords: Micro injection, conditions. flow behaviours, crystalline, polymer melt, numerical.

S15-408

Bourg Violette, Ienny Patrick, Le Moigne Nicolas, Guillard Valérie, Bergeret Anne

Linear and Branched Polybutylene Succinate Blends for Packaging Applications: From

Rheological Behavior to Functional Properties of Films

In 2012 packaging represented 40% of the European plastic consumption as only 20% of the wastes of the total production were recycled. To decrease the packaging impact on waste management, an alternative consists in using biodegradable polymers. Among these, Poly(Butylene Succinate) (PBS) is considered as an interesting candidate for replacing polyolefins, mostly used for packaging purposes [1]. It is well-established that drawing conditions in processes such as cast-film or blowfilm extrusion- which are the two main processes used to convert polymers into filmscan dramatically affect final properties especially mechanical, impact, and optical properties [2]. In this work, we studied the relationships between processing conditions and microstructural features on the development of specific morphologies and packaging related properties of PBS films. Linear PBS blended with different amounts of long-chain branching (LCB) PBS were processed by cast-film extrusion into films at increasing draw ratios. The rheological behavior, the microstructure in terms of degree of crystallinity and overall molecular orientation as well as respective orientation of crystalline and amorphous phases were investigated by differential scanning calorimetry (DSC), birefringence, infrared linear dichroism (IRLD), wide angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM). Finally, the functional properties of tear and puncture of the films were studied. Results show that the presence of LCB does not lead to major modification of the rheological behavior under shear flow while strain hardening is observed under elongational flow. The addition of only 20% of LCB PBS in the blend drastically enhances the overall orientation. SEM micrographs and crystalline phase orientation show that increasing the amount of LCB PBS leads to "row-nucleated-like" type structure. The notchedtear strength of the films was found to be degraded when adding LCB PBS, whereas an enhancement of the puncture resistance is found. [1] M. Garin, L. Tighzert, I. Vroman, S. Marinkovic, B. Estrine, J. Appl. Polym. Sci. 131(2014) 1–7. [2] S. Tabatabaei, P. Carreau, A. Ajji, Polymer. 50 (2009) 3981-3989.



S15-475

Vincent Michel, Hondros Vassilis, Haudin Jean-Marc, Ville Laurence, Francois Guillaume

Modeling of the packing stage for semi-crystalline polymers: PVT data and no-flow criteria

During the packing stage in injection molding of thermoplastics, a compressible flow under imposed pressure allows to counteract the effect of the thermal shrinkage. PVT curves are important data for the numerical simulation of this flow. They are usually obtained by measuring the volume change of a given mass of material at constant pressure and at a cooling rate usually much lower than in the process. The sharp volume decrease at crystallization may not be correctly captured. A second issue concerns the prediction of the solidified layer which grows in contact with the mold walls until full solidification. To address these two issues, we characterized the crystallization kinetics of a polypropylene either at room pressure up to a cooling rate of 100 K/min by DSC, or under pressure up to 90 MPa in isothermal conditions in the Cristapress device developed in the laboratory. This allows obtaining crystallization the temperature as a function of the cooling rates and pressure. The crystallinity ratio is used to obtain the specific volume in the crystallization range, as a function of the specific volumes of the amorphous and crystalline phases. For the no-flow criteria, instead of using a no-flow temperature, we used a criteria related to the crystallinity ratio. We performed injection molding tests and measured the pressure on three transducers located in the cavity, the mass of the molded part for different packing pressures and times. We used the Rem3D® software package to test the models for the PVT data and no-flow criteria. The agreement is correct.

S15-576

Bicalho Luciana Assumpção, Silva Jorge Manoel Jardim, Canevarolo Sebastião Vicente

Thermo-optical characterization of polyester fiber in real time via quantitative cross-polarized optical microscopy

А real time quantitative thermo-optical characterization of polyethylene terephthalate PET fiber was performed using a modified crosspolarized optical microscope. The thermal cycles were produced by a hot-stage CSS 450 and the quantitative optical measurements were done by placing an optical module, recently developed in our research group, into the slot of the microscope's analyzer. The module has two adjacent photocells, one of them covered by a polarizer filter. The first photocell measures changes in the transmitted light intensity resulted by the scattered light (i.e. turbidity) and the second (covered by the filter) the cross-polarized light intensity. The signals are collected via software, developed in the LabView 8.6 platform, which in real time calculate, present in the screen and save the data. In addition, it also controls all parameters set on the CSS 450. Finally, a digital camera was coupled in the ocular tube of the microscope to allow for both colored image capturing and video recording. The structural changes in the fiber arising from the thermal protocol were assessed by both optical signals, which reveal the PET thermal transitions: glass cold crystallization transition, and melting. Additionally the observation of the interference color formed during the thermal cycles, quantitatively as optical path differences, is another way of displaying the thermal transitions as a function of temperature. This helps understanding the PET molecular mobility including glass transition, cold crystallization and melting. As control the optical signals were compared with DSC scans showing good reproducibility, validating the thermo-optical method. Furthermore it has the advantage in providing additional information including level of fiber orientation and stretching.

S15-591

Navard Patrick, Girones Jordi, Freire Lionel, Haudin Jean-Marc

Miscanthus x giganteus stem fragment-reinforced polypropylene composites. Influence of a compatibilizer on the isothermal crystallization kinetics



Crystallization kinetics of PP-based composites reinforced with miscanthus stem fragments was studied by DSC and optical microscopy with or without the addition of MA-g-PP. The presence of miscanthus fragments has a clear and noticeable effect onto the crystallization of the PP matrix, with the crystallization peak being shifted from 113°C to 119°C, due to nucleating effect of miscanthus fragments for the crystallization of PP. However, the size of the miscanthus fragments has a negligible effect onto the crystallization of PP. Isothermal crystallization curves at 130°C evidenced that crystallization started earlier for composite materials coupled with MA-g-PP, as also shown by Avrami parameters. The coupling agent does not only affect the nucleation process but also increases the crystallization kinetics. In addition to the crystallization acceleration caused by MA-g-PP, the size of the fragments also affect the crystallization kinetics. However, fragment size only seems to affect the crystallization process if there is a good interaction with PP matrix Seen by optical microscopy, composites coupled with MAg-PP had a higher number of nucleation sites, started the crystallization earlier and at a faster rate than composites without coupling agent. Crystallization started independently at the surface of the fibers and on the polymer matrix. These results put in light the effect of a coupling agent on the crystallization of a polymer matrix, here polypropylene.

S15-60

Oda Naoto, Nakano Ryoko, Sekiguchi Hiroshi, Yao Shigeru

Structure construction of amorphous polymer at long time region and their mechanical properties.

Polymer is thought to be constructing a random structure in molten state. Especially, longer the longest relaxation time, polymer is in a relaxed state with lost the orientation history. Moreover, the amorphous polymer, cooled and solidified from such molten stage is thought to have no structural morphology and show stable mechanical property. However, in this time, we investigated holding time of molten stage dependence to tensile properties by using polystyrene virgin pellet and found that the tensile properties much depends on the holding time and became ductile. And also, we got the results that obvious structural construction were occurred by SAXS and WAXS measurements. These results shows that amorphous polymer construct ordered structure in the molten stage.

S15-606

Bourg Violette , Saffar Amir, Ajji Abdellah

Influence of a dispersed elastomeric phase on the orientation of hot-drawn Poly(ethylene Terephthalate)

For years, it is well-established that properties of polymeric materials strongly depend on their orientation state. However, if orientation causes a favorable anisotropy in the drawing direction, it also results in drawbacks such as a reduction of the same properties in other direction(s) that is generally accompanied by a reduction of the elongation at break. To overcome this loss of properties, it is possible to disperse an elastomeric phase that will either be stretched or teared and debonded upon stretching and therefore alter the state of stress in the brittle matrix. Scarce studies investigated the influence of such a dispersed phase on the orientation of the matrix. Chapeleau et al. studied the effect of different drawing techniques on the orientation of a PET modified with a metallocene ethylene-octene polyethylene (m-PE) copolymer, and the effect of grafting with glucidyl methacrylate as a compatibilizer (GMA). By following the evolution of the orientation function of the 1340 cm-1 infrared band with the draw ratio, they showed that the trans conformers orient less for the modified PET than for neat PET and even less for the grafted modified one. In our work, PET is modified with PE and/or Ethylene-Polypropylene Diene terpolymer (EPDM), grafted with GMA, and drawn from the amorphous state at 90°C with an increasing draw ratio. Due to the higher thicknesses that are used, saturation issue prevent from determining the orientation function of PET from the band at 1340 cm-1. Therefore, a combination of Infrared Linear Dichroism (IRLD) using a Near Infrared (NIR) band (overtone or combination of



the fundamental vibration of the mid-infrared region) and Wide Angle X-ray Diffraction (WAXD) technique is used to determine the orientation of the crystalline and amorphous phase separately. An investigation of the morphology in terms of crystallinity and structure is also performed with Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy (SEM).

S15-618

Bakis Gökhan, Brückner Alexander , Zeiler Rico, Deutges Holger, Altstädt Volker

Fatigue crack propagation behavior of simultaneously toughened and electrically conductive epoxy composites

Simultaneously conductive and very tough thermoset formulations are desired for applications such as lightning strike protection or electrostatic dissipation for aerospace industry. Within the scope of this research, diglycidylether of bisphenol A (DGEBA) cured with 4,4'-diaminodiphenyl sulfone (4,4'-DDS) is chosen as the reference epoxy system and modified with an industrially available, electrically conducting carbon black in combination with various types of tougheners to simultaneously increase the resistance to the fatigue crack growth and electrical conductivity. As toughening agents core-shell particles and two different grades of functionalized tri-block copolymer of PMMA-b-PBA-b-PMMA were used up to 10 wt%. Electrical conductivity of above described multifunctional nanocomposites are characterized with 2 point conductivity measurements. In addition, the effect of the tougheners morphology on the electrically conductive network formation of the carbon black and as well the fatigue crack growth resistance is studied systematically. Addition of carbon black and various tougheners did not affect the Tg of the DGEBA-4,4'-DDS. The addition of all tougheners increased the fatigue crack growth resistance the neat (da/dN)of system. Especially heterogeneously distributed core shell and M52N increased the resistance to initiation of crack propagation and as well the critical failure. Tougheners with the homogeneous dispersion and heterogeneous distribution promoted the

conductive network formation of carbon black even further and increased the electrical conductivity almost 100 times compared to the nanocomposites of only carbon black. On the other hand, nanophase separated toughener with homogeneous dispersion and distribution having averagely 30 nm soft-phases hindered very strongly the conductive network formation of carbon black.

S15-630

Nassar Samira Fernandes , Stoclet Gregory, Guinault Alain, Sollogoub Cyrille, Delpouve Nicolas, Domenek Sandra

Confined Crystallization of PLLA in Nanolayered Films

Because the classical 3D crystal growth is frustrated, crystallization under confinement can lead to unique crystal morphologies and orientations. Such unique features can eventually lead to enanched propreties, like gas barrier properties1. The nanolayer coextrusion is a novel and innovative process that allows, through layer multiplying elements, combining two polymers in a layered structure, creating nanolayered films with continuous and regular layers down to 10 nm thick. It appears to be a relevant tool to study the structure-property relationships of confined polymer crystallization2 and to determine the critical factors that control the confined structures. In this work, PLLA was confined by poly(styrene) (PS) and polycarbonate (PC) using nanolayer coextrusion. Ten multiplying elements (2049 layers) were used in order to reach 20 nm continuous layers of PLLA, confined between slightly thicker PS or PC layers (around 60 nm) in final 100 µm thick films. Those films can be studied as extruded and after a subsequent annealing at different temperatures above the glass transition temperature of PLLA but below the glass transition temperature of the confining polymer, in order to maintain the layered structure. The effect of the confinement and of the annealing has been investigated on the crystallization morphologies and orientations, using mainly X Ray diffraction.

S15-690

Toquet Fabien, Cassagnau Philippe, Schlegel Brice, Guy Laurent, Fulchiron René

Increase of UHMW-PE crystallinity with the addition of naphthenic oil and silica in PEmembranes for battery separator application

The used material for battery separator membranes for automotive applications is generally based on Polyethylene. These PE separators are porous membranes composed of a blend of ultrahigh molecular weight polyethylene (UHMW-PE), naphthenic oil and precipitated silica. During the elaboration process, the membrane is formed at a temperature higher than the melting point of UHMW-PE and then the material is cooled. This cooling generates two phenomena, the UHMW-PE crystallization and a phase separation between UHMW-PE and naphthenic Oil. The membrane's porosity is finally obtained by extraction of the naphthenic oil. With the aim of understanding the membrane structuring mechanisms, we studied the influence of silica and oil concentrations on the UHMW-PE crystallization. Blends with polyethylene/precipitated silica/naphthenic oil were performed in an internal mixer and analyzed by Differential Scanning Calorimetry (DSC) and by Thermogravimetric Analysis (TGA) to study UHMW-PE crystallization. Three kinds of polyethylene have been studied, UHMW-PE, HDPE (High Density Polyethylene) and L-LDPE (Linear Low Density Polyethylene). Results have shown that, for each polyethylene, the crystallization temperature is controlled by the Oil/PE ratio. Moreover, only crystallinity of UHMW-PE is controlled by the Oil/UHMW-PE ratio of the blend. Crystallinity of UHMW-PE varies from 40% to 65% and the initial high crystallinity ($\chi c \approx 65\%$) of UHMW-PE can be recovered in the membrane with a high Oil/UHMW-PE ratio in the membrane. Furthermore, indirectly precipitated silica contributes in increasing the UHMW-PE crystallinity by increasing the possible oil content in the blend.

S15-754

Sowinskia Przemyslaw , Piorkowska Ewa , Boyer Severine, Haudin Jean-Marc

DMBS-Induced Nucleation Of Isotactic Polypropylene Under High Pressure In Isothermal And Non-Isothermal Conditions

Recently, we have conducted a fine study dealing with the nucleation of the gamma-form in isotactic polypropylene (PP) under high pressure. To nucleate crystallization of PP three nucleating agents were used, namely alpha-nucleants (Hyperform HPN-20E, PTFE submicron particles [1]) and a beta-nucleant (calcium pimelate). The study utilized a 'model' PP (3250MR1, Atofina). During processing crystallization is non-isothermal, hence the study has focused on nucleation of the gamma form in PP under high pressure in isothermal conditions [2] as well as during cooling [3]. The present study focuses on a specific alphanucleant, 1,3:2,4-bis(3,4-dimethylbenzylidene sorbitol) or DMBS, named Millad 3988i (Milliken Chemical). As its homologues, neat PP and PP with 0.2 wt% of Millad were crystallized in a highpressure cell [4], under pressure ranging from 50 to 300 MPa, with i) annealing at 200°C for 15 min or annealing at 200 MPa for 2 min, 15 min, 1h and 4h), and ii) during cooling at approx. 8 °C/min. Crystallinity, contents of crystallographic forms and spherulitic structure were then analysed. Compared to its homologues, nucleation of the gamma-form induced by Millad showed a different behavior. It was pressure-dependent for both isothermal and non-isothermal conditions. Millad increased crystallization temperature and reduced the grain size at 100 MPa, indicating intense nucleation. Under 200-300 MPa, large spherulites were embedded in fine-grain structure; most probably the large ones were nucleated as in neat PP while the small ones were nucleated later, when larger spherulites were growing, at lower temperature by Millad; crystallization temperature did not increase. So it means that high pressure cancelled the effect encountered at 100 MPa; this was not observed for Hyperform HPN-20E and PTFE submicron particles. Direct nucleation of gamma-form on the substrate can be envisaged as a possible mechanism [1] Masirek R, Piorkowska E (2010) Eur Polym J 46:1436-1445 [2] Sowinski P, Piorkowska E, Boyer SAE, Haudin JM, Zapala K (2015) Colloid Polym Sci 293:665-675 [3] Sowinski P,



Piorkowska E, Boyer SAE, Haudin JM (to be published)

S15-759

Bergeret Anne , Fernandeza J. Acera , Testoni G. Apolinario , Le Moigne N., Corn S. , Leger R., Ienny P. , Haudin J.M. , Le Duc A. , Lozachmeur M. , Bono P.

Effect of flax fabrics chemical extraction treatments and processing conditions on the microstructure of flax fabrics reinforced thermoset biocomposites

Flax fibres based composites are increasingly used as alternatives to glass fibres based ones mainly because of their low density, good mechanical properties and positive life cycle assessment. In contrast to glass fibres, flax fibres present a complex hierarchical and layered structure made of several biopolymers. Moreover, the production of flax fabrics from bast fibres to textile and composite applications requires several transformation steps involving mechanical processes and chemical treatments that have a significant influence on the biochemical composition, the structure and the properties of flax fibres, and hence strongly influence the microstructural and mechanical properties of biocomposites. As well, the processing techniques used for manufacturing flax fibres based composites influence greatly these properties. In a first part, this study compares the microstructure of thermoset polyester/flax fabrics composites processed through vacuum infusion and thermocompression. Results show that vacuum infusion produced lower fibre content in composites with lower matrix porosity and yarns packing. Mechanical properties are therefore lower but the fibers are less degraded because of the low pressure setting. The second part investigates the effect of different chemical extraction treatments on properties the flax fabrics (biochemical composition, fabrics dimension and density) and on the microstructure (reinforcing rate, porosity, bundles dispersion, crosslinking rate) of thermocompressed epoxy/flax fabrics composites. A gradient of solvation capacity of flax cell wall components was obtained with selected chemical extraction treatments. The analysis of flax yarns

dispersion within composites showed that the chemical extraction treatments induced а pronounced individualization of the fibre bundles in elementary fibres and favored the diffusion of epoxy resin within the yarns during processing resulting in variations in fibre content and mechanical properties. Keywords: thermoset biocomposite, flax fabrics, vacuum infusion, thermocompression, chemical extraction treatment, fibre dispersion.

S15-92

Kuzmanovic Maja, Delva Laurens, Ragaert Kim, Cardon Ludwig

The Effect of Injection Moulding Temperature on PET Particles/Fibrils in PP/PET Blends and MFCs The microfibrillar composites of polypropylene (PP)/poly(ethylene terephthalate) (PET) have been

prepared by twin-screw extrusion, followed by hot stretching. The employed stretch ratio was 4. Further processing was done by injection moulding at three different processing temperatures (210°C, 230°C, 280°C) on PP/PET blends with wt% 70/30 and 85/15. Establishing relationships between the processing parameters, mechanical properties and morphology of composites is of huge importance. subjected to the Samples were extensive characterization in each step of MFC preparing. Fourier Transform Infrared (FTIR) spectroscopy was employed to determine the nature of the interaction between the polymers in the composites. Linear viscoelastic shear oscillations and start-up shear flow experiments were performed using a Dynamical Shear Rheometer. Thermogravimetric Analysis (TGA) were used to degradation investigate of polymers. The crystallization, melting behaviour and the crystallization morphology were investigated by Dynamic Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM). Influence of processing temperature on morphology was investigated by using Scanning Electron Microscopy (SEM). The observations from the fracture surfaces were discussed and compared with the mechanical properties, and results have shown significantly influence of injection moulding parameters on morphology development.



Poster

S15-137

Wang Ke, Zhang Qin, Wu Zhiqiang, Fu Qiang

Facilely Assess The Soluble Behaviour of Nucleating Agent by Gradient Temperature Field for Construction of Crystalline Frameworks in iPP

Nucleating agent (NA) species with solubility and self-assembly ability can readily and effectively manipulate the crystalline morphology of semicrystalline polymers through construction of heterogeneous frameworks prior to primary crystallization of basal resins. However, the solubility of NA is difficult to be assessable by current traditional methods. In this study, gradient temperature field (g-T field) was utilized to ascertain the dissolution and self-assembly behaviors of beta-NA in the melts of isotactic polypropylene (iPP). The g-T field technique can facilely assess the soluble behavior of beta-NA through determining the transformation between several NA frameworks, namely, needle-, flowerand dendrite-like supermolecular structures. Clarifying the soluble behavior of beta-NA is of great significance to guide the formation of various crystalline frameworks under the homotemperature fields and control the resultant crystalline morphology of beta-modification iPP. Some interesting findings are summarized as: (1) an in-situ observation under g-T field clearly indicates the sequential occurrence of various nucleation and crystallization events on the same observed window, and approves for the migration of well molten beta-NA, (2) the exact correlation between Tf and framework type reveals that an abrupt transformation (over narrow temperature range of 1oC) occurred between needle-like and dendritelike frameworks, (3) the primary crystallization of iPP is strongly depending on the construction mode of beta-NA framework.

S15-185

Structural evolution of isotactic-polypropylene during creep under sub-yield stress: a study by in situ synchrotron small angle X-ray scattering

The objective of this study is to explore the structure evolution of isotactic polypropylene (iPP) during creep under sub-yield stress by in-situ synchrotron small angle X-ray scattering (SAXS). Generally, creep curve of iPP at relative high force can be split into four regions. In region I, strain grows nonlinearly to a value smaller than 15 % at sufficiently small times. In this region, only the long period along drawing direction (La) increases with the increase of time, whereas the long period perpendicular to drawing direction (Lp) keeps constantly. The increase of La is caused by elastic deformation of the non-crystalline phase in the polar region of iPP spherulites. In region II, strain linearly increases with time, and both La and Lp increase as time increases. Two possible reasons are proposed for the increase of long period. One of them is annealing induced crystalline perfection by melting-recrystallization and the other one is straininduced increase in free volume. In region III, strain grows dramatically with time, and the yielding of iPP occurs in this region. In this region, the peak intensity positions of the lamellae reflection in 2D-SAXS patterns change from a circle or light ellipse to a distinct ellipse. This significant transition indicates that the lamellae is tilted and rotated during the yielding process. In the last region, strain grows linearly with time again. The lamellae reflection grows from distinct ellipse into two spots, which means that lamellae aligned mainly along the drawing direction after yielding. What's more, a streak perpendicular to the drawing direction shows up in this region. After evaluating the intensity of the streak, it is proposed that the streak is a signal of shish, instead of cavity. Employing the Ruland's streak method, it is calculated that the length of shish is ca. 10 nm and grows to ca. 15 nm with the increase of time.

S15-330

Hasanabadi Noushin, Lattuada Marco, Nazockdast Hossein

Chang Baobao, Schneider Konrad, Heinrich Gert



Morphology development of block copolymer containing Carbon Nanotube

The aim of the present work was to study the effect of multiwalled carbon nanotube(MWCNT) on the microphase separation kinetics and its influence on the morphology development of polystyrene-bpoly(ethylene-co-butylene)-b-polystyrene (SEBS) copolymer with cylindrical domains using dynamic rheological technique. The results of temperature sweep experiment showed small increase of microphase separation temperature which could be attributed to nucleating of nanoparticles. In order to evaluate the structural recovery of block copolymer and MWCNT filled samples, the samples were presheared for certain time and the storage modulus (G') was monitored as a function of time after the cessation of shear flow. The addition of MWCNT was found to have a reducing effect on the structural recovery kinetics and this effect was much stronger above the rheological percolation of nanoparticles. It was demonstrated that the rheology can provide a valuable insight in to understanding the MWCNT induced morphological changes of this nanocomposites system. Keywords: Block copolymer, MWCNT, Rheology, Morphology development, Structural recovery

S15-345

Wu Hong, Wang Cuilin, Wang Jianfeng, Guo Shaoyun

Tunable crystalline morphologies and enhanced mechanical properties of isotactic polypropylene under multistage combined stress

Homo-polypropylene sheets with different orientation structure were prepared by multistage stretching extrusion technology. By changing the number of force assembly elements (FAEs), the shear and extensional stress-induced anisotropic structure were investigated. Wide Angle X-ray Diffraction (WAXD) and Microscope Polarized Fourier Transform Infrared (M-FTIR) results showed the number of FAEs plays a vital role on the tunable crystalline morphologies, which was also confirmed by Scanning Electron Microscopy (SEM) and Polarized Optical Microscope (POM)

images. With applying amounts of FAEs, the crystalline and amorphous phases are alternately aligned in the thickness direction. Melting behaviors revealed the force assembly process would enhance the melting temperature, thicker lamellar were obtained during the process. Tensile tests showed enhanced mechanical properties in machine direction (MD) with increasing FAE number, further improvement were observed after annealing at higher temperatures. The Dynamic Mechanical Analysis (DMA) demonstrated large enhancement of storage modulus with increasing FAE number and annealing temperature, moreover, storage modulus in MD was higher than that of transverse direction (TD).

S15-425

Mao Chaoying, Huang Yajiang, Kong Miqiu, Yang Qi, Li Guangxian

Droplet coalescence and clustering behavior in microsphere-filled PIB/PDMS blends under shear flow: The key role of component ratio

The flow-induced morphology of ternary polymer blends consisting of two Newtonian fluids, namely polyisobutylene (PIB) and polydimethylsiloxane (PDMS), and a small fraction of solid polystyrene (PS) microspheres are explored by direct flow visualization. The results suggest that the asymmetric affinity of interfacially located PS microspheres to two fluid components leads to diverse flow-induced morphology in PIB/PDMS blends with different compositions. In 10/90 blends which microspheres are preferentially wetted by the PIB droplets, significantly promoted coalescence of PIB droplets is observed. Increasing the loading of particles or changing the shear rate will alter the size and spatial distribution of PIB droplets. In contrast, in the inverse 90/10 blends which microspheres are wetted by the continuous PIB phase, bridging of PDMS droplets is found, leading to the generation of string-like structure or grape-like clusters. These results indicate that the flow-induced morphology of PIB/PDMS blends in the presence of PS microspheres is not only determined by the experiment conditions (shear rate and degree of wall confinement) but also to a

large extent by the component ratio (concentration of PS microspheres and composition ratio of blends).

S15-435

Sundararaj Uttandaraman

Morphology Development Mechanisms of Viscoelastic Polymer Blends

Polymer blends provide an efficient way to produce new materials. It is known that the final morphology of polymer blends develops rapidly during the blending process. During the initial stages of polymer blending, lamellar structures or sheets are formed and this is an effective way to achieve quick reduction in size. Thus, the millimeter sized polymer pellets are deformed and broken up into sub-micron sized droplets rapidly. Studying the deformation and breakup of a polymer drop in a second polymer melt will help us to understand how one polymer disperses into another, and will give valuable insight into how the final drop distribution is obtained. Visualization studies on drop breakup in polymer systems suggest that the normal stress plays an important role for polymer-polymer systems, and contributes to phenomena such as widening of drops or elongation in the vorticity direction. A good understanding of the mechanism of drop deformation and breakup is crucial to control the dispersion in polymer blends. A specially designed twin-screw extruder and a special transparent Couette flow cell were used to study drop breakup at high temperature. During Couette experiments, the two cylinders counter-rotated to keep the drop in a stagnation position. In polymer systems, it was found that drop breakup occurs even when the viscosity ratio is greater than 3.5 (impossible for Newtonian systems). It may be inferred that the critical breakup condition for polymer systems is different from that for Newtonian systems since polymers are viscoelastic and shear-thinning. The drop size determines to a great extent, the type of drop breakup mechanism and the critical point when the mechanism changes. There is a big jump in the critical shear rate when the mechanism

changes from breakup in the flow direction to breakup in the vorticity direction.

S15-46

Talhi Fatima Zohra, Belhaneche-Bensemra Naima, Benaniba Mohamed Tahar , Massardier Valérie

Characterization of old welded polyethylene gas pipes in service for up to 29 years

The main purpose of this work is to evaluate the long term performance of butt welded polyethylene pipes in comparison to not welded counterparts. Therefore, old welded and un-welded medium density polyethylene (MDPE) pipes used in Algerian gas distribution systems for up to 29 years were investigated. They were characterized using several techniques including dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Characteristics were compared to un-aged samples which have the same basis material as old ones. The DMA results revealed that the melt viscosity of material at the weld is influenced by ageing while TGA and DSC measurements showed that welds are more sensitive to thermal and oxidative degradation than the rest of the pipes.

S15-516

Rodriguez Luis A., Garcia Carla, Grace Landon R.

Three-Dimensional Hygrothermal Anisotropic Moisture Uptake in Bismaleimide/Quartz Laminates

The effect of elevated temperature on threedimensional, anisotropic moisture diffusion behavior is explored via full immersion of a quartzreinforced 6-ply bismaleimide (BMI) laminate. The balanced, 8-harness satin weave quartz fabric reinforced laminates were machined into three different aspect ratios and immersed at three different temperatures. The dimensions of the machined samples were chosen to provide three significantly different ratios between planar surface area and edge surface area available for diffusion in an effort to facilitate the determination of the threedimensional diffusion parameters. Five samples of



each aspect ratio (5, 12.5, and 20) were fully immersed in distilled water at 25°C, 37°C, and 50°C. The rate of the initial, linear uptake is heavily influenced by temperature; moisture content by weight of 1% was reached at 900, 576, and 324 hours of immersion for temperatures of 25°C, 37°C, and 50°C, respectively. Prior work has demonstrated conformance of this material to the Hindered Diffusion Model for room temperature diffusion. Deviation from Fickian behavior, as indicated by slope deviation from the Fickian plateau, exhibits an increase proportional to temperature. Results indicate a temperaturedependence of the hindrance coefficient, similar to the temperature dependence observed for the diffusivity parameter. These results further demonstrate the complexity of polymer diffusion behavior, and reinforce the necessity of accurate prediction techniques.

S15-666

Xiang Meng, Ye Lin

Synthesis and Structure of Permanently Antistatic Monomer Casting Nylon-6-b-Polyether Amine Copolymers

MC nylon-6-b-polyether amine copolymers were synthesized with macro-initiator based on aminoterminated polyether amine (PEA) functionalized with isocyanate via in-situ polymerization. It was found that introduction of PEA delayed the polymerization process of caprolactam bv decreasing maximum heating-rate (Rmax) and prolonging the time (tmax) corresponding to Rmax, resulting in the decrease of molecular weight of MC nylon-6. High grafting efficiency of PEA can be achieved. With the increase of PEA molecular weight, Rmax and grafting ratio decreased slightly. With increasing content of PEA, the melting peak became declining and widening, while the crystallinity and crystal grain size decreased gradually, indicating that the crystallization ability of nylon-6 matrix was weakened by incorporation of PEA molecular chains. In the meantime, the fracture surfaces of the copolymer changed from irregular mosaic to the striation, presenting tough fracture characteristic, and the notched impact

strength of the copolymers were improved dramatically. Noteworthy is that the remarkable increase of crystallization ability and mechanical property can be observed with increasing PEA molecular weight. The electrical resistivity of the copolymers was increased by three orders of magnitude, and kept stable with the prolongation of storage time, indicating a permanently antistatic ability. The improved antistatic mechanism of the copolymers was deduced by the increase of concentration of oxygen atom and C-O group on the surface of the copolymers with the increasing PEA content. The water contact angle decreased and surface tension increased, and finally the hydrophilicity of the copolymers was enhanced, resulting in the fairly good antistatic behavior of the copolymers by absorbing moisture from air.

S15-118

Seo Yongsok

Nonisothermal Crystallization Behaviors of Nanocomposites Prepared by In-Situ Polymerization of High-Density Polyethylene on Tungsten Oxide Particles

Morphology development and thermal properties of polyolefin composites (tungsten oxide (WO3)/ high density polyethylene (HDPE)) were characterized by differential scanning calorimetry, polarized optical microscopy, and nonisothermal crystallization kinetics. Tungsten oxide (WO3) and HDPE composites were prepared by the in-situ polymerization method metallocene which consisted of attaching a metallocene catalyst complex onto the surface of the nuclei (WO3) and followed by the surface-initiated polymerization. A kinetic equation proposed by Seo was employed to analyze the nonisothermal crystallization characteristics of the composites. The polarized optical microscopy and the Avrami exponent verified the importance of the interaction between the HDPE molecules and the nuclei surface for the HDPE molecular ordering around the metal powder as well as the morphological development in the early stage. The Avrami exponent, n, determined from the nonisothermal crystallization kinetics analysis indicates random 3-dimentsional



morphology development for the WO3/HDPE composites. Dispersed WO3 accelerated the crystallization rate due to heterogeneous nucleation effect as indicated by the shift in the crystallization peaks to higher temperatures. The obtained crystalline structures were compared to those for the neat polyethylene resins and carbon nanotube (CNT)/ HDPE composites.



B. Special Symposia

S16- Plastic Solutions for Ecoconception

Keynotes

S16-196

Isayev Avraam I.

Decrosslinking Of Peroxide Crosslinked Hdpe Using Ultrasonic Twin Screw Extrusion: Simulation And Experiment

Decrosslinking extrusion technology for recycling crosslinked polyolefins was developed by using ultrasonically aided twin-screw extruder (TSE). To better understand the decrosslinking process in this extruder, a model for ultrasonic decrosslinking of peroxide crosslinked HDPE (XHDPE) is proposed. The model is developed based on modification of our earlier model describing ultrasonic devulcanization of rubbers. The ultrasonic bubble cavitation in a viscoelastic solid containing small concentration of voids is considered. Calculation of ultrasonic power consumption and acoustic pressure in a bubble filled polymer is proposed based on the linear acoustic analysis. The rupture of network is modeled by considering the breakage of main chains caused by their deformation during bubble oscillation. The current model does not require assigned kinetic parameters to describe the rupture of network. The nonisothermal flow of the decrosslinked XHDPE in the ultrasonic treatment zone in TSE is modeled by considering a helical flow of a power-law fluid with its material parameters depending on the gel fraction. The simulation of ultrasonic under static condition reveals the dependence of ultrasonic bubble oscillation dynamics, gel fraction and crosslink density on the ultrasonic amplitude, hydrostatic pressure, bubble volume fraction and residence

time in ultrasonic treatment. The distribution of temperature, velocity, gel fraction, crosslink density and pressure in the ultrasonic treatment zone in TSE is calculated at various ultrasonic amplitudes. The simulation results are compared with experimental data. A quantitative agreement for ultrasonic power consumption is achieved. A qualitative agreement on the dependence of gel fraction and crosslink density on ultrasonic amplitude is achieved. The effect of flow rate on the gel fraction and crosslink density is over-predicted, possibly, due to the lack of proper modeling of ultrasonic bubble nucleation.

S16-222

Ragaert Kim, Hubo Sara, Van Damme Nicolas, Veelaert Lore, De Meester Steven, Du Bois Els

Design from Recycling: Identifying applications for recycled polymers

Design for recycling is a well-known strategy in which new products are developed so that they can be recycled at their end-of-life. It entails easy separation of different materials and an all-round efficient material use. The strategy is part of a virgin material's start-of-life. Design from Recycling is an altogether different approach, even though the two do not exclude one another. In Design from Recycling, the secondary raw material originating from the recycled polymer (r-polymer) waste of a previous product's end-of-life is the starting point of new product development. These materials are often quite complex (mixed plastics, contaminations...) and not so straightforward to use efficiently. Design from Recycling involves identifying the r-polymer's strengths and weaknesses through extensive characterization, as well as identifying acceptable strategies for possible upgrading of the material quality where necessary. During the stage of product design, these characteristics are taken into account and matches are found between (new) products and r-polymers suitable for producing them. Finally, the overall resource efficiency of the whole process is quantified, ensuring the best possible use of the rpolymers as well as demonstrating to the broader public the gain that is to be had by using these



secondary material sources. This paper will illustrate the principle of Design from Recycling based on an industrial case study.

S16-406

Wang Qi, Bai Shibing, Sun Fasen, Yang Shuangqiao

Recycling Waste Polymer Materials by Solid-State Shear Milling Technology

Recycling of the continuously increased waste polymer materials (WPM) is a big and challenging issue worldwide due to the difficulties in sorting and separating of the multi-component WPM and the reprocessability of the cross-linked WPM. This paper reports a novel solid-state shear milling (S3M) technology to efficiently recycle WPM. We have developed a solid-state shear milling equipment, which has a unique structure, and acts as three-dimensional scissors, therefore has multifunctions such as strong shearing, pulverization, desperation, and cutting of the cross-linked bonds, offering a way to solve the problems in recycling WPM. Firstly, the complicatedwaste polymer blends and composites could be ultra-finely pulverized to micro/nanoscale particles at room temperature. The domain size and performance of the materials were controlled by the particle size and distribution rather than the compatibility and the melt viscosity of the compounds, saving the trouble of sorting and separation of the WPM. Secondly, the cross-linked WPM could be partially decrosslinked by S3M and thermally reprocessed.A series of the WPM that can't be recycled by the conventional methods, such as waste cross-linked polyethylene (XLPE) cables, waste printed circuit boards (WPCB) as well as waste artificial turf, etc. have been successfully recycled by our novel S3M technology. Taking the recycling of waste crosslinked polyethylene (XLPE) cables as an example, the XPE cables with more than 10 kinds of componentswere pulverized to fine powders, the cross-linking structure was partially destroyed, the gel fraction decreased from 67% to 24%, endowing the recycled material good thermal processability. The tensile strength and the elongation at break of the recycled XLPE samples reached 24MPa and 700% respectively, comparable to that of the

pristine HDPE material. The recycled XPE was successfully used to manufacture geomembranes, etc. This work was supported by national high technology research and development program (2012AA063003) of China.



Oral

S16-134

Oguz Oguzhan, Menceloglu Yusuf Ziya

Green composite materials with enhanced stiffness and impact resistance

Environmental and economical concerns are stimulating research in the mass production of sustainable materials for markets require low costs and high production rates. Physical modification of biodegradable thermoplastics such as Polylactic acid (PLA) based on blending with natural fibers and/or elastomers is an economical way to produce green composite materials preventing further stresses on the environment. Although PLA finds use in a wide range of applications due to its intrinsic properties, such as low density and biodegradability, the poor impact resistance is a major problem for many industries. Furthermore, the common use of cellulose based short fibers, which are not suitable to reuse in textile industry due to their length, (natural wastes) and elastomers (synthetic wastes), is becoming a world-wide waste disposal problem. To address these issues, our study is an effort to create a new horizon for the mass production of the advanced green composite materials by the processing of the renewable sources and biodegradable thermoplastics in a high-shear thermokinetic mixer. Here we modified PLA, as a green thermoplastic matrix, by cellulose based short fibers (w-CF) and crosslinked Polyurethane wastes (w-PUR), as renewable reinforcing agents, with various content (1-30% by weight). We produced PLA/w-CF and PLA/w-PUR green composites with enhanced stiffness and impact resistance. Briefly, we achieved 50% increase in elastic modulus and 5-fold increase in impact resistance of PLA by the addition of 30% w-CF and w-PUR, respectively. The results suggest that our approach can be applied, as a practical way, to ensure sustainability and reduce environmental and economical costs in the mass production of biodegradable materials. The main

conclusion of the study is that the extensive blending technology gives us the ability to produce high performance green composite materials as well as managing the world-wide waste disposal problem by reusing of synthetic wastes.

S16-202

Li Guangxian, Huang Yajiang, Yang Junlong, Liu Shixiang, Zhao Jincan

Graphene nanosheets: a promising multifunctional antioxidant to improve the thermo-oxidative stability of isotactic polypropylene

Nowadays, graphene materials have been receiving tremendous attention due to their extraordinary abilities in enhancing the electric/thermal conductivities and mechanical properties of polymeric materials while their potential in the thermo-oxidative stability improving of materials is seldom touched. In this study, the effect of graphene nanosheets (GNS) on the thermooxidative stability of isotactic polypropylene (iPP) different is explored by thermoanalysis technologies. Our preliminary results show that GNS exhibit noticeable positive impacts on the thermo-oxidative stability of iPP, especially in oxygen-rich environments. The underlying mechanism is closely related with the unique physicochemical characteristics of GNS which play a crucial role in the degradation process. It is suggested that the decline both in the concentration of peroxy radicals due to the acceptor-like electronic property afforded by the long conjugated C=C bonds and the lower oxygen permeability due to the barrier effect of GNS are responsible for the improved thermo-oxidative stability of iPP observed. The possible interactions between GNS and conventional antioxidant are also discussed. The utilization of dispersion strategies such as surface grafting or coating is found to be beneficial in updating the stabilization efficiency of GNS. Meanwhile, the mechanical properties of iPP such as tensile creep resistance also exhibit a noticeable improvement upon the incorporation of GNS. Therefore, our findings suggest that GNS can serve as a promising multifunctional antioxidant for



polymeric materials. Keywords: graphene; isotactic polypropylene; thermo-oxidative stability References [1] Yang JL, Huang YJ, Lv YD, Li SR, Yang Q, Li GX. Carbon 2015;89:340-349. [2] Yang JL, Huang YJ, Lv YD, Zhao PF, Yang Q, Li GX. Journal of Materials Chemistry A 2013;1(37):11184-11191.

S16-257

Almusawi Aqil Mousa, LACHAT Remy, ATCHOLI Kokou Esso, TIÉ BI Salima

Manufacturing and characterization of thermoplastic composite of hemp shives and recycled expanded polystyrene

In our study, we are interested in the expanded polystyrene (EPS). In fact, due to its huge volume, it represents two main problems: the large space needed if disposed of in the landfill and the transport cost if we decide to recycle it. Therefore, two process are executed consequently: the first one is the process of recycling the EPS by a recycled solvent, that allow separating the EPS from other plastic waste and reducing the volume to more than 95%. Then the resulting fresh saturated paste is used in the second process as a binder with 60% wt of hemp shives to produce biobased thermoplastic composites. This allowed modifying the mechanical improving the degradation properties, and reducing the overall cost. In addition, adding the hemp shives will significantly reduce acetone evaporation time to 3 hours instead of 3 weeks for drying the pure paste of EPS. Consequently, it reduce the time for recycling the evaporated acetone. We used the thermogravimetric analysis tests (TGA), to estimate, firstly, the acetone quantity required to dissolve the EPS. Secondly, the acetone residual in the final composite. To identify the physic-mechanical properties, we used the Density measurement and the 3-points of load test. As a result, we have succeeded to manufacture a lightweight composite without using the thermoforming process. Indeed, in a second phase, we have used the thermoforming process that has improved, once again, the mechanical properties of this composite to be better than the pure polystyrene.

S16-270

Thoden van Velzen Ulphard, Jansen Michael, Brouwer Marieke, Feil Alexander, Molenveld Karin, Pretz Prof. Thomas

Efficiency of recycling post-consumer plastic packages and their recyclate properties

Recycling of post-consumer plastic packaging involves separate collection, mechanical recovery from MSW, sorting and mechanical recycling. The first two steps in this recycling chain are welldocumented. The subsequent step (e.g. the conversion of sorted fractions into washed milled goods) has, however, not scientifically been described, yet. Therefore a dedicated laboratory was set-up to mimic the mechanical recycling process. This process consists of a shredder, washing mill, density separation vessel, centrifuge and an oven, which converts a sorted fraction into dried washed milled goods, waste products and waste water. This set-up has been used to determine the mechanical recycling yields of the five sorted fractions in a systematic manner, with sorted fractions from both collection systems. These technical processing yields are essential data for a technical recycling chain analysis and environmental studies. The recycled polyolefines were subsequently converted by extrusion and injection moulding and/or kneading and compression moulding into test specimens. These specimens were analysed by FT-IR, DSC and TEM. Also the mechanical properties were measured. This analysis reveals that recycled polyolefines should be regarded as blends. The properties of test specimen made from recycled polyolefines could approach those made from virgin polyolefines in case the extrusion / mixing was intense and the cooling was instantaneous. A model study with the sorted fraction PE was performed to understand the relation between the composition of sorted fractions and the properties of the produced recyclates better. In a systematic manner different types of contaminants were removed and the effect on the recycling process and the recyclate properties were studied. Preliminary results of this study reveal that most contaminants impact the quality of the recyclates.



S16-327

Van Kets Karen, Van Damme Nicolas, Delva Laurens, Ragaert Kim

The effect of the compatibilizer SEBS-g-GMA on the blend PP-PET: virgin and recycled materials

When poly(ethylene terephthalate) (PET) and poly(propylene) (PP) are used for carpet manufacturing, the polymers are attached to one another and become physically inseparable for the purposes of mechanical recycling. In this experiment a blend with a matrix of 80 wt% PP and a dispersed phase of 20 wt% PET were made. Because these two polymers are immiscible in the melt state, the compatibilizer SEBS-g-GMA was added. This compatibilizer was selected by previous research (E.P.A. Van Bruggen, 2014), where it was found to sufficiently induce the brittle-to-ductile transition for an added percentage of 2,5 wt% to a mix of 80:20 PP with amorphous PET (PETg). In the current research, it was found that functionality of SEBS-g-GMA the is transferable from amorphous PET to semicrystalline PET. But as compared to the blend without SEBS-g-GMA, the amount of crystallinity in PET decreases due to the copolymerisation between the compatibilizer and the PET during melt blending. At the other hand, the crystallinity of the matrix increased since the spheres of the dispersion phase became smaller. SEBS-g-GMA was also added to a mixture of post-industrial PP (originated form carpet fibres) and post-consumer PET (origin unknown). When recycled materials were used, the amount of compatibilizer was realize the insufficient to brittle-to-ductile Possible causes include unknown transition. contamination and additives in the recycled polymers. They will, according by their interfacial tension, prefer to migrate in one of the polymers or they will prefer to be in the interface. This could cause interaction with the compatibilizer, but also influence the migration of the dispersed phase in the matrix phase what leads to a different size of the droplets of the dispersed phase compared to the bled of the virgin materials.

Cherukupally Pavani, Hinestroza Juan P, Farnood Ramin, Bilton Amy M, Park Chul B

Adsorption Mechanisms of Emulsified Crude Oil Droplets onto Hydrophilic Open-Cell Polymer Foams

Currently, there is lack of economical and sustainable treatment methods for removal of dissolute and emulsified organics from oil sands tailings water. As a result, open-cell polymer foams are being examined as a potential material for adsorbent filtration treatment. Adsorption experiments using polyester and polyurethane open-cell foam have shown substantial removal of the oil from surrogate tailings emulsions. This substantial oil uptake is unexpected due to the hydrophilic nature of polyester and polyurethane. This paper examines the mechanisms of this unexpected crude oil droplet attachment to enable the design of an adsorbent filter. In particular, the effect of emulsion acidity on adsorption is experimentally studied. In this study, the pH is adjusted to result in acidic (pH 2), neutral (pH 7), and basic (pH 11) emulsions to adjust the oil droplet positive, neutral, and negative surface charge and verify if the attachment onto the foam is due to electrostatic forces. Droplet surface charge, an indicator of emulsion stability was measured through zeta potential. Batch adsorption experiments were performed with foam and model emulsions at 1%, 3%, and 5%, by volume fractions, at 40°C and 200 rpm for 5-10 hrs. There was substantial oil removal at acidic (pH 2) and neutral conditions (pH 7) in approximately 3-5 hrs however, under basic conditions, no significant removal has occurred after 10 hrs. These results indicate the crude oil adsorption onto the hydrophilic foam is due to electrostatic and van der Waals attraction forces. The source of this oil wetting behaviour could be due to the presence of oleophilic surfactants at the polymer surface. Although, the emulsions under acidic condition showed significant oil removal, it could also reduce the net amount of oil droplets deposition onto the surface and/or reusability of the foam.

S16-388

S16-593



Mani Skander

A New Continuous Extensional Flow Mixer for **Compounding and Recycling of Complex Polymer** Blends

The aim of this work is to implement a novel process that combines plastics compounding and recycling into one processing step, thereby developing of a new extensional flow mixer at pilot scale. The original screw-barrel system design of the new mixer, METEOR, is based on creating strong extensional flow to achieve efficient dispersive and distributive mixing. Indeed, the high mixing efficiency of METEOR is the result of multiple passes and surface reorientation of fluid elements through the high stress regions. Extensional flow not only achieves more effective dispersion, but also creates less viscous dissipation than shear flow. Obviously, the temperature rising and the power consumption in METEOR are less than in conventional mixing devices like single and twin screw extruders. The mixing efficiency of METEOR has been compared to three extrusion technologies such as, twin screw extruder, high shear extruder and Buss technology. The effect of methods on these processing morphology development, mechanical, rheological and thermal properties of virgin and recycled polymer blends are investigated.

S16-623

PPS[®]32

Holzer Clemens H., Katschnig Matthias, Purgleitner Bianca, Hornitschek Birgit, Höllebauer Andreas, Link Offenberger Ewald, Hierzenberger Peter, Jürgen, Brzezowsky Klaus, Wind Christian, Dobiasovsky Regina, Ruhaltinger Otmar, Ramsl Martin, Daucher Monika

Upcycling of POM for Catch Springs by Using the **Rec2TecPart Process**

Moving towards sustainability is a social challenge that obliges society and politics the same way. Resource efficiency is thereby an important approach. Regarding plastics a material flow from cradle to cradle (C2C) would be a desirable solution consecutively. C2C already exists in producing simple products out of down-cycled plastic waste.

> 32nd PPS International Conference 2016, Lyon, France

high-quality products, that need engineering plastics, are still far away from implementing recycled polymers on a larger scale. Reasons are for instance rigorous material specifications, demanding RoHS compliance and the need for reproducible supply. Hence, we mostly incinerate engineering plastic waste in Europe, which is neither resource-efficient nor saving CO2. Rec2TecPart (Recyclates to Technical Parts), a project based on a network of small and mediumsized companies in Austria, delivers a process design, that upgrades engineering plastic waste by compounding to fabricate tailor-made materials ("RecHQ") for technical components using the socalled Rec2TecPart process. This process is separated in modules (supply logistics, input producing formulation, and component) which simplifies the implementation later on. To verify the process design we have chosen catch springs made out of recycled POM as a case study. In the beginning, a company analysis has provided weaknesses and strengths of the actual processes, implementation of the needed Rec2TecPart modules led to an adapted process. Subsequently post-industrial POM was upcycled

S16-670

However,

management,

Tominaga Aya, Sekiguchi Hiroshi, Nakano Ryoko, Yao Shigeru, Takatori Eiichi

using the new process design. Moreover, we

conducted a life cycle assessment of the POM-based

RecHQ. The emphasis has lain on controlling data

uncertainty by means of scenario/sensitivity

analysis and Monte Carlo simulation. The results confirmed the new approach, catch springs based

on POM RecHQ save at least 25 % CO2 eq. and 30 % costs providing technical equal material

properties compared to new polymer.

recycling process Fabrication of advanced considered from the perspective of the physical degradation

To address the dual problems of the depletion of natural resources and the environmental impact of a growing volume of wastes, effective recycling of various products and materials has become an important challenge. Especially, the amount of
plastic waste is extremely large, and thus it is very important to establish effective process of recycling them as soon as possible. However, the mechanical properties and durability properties of the products made from waste plastics are very inferior compared to those of products molded from virgin plastics, and thus their application area is presently limited. Usually, the reason of above phenomena has been thought to be caused by chemical degradation and there is no way to improve them. Recently, we found that recycled pre-consumer polypropylene (Pre-RPP), that was not chemically degraded and had almost same molecular properties of virgin polypropylene (VPP), shows very different inner structure and very poor mechanical properties compared to VPP. And by choosing suitable molding temperature, molding time, and cooling condition, the mechanical properties of Pre-RPP had changed very much and some of them became almost same properties of VPP. By referencing of this research results, we had dramatically improved the mechanical properties of containers and packaging recycling plastics by changing molding process.

S16-742

Tavares Beatriz, Fressato Dayanny C. F., Leão Alcides L, Chaves Marcia R. M.

Recycled plastic boxes of automotive batteries: effect of the reprocessing number on the mechanical properties

Currently the automotive industry is responsible for using a lot of plastic, so the interest in recycling has been growing. Polypropylene (PP) is a low cost thermoplastic, easy molding, good impact resistance, good thermal stability, among other advantages, justifying its use as raw material in the automotive industry. These characteristics make the PP polymer the best choice to produce boxes of automotive lead-acid batteries. In this context, this study was conducted to determine the effect of number of cycles on the mechanical properties of new boxes produced by blends using recycled PP. The aim was investigate the processing conditions of the blends without the PP loses the usage essential properties. The behavior of the recovered

addition of PP (battery scrap) to original PP in various proportions, and in their original forms (PP recovered 100% and 100% original PP) was The blends were obtained evaluated. in homokinetic and extruder mixer, a total of four thermo-mechanical processing cycles. Samples for mechanical testing were injected. Flow testing, tensile and impact strength were determined. The samples were analyzed for iron and lead content. The results indicated that recycling can be done up to four times without loss of product quality, compared with the standards established for the battery box.



Poster

S16-49

Benaniba Mohamed Tahar, Massardier Valerie

Thermal Stabilisation and Flexibility Improvement of Plasticised Poly(vinyl chloride) using Biobased Plasticisers

Biobased blends present potential use as nontoxic, sustainable plasticizers and as replacement of commonly used phthalate plasticizers. Epoxidised sunflower oil (ESO) and epoxidized sunflower oil methyl ester (ESOME) were prepared respectively by epoxidation and esterification reactions of sunflower oil (SO). Samples prepared by different combinations of ESO, ESOME, isosorbide (ISB) and acetyl tributyl citrate (ATBC) were blended with poly(vinyl chloride) (PVC) using two roll mills at 160¢XC. Discoloration sheets, mechanical properties, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) dynamical mechanical analysis (DMA) and scanning electronic microscopy (MEB) were used to characterise the plasticised PVC. The plasticizer combination system increased the thermal stability and the elongation at break. All samples exhibited both single Tg and Tan £_ obtained by DSC and DMAfw, which is in agreement with good miscibility of our formulations. Thus, combination of ESO, ESOME, ISB and ATBC performs a dual role in the stabilization and plasticization of PVC.

S16-302

Takenaka Nozomi, Tominaga Aya, Nakano Ryoko, Sekiguchi Hiroshi, Yao Shigeru

Effective Pelletizing condition of recycle containers and package plastics.

The mechanical properties of recycle containers and packaging plastics are thought to be very poor. However, we have suggested that the main reason of this phenomena is physical degradation. We also suggested the physical regeneration molding condition of those recycled plastics. In this time, we investigated pelletizing condition dependence of mechanical properties of recycle containers and package plastics. We found that the mechanical properties of injection molded sample also depends on the pelletizing condition that is estimated from the previous consideration.

S16-433

Kuwabara Kou, YASUHARA Toshiyuki

Mechanical Joining of Metal Sheets and CFRTP by Using High Frequency Induction Heating

Now a days, CFRTP (Carbon Fiber Reinforced Thermo-Plastic) is strongly expected for losing weight of motor vehicles because of its good productivity. Though bolts or rivets are usually using as joining methods for joining between CFRTP and metals, some problems occur such as gaining weight or break-point from drilling holes. In this study, joining method for metal sheets and CFRTP without break of carbon fiber induced by drilling was developed and joining strength by tensile test was investigated. Cross-ply composite of CFRTP impregnated by PMMA and A5052 aluminum sheet were used as specimens. Joining method of this study shows as follows. First of all, aluminum sheet of 0.3mm-thick was fabricated that mechanical anchors was formed like a pin holder and projection shape was almost 1 mm squared. Next, CFRTP sheet of 10mm-wide and 30mm long was set into the induction heating coil. Then the carbon fibers situated among CFRTP were heated by high frequency induction heating and surface of the CFRTP was heated up to 170 degrees C. the press mold with a punch made of ceramic material of 10mm-square was closed and aluminum sheet specimen and molten CFRTP was pressed. The compression force of about 2kN was applied. Tensile shear tests of these specimens were carried out. As a result, maximum tensile strength was about 60MPa. This value was almost twice larger than that of the pristine PMMA sheet and A5052 specimen. This result indicates that the mechanical anchors of the aluminum sheet contribute to the enhancement of the joining strength. Consideration of prevent method for galvanic corrosion of



between CFRTP and metal and also investigation of peel strength are future works.

S16-595

MANI Skander

A New Continuous Extensional Flow Mixer for Compounding and Recycling of Complex Polymer Blends

The aim of this work is to implement a novel process that combines plastics compounding and recycling into one processing step, thereby developing of a new extensional flow mixer at pilot scale. The original screw-barrel system design of the new mixer, METEOR, is based on creating strong extensional flow to achieve efficient dispersive and distributive mixing. Indeed, the high mixing efficiency of METEOR is the result of multiple passes and surface reorientation of fluid elements through the high stress regions. Extensional flow not only achieves more effective dispersion, but also creates less viscous dissipation than shear flow. Obviously, the temperature rising and the power consumption in METEOR are less than in conventional mixing devices like single and twin screw extruders. The mixing efficiency of METEOR has been compared to three extrusion technologies such as, twin screw extruder, high shear extruder and Buss technology. The effect of these processing methods on morphology development, mechanical, rheological and thermal properties of virgin and recycled polymer blends are investigated.

S16-596

de Sousa Fabiula D. B. , Scuracchio Carlos H., Hu Guo-Hua, Hoppe Sandrine

Devulcanization Of Waste Tire Rubber By Microwaves

It is well known that the disposal of solid residues is an enormous problem, especially in the case of vulcanized rubbers like tires. The old practice of landfilling is out of using due to the rising land costs, environmental concerns, fire risks and the possibility of proliferation of mosquitoes and other disease-carrying vectors. Attempting find а solution, the devulcanization has been shown to be an effective technique, making possible to the rubber to flow and to be remolded. However, the process not only breaks sulfur links, but also creates new other bonds, modifying the structure of the material as a whole. In order to help the understanding of the structural modifications on the GTR as a result of devulcanization by microwaves, this work proposes an in-depth study of the chemical modifications as function of the exposure time of the GTR to microwaves. Some important conclusions were that the final temperature reached by the sample is the determining factor for the success of the process. Depending on the final temperature of the sample, different types of sulfur bond can be broken and along the treatment there is a balance between breakings and formation of new bonds. So, the process must be well controlled, also to avoid degradation of the main chains.



S17- High Performance Composite Processing

Keynotes

S17-770

Felix Behnisch, Rosenberg Philipp , Weidenmann Kay André, Henning Frank

Manufacturing of CFRP with Epoxy and Polyurethane Systems in HP- RTM Process and Investigation of the Matrix Influence on the Laminate Properties

The High Pressure Resin Transfer Molding (HP-RTM) process has the potential for high-volume production of high performance fiber-reinforced components in the automotive industry. The development of robust equipment, new process variants and highly reactive matrix systems lead to significant reductions of the cycle time in recent years. The paper addresses the manufacturing of carbon fiber reinforced laminates with different Polyurethane (PUR) and Epoxy (EP) resin systems. To evaluate the matrix influence on the material properties, matrix dominated test methods were selected to characterize the manufactured parts. The laminates were manufactured using HP-RTM equipment for precise dosing and mixing of highly reactive resin components with relatively high throughput rates. The test samples were produced with constant process parameters using carbon fiber reinforcements. Only the matrix-specific supplier instructions for processing of the matrix mixing systems ratio, (e.g. component temperatures) were considered in the study. Three PUR systems and one EP system were examined and compared. For the evaluation of the matrix influence on the laminate properties, the interlaminar shear strength and the damage tolerance under impact loading were investigated. To characterize the interlaminar shear properties, two test methods were selected and compared to

each other: the Short-Beam Shear (SBS) test and the Edge Shear test. To obtain the damage tolerance under impact loading Compression after Impact (CAI) tests were carried out. The results show the impact of the Epoxy and Polyurethane matrix systems on the laminate performance Keywords: CFRP, HP-RTM, Fiber volume content, ILSS, Short beam shear test, Edge shear test, Compression after impact, CAI, Epoxy resin system, Polyurethane resin system.



Oral

S17-188

Chen Ning, Qi Fangwei, Wang Qi

Preparation and Selective Laser Sintering of PA11/ TiBaO3 Piezoelectric Composite Powders

Selective Laser Sintering (SLS), as an important 3D printing technology, can create any complicated shapes and structures that can not be achieved by conventional fabrication techniques. However, at present, SLS usually uses sole-component polymer powders due to the limitation of processing conditions, which can hardly meet the mutifunctional requirement for high-tech devices. This paper reports a novel polyamide11/barium titanate (PA11/ TiBaO3) piezoelectric composite powders prepared through organic/inorganic hybrid and solid state shear milling (S3M) technique so as to make the 3D printing products with required shapes and multi-functions. Solid state milling equipment is our patent equipment, which has a unique structure and acts as three dimensional scissors, making polymer/inorganic materials finely pulverized and well dispersed at room temperature. The particle size and size distribution, thermal behaviors, as well as the bulk and flow characteristics of PA11/ TiBaO3 powders were studied. The results indicated that polyamide 11 pellets with average particle size of 3-6 mm could be pulverized to fine powders with average particle size of 63.9µm and a narrow particle size distribution. The TiBaO3 particles were well dispersed in PA11 matrix with good interface compatibility. The sintering window for PA11 and PA11/TiBaO3 powders, between the onset temperatures of crystallization and melting, was approximately 12°C. The bulk density and flowability of powders were greatly improved with addition of TiBaO3 particles. For example, the bulk density of powders with 40wt% TiBaO3 was increased from 0.096 g/cm3 to 0.172 g/cm3, while the angle of repose decreased from 47.5° to 40.3°. By Farsoon-HT251P the SLS machine, the

292

PA11/TiBaO3 powders were sintered to complicated shape parts with good piezoelectric properties by adjusting the sintering process parameters. The S3M technology offers a new way to efficiently produce polymer based powders with multi-function suitable for SLS processing, thus develop new applications for SLS technology. This work was supported by the National Natural Science Foundation of China (51433006).

S17-332

Polychronopoulos Nickolas D., Papathanasiou T. D.

Some New Results in Optimal Fluid Infiltration in a Flexible Permeable Substrate Moving Past a Rigid Cylinder

We present a numerical analysis for the liquid penetrating a thin, deformable and permeable substrate moving in close proximity over a rigid stationary cylinder. The flow in the liquid film separating the substrate from the cylinder is described by lubrication theory, while fluid transport into the substrate is governed by Darcy's law. The deformation of the thin substrate at each position is assumed to be a linear function of the local hydrodynamic pressure in the gap. Our results indicate that the liquid/fluid interface is forced away from the cylinder surface as it approaches it and tries to come closer as it moves downstream. We elucidate that this pushing from and pulling towards the cylinder behavior breaks the symmetry of the gap and results in a final fluid penetration which is not possible when the substrate behaves as completely rigid and permeable. Under specific deformability (expressed by Young's modulus E) and permeability conditions of the substrate, the final amount of fluid that infiltrates is maximized. This may aid into optimization of relevant coating/printing processes as well as in the pultrusion of composites, where the fluid infiltration depth essentially defines the final product properties.

S17-402

Suenaga Hiroto, Ishigami Akira, Taki Kentaro, Inoue Takashi, Ito Hiroshi



Engineering Properties and Structure of Reactive Molded Polymers and Its Fiber Reinforced Composites

Recently, fiber reinforced thermoplastics (FRTP) has attracted attention in the automotive and aviation fields. However, the thermoplastic resin is used as the matrix of FRTP is very difficult to the fiber bundles impregnate at a high melting temperature and high viscosity. Therefore, it has to be noted that in-situ polymerization using monomer with a low melting temperature and low viscosity is the one of the attractive alternative method. Here, we study the in-situ polymerization of å-caprolactam as a monomer in order to fabricate polyamide 6 (PA6) and its composites by using reactive molding. The thermal property and the higher order-structure of polymerized PA6 and its composites were analyzed by differential scanning calorimeter (DSC). The engineering mechanical properties as bending and impact behaviors were evaluated. It found that increasing crystallinity of PA6 has resulted in enhance the flexural modulus and flexural strength in a linear relation. In the case of FRTP using PA6, the flexural modulus and flexural strength of Carbon and Glass FRTP showed high values, respectively, as compared with common PA6 composites materials.

S17-551

Giusti Ruggero, Lucchetta Giovanni

Analysis of the State of Tension at the Bonding Area Between Components of a Full Thermoplastic Hybrid Composite

The adhesion between two components of full plastic hybrid composite parts is ensured by the macromolecules interdiffusion across the interface. Technologies that are usually involved, such as injection overmolding and in mold forming, require temperature high enough to promote this phenomenon. The aim of this work is to evaluate the warpage effect along the bonding area in relation to process setting and to evaluate the effect of an annealing treatment. A T-joint specimen was produced with polypropylene-matrix composites and it was made of a rectangular sheet base, which is glass woven fabric reinforced, and a short glass fiber reinforced stem. The molding process was numerically simulated and the results, after a deep analysis of available outputs, were post-processed with a structural code. The coupling of the software allowed to convert the warpage output in to a residual stress at the interface. The most significant process parameters effects on tensile strength were investigated in accordance to a design of experiments approach. Tensile test results of asmolded samples and after annealing samples were compared.

S17-755

Dkier Mohamed, LAMNAWAR Khalid, Maazouz Abderrahim

Rheokinetic studies of polyamide for T-RTM process

The main goal of this work is to develop study and characterize the structural evolution of thermoplastic matrix during the Resin Transfer Molding (T-RTM) process. To attain this objective, the reaction kinetic and its properties for forming process of PA-matrix were investigated as an alternative for the production of thermoset systems. Through this work, various formulations of PA with anionic polymerization from caprolactam were studied. Reaction kinetic and crystallization were determined depending on processing parameters and chemistry. Besides, we present some promising routes to in-situ monitor the process of thermoplastic composites with tailored mechanical and physical properties. The dielectric analysis technique coupled to rheology was used to monitor the reaction versus time, temperature and the type of catalyst. Indeed we characterize both the structure and chemorheological properties of PA formulations. Based on the obtained results, the T-RTM cycle processing window were purposed as well the injection time, the reaction temperature and composition. Keywords: T-RTM, Anionic Polymerization, Rheokinetics

S17-777

Ram Ranvijai , Khastgir Dipak



Mechanical, electrical, dielectric and thermal property of Polyvinylidene fluoride (PVDF)/Conducting Carbon Black (CCB) and Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)/(CCB) composites

The PVDF/CCB and PVDF-HFP/CCB composites were prepared by solution casting technique. The PVDF/CCB and PVDF-HFP/CCB composites show composition dependent morphological, mechanical, and electrical properties. It reveals from mechanical properties of PVDF/CCB and PVDF-HFP/CCB composites that CCB is non-reinforcing filler for both the polymer matrices. Hardness (Shore D) is highly affected by CCB loading in both the matrices (PVDF and PVDF-HFP). The AC conductivity of PVDF and PVDF-HFP is frequency dependent and it increases with increase in frequency. The AC conductivity of PVDF/CCB and PVDF-HFP/CCB composites is frequency dependent before percolation and frequency independent after percolation threshold. Dielectric loss decreases with increasing frequency. Thermal conductivity of PVDF/CCB and PVDF-HFP/CCB composites is highly influenced by temperature as well as CCB content in both the polymer matrices. The field emission scanning electron microscopy (FESEM), of PVDF/CCB and PVDF-HFP/CCB images composites of cryo- fractured samples show the surface morphology, dispersion and distribution of CCB in PVDF and PVDF-HFP matrices. Keywords: Percolation threshold, composite, Young modulus, thermal conductivity.

S17-84

Hopmann Christian, Beste Christian, Boettcher Arne, Fischer Kai

Compression moulding of LFT components with increased quality by variothermal mould technology

For the production of composite components made of long-fibre reinforced thermoplastics (LFT) the economic compression moulding process is well established. However, the low temperature of the compression mould during processing leads to a and in the compression force in particular for thinwalled components. In addition low surface qualities result which prevent the application of such components in visible areas. To overcome these disadvantages, a variothermal compression molding process has been developed at the Institute of Plastics Processing (IKV) at RWTH Aachen With University. the variothermal mould technology a reduction of the viscosity of the moulding compound during processing is achieved. This results in a reduction of compression force by about 60 %. Additionally, moulding compounds with higher fibre contents (up to 60 % by weight) can be processed and the surface quality of LFT compression moulding components can be significantly increased for the application in visible areas. This paper describes the functionality of the variothermal mould technology and its efficiency for the process of LFT compression moulding. Results of detailed investigations regarding the influence of the mould temperature on the process properties (compression force, rheology) and the component properties (mechanical properties, surface qualities) are presented and discussed.

significant increase in both the material viscosity



32nd PPS International Conference 2016, Lyon, France

S18- Additive Manufacturing for Plastic Components

Keynotes

S18-590

REGNIER Gilles JP

Simulation of Selective Laser Melting process for thermoplastic powder

Thermoplastic parts obtained by selective laser melting of a powder bed (SLM process) have porosities which significantly reduce their mechanical resistance. These porosities are due to trapped air between polymer grains while polymer melts and grains coalesce. To understand the physical mechanism involved in the powder densification, the anisothermal coalescence of a powder bed has been simulated after the passage of the laser beam. Firstly we show that coalescence of spheres leads to roughly the same coalescence time as cylinders. It allowed us performing a 2D simulation using a C-NEM method implemented in Matlab® to assess the importance of the different physical phenomena involved in the process: polymer powder grain coalescence, interface welding, process temperatures, powder laser energy absorption. Two polymers were considered in the simulations: a PEEK and a PEKK. Surface tension and viscosity of studied polymers, which pilot coalescence phenomenon, were measured versus temperature. The geometry of powder bed was determined by Xray tomography. Laser were absorption of thermoplastic powders identified though a specific device and а calorimeter. The simulation was validated by comparing the simulation of flows for of known simple geometries: cylinder coalescence and pendant drop. The simulation was calibrated by adjusting thermal exchange coefficients thanks to measured melted depth. We have determined thermal and time orders of magnitude of the process. We mainly show that the temperature of

the polymer may rise by several hundred degrees and decreases in a few tenths of a second, while densification process can take several tens of seconds. We have processing window for semicrystalline polymers. Then we could conclude that only amorphous thermoplastic powder with a very low molecular weight can be processed by SLM process.

S18-484

Xia Hesheng

SLS 3D printing of Thermoplastic Polyurethane Carbon Nanotubes Nanocomposites

3D printing, a manufacturing technology with innovation and intelligence, has swept around the world due to its customization and mold-free property. Selective Laser Sintering (SLS) is one of the most significant 3D printing technologies. It is a powder-based process and manufactures with laser as the power source. On the basis of CAD data, it selectively sinters the powder layer by layer into three dimensional objects. However, one limitation of SLS in a wide-range application is the narrow variety of available polymer materials. Up to date, polyamide 12 (PA-12) is the most commonly used SLS polymer material in commercial application. Other polymers with remarkable property such as PA-11, polystyrene (PS), poly ether ether ketone (PEEK), thermoplastic polyurethane (TPU) only represent a small fraction [1]. While developing new SLS polymer materials, polymer compounds based on existing polymers have been prepared to enhance the mechanical, thermal and electrical property of SLS products [2][3], of which PA-12 compounds are normally used. In this study, the multiwall carbon nanotubes (CNTs) wrapped TPU powder was successfully prepared and used for SLS 3D printing. A novel approach, i.e. using CNTs-wrapped TPU composited powder, combined with the SLS 3D print technology, was and used construct electrical proposed to conductive nanocomposite with segregated conductive network. The TPU/CNTs nanocomposite obtained by our approach has much higher electrical conductivity and lower percolation than those by conventional extrusion and injection



molding. Also the 3D printed sheet shows good flexibility, which can be stretched, bended and twisted.

laser sintered parts with an improvement of some properties.

S18-269

Wegner Andreas

Crosslinking of Laser Sintered Polyamide 12 and Polyethylene Parts

Laser sintering gets more and more importance as a small series production technique. However, there is only a little number of materials available for the process. In most cases parts are build up using polyamide 11 or polyamide 12. Therefore, parts produced with laser sintering sometimes do not have the required part properties for intended applications. Especially temperature stability or chemical resistance are sometimes not sufficient for parts made by polyamide 12. Cross-linking is a well established process for the post-processing of plastic parts in a cheap and fast single step treatment. It offers the possibility to improve temperature stability, the mechanical properties and the chemical resistance of parts. Therefore, it offers also great potential to improve part properties of laser sintered parts. However, there is only very limited knowledge on use of crosslinking for those parts. Within the performed work cross-linking is used to post-process parts made by laser-sintering. Two different laser sintering materials are considered in the study. On the one hand a standard polyamide 12 from EOS (PA 2200) is used. This is modified with a cross-linking agent on two different ways in order to test that influence on the resulting part properties. On the other hand a new polyethylene material from ROWAK, which was developed in person, is used for the tests. This material does not require an additional crosslinking agent. The laser sintered parts are crosslinked using two different radiation levels. Afterwards material and part properties like temperature stability and mechanical properties are studied for the cross-linked parts. Additionally, these results are compared to those of parts which were not treated. Results show a significant influence of cross-linking on the performance of



Oral

S18-176

Kleijnen Rob, Sesseg Jens, Schmid Manfred, Wegener Konrad

Insights into the development of a short fiber reinforced polypropylene for laser sintering

Selective laser sintering (SLS) is a powder based additive manufacturing technology, and one of the most promising technologies currently in use for the manufacturing of medium sized series of functional parts. However, the availability of suitable materials is still very limited, with polyamide-based materials taking up the lion's share of consumption. Recently, a number of polypropylene materials has come onto the market as an addition to the SLS materials portfolio. The current study focused on the improvement of mechanical properties of one of these materials by fiber reinforcement, a method well known in traditional polymer processing. In a systematic manner, varying amounts of wollastonite and glass fibers of different lengths ($\sim 50 - 150 \mu m$) were dry blended with two varieties of bonding agents and the polypropylene powder. The processability on an SLS machine of the produced blends was assessed, and the mechanical properties of produced parts were determined via tensile and impact resistance tests. Additionally, the nature of fracture was investigated using microscopy. Through simple dry blending, homogeneous distributions of fibers could be achieved. It was found that both fiber length and amount play a critical role with respect to powder flowability, and therewith processability. In addition, the nucleating effect of wollastonite fibers caused a narrowing of the processing, or sintering window. Since the fibers were all assumed to be shorter than the critical length, the most important parameter to be influenced is adhesion of the fibers to the polypropylene matrix. The adhesion was found to depend largely on choice of the bonding agent and its particle size distribution, and could be improved

by changing certain process parameters. Ultimately, it was possible to produce parts that showed both increased tensile modulus and strength, in comparison to unfilled materials.

S18-20

Mead Joey, Barry Carol

Nanomanufacturing Processes for Printed Polymer Structures

The Nanomanufacturing Center at UMass Lowell processes has developed to enable the nanomanufacturing of polymer based products. Bulk properties can be tailored for preparing novel nanomaterials for use printing materials or as substrates. This work will focus on the ability to tailor the surface for specific applications or enabling the printing of structures onto the substrate. For example, the surface chemistry and structure can be tailored for superhydrophobic or omniphobic properties. Tailored surfaces for controlling the printing of secondary structures by patterning of hydrophobic and hydrophilic surface patterns as well as nano or micro-structured surfaces with patterns of different polymers or nanoparticles can be made with directed assembly and transfer to a polymer substrate. The process can be scaled to a roll to roll process. A critical aspect is the transfer process, which is controlled by the interfacial attraction between the substrate and the patterned nanomaterial and the process parameters (melt temperature, rates). These structures can be used in applications such as metamaterials, flexible electronics, sensors, and structural materials. The environmental, health, and safety aspects of nanomanufacturing are also addressed.

S18-23

Knoop Frederick, Kloke Agnes, Schoeppner Volker

Quality Improvement of FDM Parts by Parameter Optimization

Fused Deposition Modeling (FDM) is an Additive Manufacturing (AM) technology which is used for prototypes, single-part-production and also small

batch productions. For use as a final product, it is important that the parts have good mechanical properties, a high dimensional accuracy and smooth surfaces. The knowledge of the mechanical properties is very important for the design engineer when it comes to the component design. End-use parts out of the FDM process have to resist applied forces. In this paper, investigations were conducted with the polymer ABS-M30 from Stratasys Inc. To achieve a quality improvement of FDM parts, various toolpath parameters and orientations were used. Within the mechanical properties, the tensile, flexural and impact strength were evaluated. Furthermore, the tensile strength of FDM parts is compared to injection molded specimens. With optimized parameters, an increase of the tensile strength by up to 28% and a doubling of the impact strength was possible.

S18-251

Chaunier Laurent, Leroy Eric, Della Valle Guy, Dalgalarrondo Michèle, Bakan Bénédicte, Marion Didier, Madec Baptiste, Lourdin Denis

3D Printing Of Maize Protein By Fused Deposition Modeling

Additive Manufacturing (AM) opens new perspectives for biopolymers in functional material applications, as for the production of biomedical devices, exploiting their biocompatibility and resorbability. Plasticized materials from zein, a storage protein from maize seed endosperm, could display thermomechanical properties matching with Fused Deposition Modeling (FDM). The objective of this work was to evaluate their thermorheological behaviour during processing, in relation with their structural modifications. For this purpose, 20% glycerol was added to commercial zein, containing naturally about 4% lipids and 5% water. After storage at intermediate relative humidity (RH=59%), its glass transition temperature, measured by DSC, was Tg=42°C. The principal mechanical relaxation, measured by DMA, was found at T α =50°C, leading to a drop of the elastic modulus from E'=1.1GPa, at ambient temperature, to E'=0.6MPa at T α +100°C. These values are in a similar range as those of standard

polymers used for AM-FDM processing, such as PLA and ABS. The molecular structure of zein was characterized at different scales by SDS-PAGE, reversed-phase HPLC, FTIR and WAXS, at each processing stage: (i) the initial formulation of the plasticized powdery material, (ii) after extrusion at 130°C for shaping printable filaments, and (iii) after deposition through the 3D printer nozzle (Ønozzle=0.5mm, Tprinting=130°C, vprinting≈10mm/s). The presence of disulfide bond cross-links was evidenced in extruded filaments and remains at the same level after printing. It was checked by WAXS that, in these conditions, no molecular orientation was obtained in the deposited material. These results lead to the setting up of zein-based printable compositions, bv shedding light on the structural changes of these materials during processing. This opens the field of their processing as resorbable printed parts, with a controlled geometry and a designed tridimensional structure.

S18-254

Alig Ingo, Wohlgemuth Florian

Viscoelastic modelling of gas pore collapse during polymer sintering

Based on of Frenkel's viscose flow approach [1] and Mackenzie and Shuttleworth [2] extension considering trapped gas, a model for the shrinkage of a gaseous pore in a viscoelastic melt driven by surface tension was developed. The viscoelastic flow of polymeric materials was considered by using a simple viscoelastic model described by Bellehumeur [3]. In the simulation the viscoelastic relaxation has a pronounced effect on the time scales of the shrinkage, but does not alter the final equilibrium gas sphere diameter. First attempts at including gas diffusion motivated by the works of Kontopoulou and Vlachopoulos [4] and Gogos [5] will be given. Numerical solutions using our simplified model show, that the inclusion of gas diffusion leads to a complete collapse of the pore. The rate of diffusion can change the time dependence of the collapse mechanism tremendously. [1] Frenkel, Journal of Physics, vol. IX, no. 5, pp. 385-391, 1945. [2] Mackenzie and



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Shuttleworth, Proc. Phys. Soc. B, vol. 62, p. 833, 1949. [3] Bellehumeur, Kontopoulou and Vlachopoulos, Rheologica Acta, vol. 37, no. 3, pp. 270-278, 1998. [4] Gogos, POLYMER ENGINEERING AND SCIENCE, vol. 44, no. 2, pp. 388-394, 2004. [5] Kontopoulou und Vlachopoulos, POLYMER ENGINEERING AND SCIENCE, Bd. 39, Nr. 7, pp. 1189-1198, 1999.

S18-274

Kukla Christian, Duretek Ivica, Schuschnigg Stephan, Gonzalez-Gutierrez Joamin, Holzer Clemens

Effect of Particle Size on the Properties of Highly-Filled Polymers for Fused Filament Fabrication

Fused Filament Fabrication (FFF) could replace injection moulding as the shaping step in a process similar to powder injection moulding (PIM). Herein after shaping by using a highly-filled polymer the part is debound and sintered to obtain a solid part of metal or ceramic. New feedstock materials have been developed that can be printed using conventional FFF equipment, debound and sintered to obtain stainless steel parts. However, there are many parameters that can affect the performance of the FFF feedstock materials. One important parameter is the particle size distribution of filler particles. In this paper, feedstocks containing 316L different steel powder with particle size distributions were characterized in terms of viscosity and mechanical properties, and tested regarding the printability using a conventional FFF machine. It has been observed that particle size significantly affect the properties of feedstock materials.

S18-338

Verbelen Leander, Van Puyvelde Peter

Screening methodology for the identification of new polymers for Laser Sintering

With the increasing use of laser sintering as a form of Additive Manufacturing, there is considerable interest in developing new polymer materials for this technique. Due to the complexity of the process, however, materials have to fulfill very specific requirements in order to be easy processable. In this study, a screening methodology was developed that encompasses all material properties essential for laser sintering. This methodology consists of both traditional techniques to evaluate coalescence, melt flow and crystallization kinetics, as well as newly developed techniques to measure powder flow and crystallization shrinkage. Using this methodology, existing sinter materials such as polyamide-12 have been investigated, but also some new promising materials have been identified that could increase the material choice for laser sintering.

S18-360

Jarry Thomas, Barrès Claire, Charmeaux Jean-Yves

Investigation of the laser sintering process from the melt side

Laser Sintering (LS) is widely used to produce plastic parts with complex designs, for prototyping or custom low volume production. But achieving good and reproducible mechanical properties, suitable for end-use parts, is still a challenge. The aim of this work is to better understand how the physical mechanisms of the material transformation influence the final part properties. LS parts are known to exhibit less ductility than their injectionmolded counterparts. The crystalline microstructure is not the only feature affecting the mechanical properties. The degree of "welding" between powder particles and the residual porosity certainly have a major role, too. A variety of parameters influence the parts final microstructure, especially the LS machine settings and the physical features of the material. It is well known that heat control throughout the entire processing is crucial in determining the parts final properties. Previous work has shown some relations between the variables of the laser exposition, part microstructure and mechanical properties. The present study addresses specifically the phenomena occurring in the molten phase, which contribute to the consolidation and densification of the layer prior to its solidification. In a semi-crystalline



polymer powder under laser exposure, particles first melt, then viscous coalescence occurs, followed by a densification step through gas bubbles removal. The anisotropy of mechanical properties in LS parts suggests that macromolecular diffusion is a key phenomenon to the bulk formation. In this work, a PA12 powder was chosen to investigate the polymer interdiffusion dynamics through interfaces and the bubble resorption through gas diffusion in the melt. These results allow to better understand how material characteristics and process conditions can affect the bulk formation and the resulting correlate with microstructure in order to mechanical properties.

S18-449

Baumann Stéphanie, Eisenträger Frank, Niessner Norbert, Meiners Josef, Schmidt Hans-Werner, Bastian Martin

Relationships between ABS Copolymer Composition, Filament Quality and 3D Printing Performance in FDM Process

Fused Deposition Modeling (FDM) is a well-known additive manufacturing process used for producing household objects as well as industrial prototypes and end-use parts directly from three dimensional computer aided design (CAD) models. The FDM technology generates 3D printed products by feeding a filament of thermoplastic material through a heated extrusion nozzle which deposits material strands onto a platform from the bottom up, layer-by-layer. The most widely used FDM material offering a good heat, moisture and chemical resistance is acrylonitrile butadiene styrene (ABS). Besides process parameters, such as extrusion and building chamber temperatures, building orientation, filling raster angle and air gap, the material characteristics also play a significant role in the performance of the 3D printed parts, but they have still not been sufficiently investigated. Over the course of our research, we studied the relationships between the ABS copolymer composition, the filament quality and the 3D printing performance in the FDM process. A series of ABS materials made up of diverse styrene acrylonitrile (SAN) copolymers and different

butadiene (BR) amounts were prepared using compounding process by blending diverse SAN matrices with different amounts of SAN-grafted butadiene rubber (BR-g-SAN). Filaments from the ABS materials were fabricated using extrusion process, analyzed with regard to their diameter consistency and roundness and tested on a FDM 3D printing machine. For the assessment of the 3D printing performance, appropriate test specimens were printed and characterized. The evaluated properties included dimensional accuracy, overhang and bridge building ability as well as tensile characteristics like tensile modulus, tensile strength and elongation at break. The results show a correlation between the butadiene amount and the evaluated properties. The findings form the basis for further FDM material qualification and development.

S18-464

Van den Eynde Michael, Verbelen Leander, Van Puyvelde Peter

Influence of Temperature on the Flowability of Polymer Powders in Laser Sintering

Powder flowability depends on many variables. Not only intrinsic powder characteristics, such as particle size and shape distribution, contribute to the quality of the powder flow, also external parameters such as temperature and humidity play a large role[1-2]. Therefore, it is advisable to check the extent of their influence on powder flowability in the intended application. The application of interest is Laser Sintering (LS), a form of Additive Manufacturing (AM) that uses polymer powder as a base material. Particles, with an average particle size of around 50 µm, are spread into thin layers of around 100 µm[3]. Temperature effects are relevant in this application, as the powder bed in a sintering machine is heated between the crystallisation and melting temperature to minimise part warpage[4]. This heating influences powder flow in two ways. Firstly, the elevated temperature may soften the polymer, thereby changing the contact between particles and thus altering flow. Secondly, the long exposure to elevated temperatures, combined with the load of the powder bed above it, can lead to



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caking of the powder. Depending on the caking strength, this affects the recycling of the unsintered powder for the subsequent builds. To evaluate the influence of temperature, two independent techniques are used. The first technique, the powder spreader, an in-house built device, mimics the LS application as close as possible on a lab scale. It evaluates the density and surface quality of deposited layers at elevated temperatures. The second technique, powder rheometry, measures the force needed to move through a powder bed. Both tests indicate a decrease in the flowability of the standard LS polyamide of EOS above the glass transition temperature. 1 A. Amado et al, RapidTech 2013 Messe Erfurt, Germany (2013) 2 R. Bhadra et al, Int. J. of Food Prop. 16, 1071-1079 (2013) 3 R.D. Goodride et al, Prog. in Mater. Sci. 57, 229-267 (2012) 4 D. Drummer et al, Phys. Proc 5, 533-542 (2010)

S18-465

Vetterli Marc, Wegener Konrad, Schmid Manfred

SLS surfaces: new insights

Powder based additive manufacturing production technologies still face important issues concerning the surface state of produced parts. Regardless of base material nature, polymer or metals, the parts present surfaces that do not match customers' expectations. Until now, the main parameters used for determining the surface state of such parts are based on profile height parameters like the arithmetic surface roughness Ra. It is legitimate to call the significance of profile roughness into question, especially when we aim at characterizing a three dimensional surface. During this talk, a novel characterization method is used that enables the computation of areal surface parameters in a rapid and reproducible way. This method is a fundamentally new way of investigating the surface of polymeric SLS parts and detecting the slightest changes in surface morphology. A DOE with different scanning parameters is implemented to analyse the surface roughness and texture of PA12 parts. The outcome of this experiment is subsequently implemented in day-to-day business

of a service bureau in order to improve the haptics of conventional SLS parts.

S18-533

Soulestin Jeremie, Lacrampe Marie-France , Krawczak Patricia

New opportunities offered by Freeformer 3D printing process

Freeformer from Arburg offers a new technology for additive manufacturing of polymers that enables to use standard pellets as raw material and gives new opportunities to manufacture parts of high quality thanks to its nozzle technology. The main advantage is the possibility to use any material commercially available. However, if printing with qualified materials (ABS, TPU, supporting material, PS) is as easy as inkjet printing, the process has to be optimized before getting parts of good quality in other cases. In the same way that for regular polymer processing technologies like injection molding, optimization of the processing parameters and the choice of appropriate grade is needed. The Freeformer technology is based on two injection molding units that enables to melt the standard granulate and to feed the printing head. The discharge unit featuring a pulsed nozzle closure generates small (down to 200 µm) molten polymer droplets to build, layerby-layer, three-dimensional parts. Thanks to the presence of two discharge units, parts of complex geometries using water soluble supporting material or parts combining hard and soft materials are easily feasible. Examples of the possibility offered by Freeform technology will be given and a comparison between parts produced using regular FDM and Freeformer technologies will be presented.

S18-545

ARAKI Kunihiro, HAMABE Goshi, DATE Keishi, TANAKA Tatsuya

The Influence of PLA Composite Filaments on Molding Product made by Three-dimensional Printing Since about 2013, it had been experiencing the boom that is the manufacturing using the three-"Additive dimensional printers called Manufacturing". "fused Even among them, deposition modeling (FDM)" type of printers are inexpensive, so they are becoming popular in a general office and a home. Poly lactic acid (PLA) and Acrylonitrile-Butadiene-Styrene (ABS) are the famous resins used for FDM type printers. The characteristics of PLA are shown below: ithe shrinkage is small when cooling time, and it is the biodegradable resin. On the other hand, as compared with ABS, PLA has defects of the impact resistance and the heat resistance. The molding products made by FDM-type 3D printing using PLA filament have same demerits. So, we attempted to improve by making and using composite filaments composed of PLA and fillers. In this study, the PLA composite filaments included cellulose or carbon nanotube were produced by a twin-screw extruder. Then, three-dimensional printing was performed using the composite filaments. After that, the comparison was performed which was between pure PLA filament PLA composite filament about the and characteristics of the molding products.

S18-560

Hebda Michael James, Caton-Rose Philip, Whiteside Ben, Coates Philip

Multi-Layered Infill Structures in FDM of thermoplastics

Fused Deposition Modelling (FDM) of thermoplastic materials such as Polylactic Acid (PLA) and Acrylonitrile Butadiene Styrene (ABS) is a rising rapid manufacturing process within the engineering and design industry. This paper takes an off the shelf consumer 3D printer, a MakerBot Replicator 2 (in conjunction with manually written custom G codes), and adapts the already known FDM technology to allow for Multi-Layered Infill Structures (MLIS). These novel structures are produced by laying down material in the X and Y axes (as normal) whilst adjusting the print bed in the z direction to form continuous 3D structures. By this method it is possible to create multiple layers

simultaneously, giving parts an added element of strength in the Z-axis in comparison to traditional FDM components. Additionally, by controlling the internal structure of printed parts, the MLIS system offers the additional possibility of mimicking complex structures such as bone for medical device fabrication.

S18-573

Schmidt Jochen, Sachs Marius, Fanselow Stephanie, Wirth Karl-Ernst, Peukert Wolfgang

New approaches towards production of polymer powders for selective laser beam melting of polymers

The opening of new fields of application of powder-based additive manufacturing methods like selective laser beam melting of polymers (LBM) hindered by the very limited currently is availability of materials showing good processability. So far, basically only polyamidebased materials are available as optimized powder materials for LBM. Two innovative methods for production of spherical polymer microparticles for LBM polymers are presented: wet grinding with subsequent rounding in a heated downer reactor and melt emulsification. Moreover, the possibilities of dry coating to tailor particle properties are illustrated. The influence of particle and powder properties, like bulk density, shape or flowability on the LBM processability and on the properties of devices obtained from the powders are outlined. The first approach (stirred media milling and rounding) is applicable for a variety of polymers. Remarkably, product particles smaller than 10 microns also may be obtained for polymers of quite high breakage elongation. The dependency of product properties, (e.g. particle size distribution, shape, crystallinity) on the process parameters in the comminution and in the rounding step will be discussed for polyesters. The second approach (melt emulsification) allows for spherical polymer microparticles in a single process step. The dependency of powder properties on process parameters will be outlined exemplarily for the production of spherical polypropylene (PP) particles. PP powders of good flowability are



obtained after spray drying of the product suspensions. The powders obtained by the two methods are characterized with respect to tensile strength, packing density and layer formation. Moreover the processability of the PP powder is proven by building single layers using a LBM device.

S18-699

Traxler Gerhard, Koepplmayr Thomas

Process Monitoring by Thermography during Fused Deposition Modeling

Fused Deposition Modeling (FDM) is a 3D printing technique in which a thermoplastic filament is unwound from a coil and extruded through a heated nozzle to produce a part in a layerwise manner. In case of a poor quality of the joint layers, mechanical consistency of the final product will be also poor in consequence. Thermography of parts while they are being printed allows the detection of surface temperature and calculation of temperature gradients within the part, which can lead to thermal stresses and geometric distortions. In our study we investigate (i) the temperature conditions along the extruder, (ii) the melt temperature of the extruded material at the nozzle exit and (iii) the temperature change of the fabricated part during printing on a heated print bed. A mid-wavelength infrared (MWIR) camera was used at a distance of about half a meter from the printed object. The emissivity of the investigated parts was high enough to capture reliable data and reflected radiation from the printhead could be deducted. Calibration of the camera was performed using a black body in thermal equilibrium combined with interpolation following Planck's law for the defined temperature range. During temperature measurement of the extruded material at the nozzle exit, microscope optics was used in order to adjust the spatial frequency of the sensor. We investigated the performance of four different thermoplastic filaments (PLA, ABS, mineral-filled PA, and graphite-filled PLA) during printing of 50x50x5 mm³ objects with 20% infill (45° grid). Heat conduction to the printbed and temporal cooling of the part were analyzed in order to evaluate the

potential of thermography for inline monitoring of the 3D printing process. Due to the low conductivity of the thermoplastic polymers heat conduction from the heated printbed to the part was low and rapid cooling by convection was observed, which indicates the importance of temperature control inside the printer to reduce thermal stresses.

S18-91

Coogan Timothy J., Kazmer David

FDM Bond Strength: Experiments and Simulations Based on Healing Models

One of the major limitations of fused deposition modeling (FDM) is part strength of the products, due to the weak strength between fibers (bond strength). This work describes the process parameters that affect bond strength, and the theories describing it. Four-sided ABS boxes with a wall thickness equal to a single fiber width were printed according to a design of experiments. A set of tensile specimens were cut from the printed box and tested in the fiber and cross-fiber directions: smaller layer thicknesses, larger fiber widths, faster print speeds, and higher nozzle and platform temperatures increased interlayer bond strength. Modeling was conducted to understand the underlying mechanisms. Reptation time governs the diffusion of polymer chains across the fiber interfaces, so the frequency response of the ABS was characterized to measure the reptation time at multiple temperatures. A one-dimensional transient heat analysis provided an estimate of the temperature profile of the interface between layers. By transposing temperature-dependent diffusion coefficients onto the interface temperature profiles, the amount of polymer chain diffusion that occurred across the layers was calculated for all the tested processing conditions. Bond strength versus total diffusion was found to match well with polymer healing models, showing that the healing models developed for polymer welding can be applied to the non-isothermal FDM process. The findings support that diffusion, wetting, and intimate contact all separately affected bond strength. Fundamental models for predicting FDM



part strength should, therefore, consider all three of these factors. This study provides processing recommendations for producing the strongest FDM parts. These recommendations can be useful for companies producing FDM products as well as companies designing printers. With the correct processing conditions, the strength limitations from FDM can nearly be eliminated.

S18-631

Larocca Nelson Marcos, Pessan Luiz Antonio

Highly filled self-assembled nanocomposites containing Layered Double Hydroxides (LDH) nanoparticles

The layer-by-layer (LbL) assembly technique is a simple, inexpensive, and versatile process for the assembly of highly ordered multilayer film of hybrid polymer-nanoparticles structures. However, each cycle in the traditional lbl dipping method takes about 5 to 20 minutes to be produced, since it depends on times of diffusion and adsorption of polyelectrolytes molecules and colloidal particles in a substrate. Therefore, macroscopic nanocomposites films with micron-size thickness can take days to be prepared. In order to speed up the lbl assembly we have produced multilayered nanolaminates by the spin-spray lbl technique. In this method, the molecular layers are formed by spraying the polyelectrolytes or nanoparticles in a high speed rotating substrate, in such a way that the adsorption of these specimens on the substrate is almost instantaneous. Consequently, we have deposited layers with cycle time as short as 1 minute by this technique, which is about 20 times shorter than in traditional lbl dipping method. In this work, utilizing spin-spray lbl technique, we have assembled nanocomposites films containing layered double hydroxide (LDH) platelets. We have achieved freestanding films with a thickness of about 10 microns comprising 1000 bi-layers produced within a time of about 8 hours. Even though these films have a high inorganic content (about 30 wt%) they are transparent. Electronic microscopy analyses unveil a structure with high spatial organization and orientation of layered

inorganic nanoparticles and low concentration of aggregates of LDH.



Poster

S18-650

Lyu Min-Young, Park J. H., Park S. J., Lee K. H.

Layer strength of FDM type 3D printed article for nozzle temperature and filament material

3D printing is getting attention in manufacturing industry recently. However there are still many supplement points for the application to industrial parts. There are several types of 3D printing method according to additive way, which are FDM, SLA, DLP, SLS, Polyjet, and so on. FDM type uses filament. Continuous filament with circular crosssection is fed into a barrel and is melted when it passes a nozzle which is heated by heating block. Melted filament is extruded through nozzle and it makes layer. Additional melted filament put on the previously made layer and this process makes three dimensional object. Layer strength in the 3D printed object is weaker than bulk material. Layer strength is dependent of tool path, nozzle temperature, nozzle moving speed, and so on. In this paper, layer strength has been examined according to nozzle temperature for PLA, PA6, and ABS filaments. Layer strengths for orthogonal direction to deposition are weaker than deposition direction by 27.9~50.3% according to filament material. Layer strengths for the deposition direction in 3D printed article have 50.2~95% of strength of bulk material. Layer strength for the orthogonal direction to deposition strongly depends on nozzle temperature and increases as nozzle temperature increases.



S19- Microtechnology and Smart Materials

Keynotes

S19-587

Kshad Mohamed Ali, Naguib Hani

Characterization of Origami Shape Memory Metamaterials (SMMM) Made of Bio Compatible Polymers

Shape memory materials (SMM) are materials that can return mechanically induced strains by external stimuli. Shape memory polymers (SMP) are a class of SMM that shown a high shape recoverability. In this paper, we present the shape memory effect on origami based metamaterials, the study shows experimental investigations of shape memory metamaterial (SMMM) made of SMP that can be used in different applications such as medicine, robotics, and lightweight structures. The origami structure made from SMP blends, activated with uniform heating. The study mainly focuses on the origami metamaterials that have negative Poisson's ratio. The effect of blend composition on the shape memory behavior was studied. Also the influence of the thermomechanical and the viscoelastic properties of the unit cell on the folding and unfolding process have been discussed, creep strain and creep recovery strain were investigated. Activation and deactivation of the unit cell has been demonstrated.

S19-672

Cakmak Mukerrem, Chen Yuwei

Large-Scale R2r Fabrication Of Piezoresistive Films (Ni/Pdms) With Enhanced Through Thickness Electrical And Thermal Properties By Applying A Magnetic Field The first successful development of a roll to roll (R2R) process that applies an external magnetic field to orient and organize magnetic nanoparticles along nanocolumns in the thickness direction of thin films to obtain high electrical and thermal conductivities in the thickness direction is reported. Utilizing a R2Rmachine that includes an in-line electromagnet, we orient and organize Ni nanoparticles in nanocolumns inside a flexible poly(dimethylsiloxane) matrix. In these films, the nanocolumns of Niparticles point in the magnetic field/thickness direction which leads to enhancement of the electrical and thermal conductivity in the thickness direction while maintaining optical transparency as the space between the nanocolumns is depleted of nanoparticles facilitating unimpeded light piezoresistivity, the transmission. Exhibiting electrical conductivity in these films increases by as much as 7 orders under moderate pressures. The thermal conductivity of the aligned composite films filled with 14 vol % Ni flakes was found to increase to 50 times the conductivity of the polymer matrix, or 13 times the conductivity of the non-aligned composite with the same concentration. This R2R method facilitates the manufacture of unique films with enhanced functional properties in the thickness direction to be used in a range of applications including Z direction heat spreaders, transparent switches, privacy protection screens and piezoresistive sensors.



Oral

S19-107

Basile Vito, Pagano Claudia, Fassi Irene

Micro-FDM Process Capability And Comparison With Micro-Injection Molding

Polymers and polymer composites are used in a wider and wider variety of applications. More recently, the demand for polymeric microcomponents is increasing for applications in several industrial fields, such as biomedical, electronics, optics and high-precision mechanical industry. Additive manufacturing (AM) technologies are becoming more and more mature and consolidated for the manufacturing of high performance functional prototypes. Among them fused deposition modelling (FDM) has become one of the most important AM technology due to its capability to produce functional prototypes with complex shape compliant with industrial applications in a cost effective way. However, industrial full-scale applications have still not gained much emphasis because of compatibility of available materials with AM technologies. Two approaches have been proposed to overcome this limitation: the development of new materials having superior characteristics but still compatible with the technology and the control of the process parameters during fabrication to improve the part properties. In this study, the dimensional and geometrical accuracy and the mechanical behaviour of miniaturized specimens produced by FDM have been studied in relation with the process parameters in order to identify the most influential parameters and optimize their effects on the component properties. The results have been used as starting point for a comparison between FDM and injection moulding. The latter is a well-known industrial process for the fabrication of a wide variety of products, also with micro dimensions features. The comparison has been done from both technical and economical point of view to highlight

advantages and disadvantages of the technologies and make a complete quantitative comparison.

S19-325

Taki Kentaro, Kondo Shunsuke, Ito Hiroshi

Curing and demolding behavior in R2R UV nanoimprint process

The Roll-to-Roll UV nanoimprint process (R2RUVNIP) is a promising technology to fabricate nanostructure on flexible films. In nanoimprint process, there is an issue how to find a feasible operating condition to peel-off the UV resin from the mold. To produce a desired nanostructure by the R2RUVNIP, the conversion and surface elasticity of UV-cured resin in the process are needed to be known precisely to optimize the UV intensity and line speed. In this study, a UV curable resin (1,6-bis(acryloyloxy)hexane) was cured in the roll-to-roll nanoimprint process. Then the conversion and surface elastic modulus of UV resin were measured with FT-IR and nano indenter, respectively. The effect of distribution of UV light on the roller mold was investigated. The sharp distribution of UV light was effective to increase surface elastic modulus at a given conversion of monomer.

S19-340

Park Beomjin, Kim Jin Kon

One-pot Route for Patterned Growth of Graphene from Selectively Crosslinked Polystyrene

Precise patterning of graphene is highly important for tailor-made and sophisticated two-dimensional nanoelectronic and optical devices. However, graphene-based heterostructures have been synthesized by delicate multi-step chemical vapor deposition methods, limiting preparation of versatile heterostructures. Here, we report singlestep growth of graphene/amorphous carbon (a-C) heterostructures from a solid source of polystyrene through selective photo-crosslinking process. Graphene is successfully grown from neat polystyrene regions, while crosslinked polystyrene regions turn into a-C because of a large difference



in their thermal stability. Since the electrical resistance of a-C is at least two orders of magnitude higher than that for graphene, the charge transport in graphene/a-C heterostructure occurs through the graphene area. Measurement of the quantum Hall effect in graphene/a-C lateral heterostructures clearly confirms the reliable quality of graphene and well-defined graphene/a-C interface. The ability to directly synthesize patterned graphene from polymer pattern opens up new possibilities for the preparation of versatile heterostructures.

S19-472

Thomson Brian, Thompson Glen, Vgenopoulos Dimitris, Nair Karthik, Duncan John, Howell Ken, Martyn Michael, Coates Phillip

Compression screws for the fixation of small bones and bone fragments using biocompatible, bioresorbable, body-temperature reverting, plasticised shape memory polymers

Orthopaedic compression screws promote fracture repair by drawing-together and stabilising adjacent bone fragments. Shape memory polymers (SMP) are smart materials that switch from one macroscopic shape to another following the application of external triggering stimuli (e.g. by shrinking in length when heated above Tg). SMP compression screws that shorten in length following implantation could potentially pull bone fragments together and facilitate fracture healing. The biocompatible, bioresorbable polymer polylactic acid (PLA) shows shape memory properties but the Tg of unmodified PLA is too high for routine clinical use. A polymer's Tg can be reduced by adding plasticisers, low molecular weight compounds that facilitate the movement of molecular chains within solid polymers. To identify plasticisers that can reduce the Tg of PLA to 37C (i.e. physiological temperatures), the Tg of plasticiser-PLA films was assessed using an identiPol machine. Shape memory properties were determined by (i) stretching the films to 200% original length at 85C, (ii) rapidly cooling to 5C without releasing the tension; and (iii) attempting to trigger shape memory reversion by brief immersion in water at 10C - 85C or more prolonged

immersion in saline at 37C. Results showed that two reportedly biocompatible plasticisers, Triacetin and Tributyl O-acetylcitrate reduced PLA's Tg in a dose dependant manner and that shape memory reversion could occur at 37C in saline. PLDLA (Purasorb 7038) plasticised with Tributyl Oacetylcitrate (2.5% v/w) showed optimal shape memory properties when pre-warmed to 45C, stretched between 2 and 3.5 fold at 47C (10 MPa) and then rapidly cooled under tension. The material was not initially birefringent, became birefringent when stretched and rapidly lost birefringence and returned to its original length when heated to 85C in water. Length was recovered completely but more gradually in saline at 37C. PLDLATAC is therefore a candidate material for SMP implants

S19-565

Vgenopoulos Dimitrios, Nair Karthik Jayan, Caton-Rose Phil, Whiteside Ben Richard, Coates Philip David

Recovery behaviour of polymers; investigating the influence of material type and processing conditions via micro-injection moulding and diedrawing.

Shape memory polymers can be used in numerous applications, such as soft tissue fixation devices in healthcare, which is the topic of this research. The recovery behaviour of a wide range of thermoplastic polymers has been investigated using two different techniques: die-drawing and micro injection moulding. Two main factors were used to assess the amount of recovery and hence morphology change that can be achieved by both techniques: a) the type of polymer, either semicrystalline (PP, PLA, PEO, PCL) or amorphous (PDLGA, PETg, PMMA) and b) the processing conditions, especially in micro-moulding. The results showed a huge advantage of amorphous polymers over semicrystalline especially in micro injection moulding, since only the former exhibits recovery behaviour. In die-drawing, both polymer exhibit recovery behaviour, however types amorphous exhibit full recovery, while semicrystalline only partial.



32nd PPS International Conference 2016, Lyon, France

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S19-569

Whiteside Ben, Babenko Maksims, Tuinea-Bobe Cristina, Brown Elaine, Coates Phil

Ultrasonic injection moulding: morphology and mechanical properties

Ultrasonic Injection moulding has emerged as an alternative production route for miniature and microscale polymeric components, where it offers some significant benefits over conventional microinjection processes. The primary advantage is the fact that heating is only performed on the volume of feedstock required for the product, so degradation problems due to extended residence time in the screw can be avoided, and the total energy required for heating is significantly lower. In addition, the ultrasonic energy can be sustained during the filling stage in the process which appears to significantly reduce the pressure requirement for cavity filling whilst simultaneously add providing the ability to add heat after cavity filling, allowing molecular chain relaxation and reduced residual stresses. Here we use a novel injection mould tool which allows the comparison of and moulding conventional ultrasonic techniques. The tool allows direct viewing of the mould cavity using high speed conventional and infrared imaging which allows direct measurement of the flow rate and thermal consistency of the polymer melt. A microscale tensile test cavity in the tool has adjustable thickness and has been used to investigate the morphology development in polyolefins and polyamides using polarised light microscopy and SAXS/WAXS. The resulting mechanical property behaviour has been investigated using small scale mechanical testing apparatus.

S19-585

Khalili Nazanin, Naguib Hani, Kwon Roy

Conducting polymer hydrogels (CPHs) for electronic skin applications

Conducting polymer based hydrogels exhibit physical properties analogous to those of human tissues. They are soft materials with high water content that can be made stimuli-responsive through altering their properties. Combining the unique features of hydrogels with the high electrical conductivity of conducting polymers, a mesh-like three dimensional network can be obtained in which the conjugated polymer acts as the single continuous conductive phase. These electrically conductive hydrogels respond to the perturbations outside pressure through а piezoresistive response which makes them promising candidates for resistive-type sensors with ultra-high sensitivity mimicking some major properties of human skin. In order to imitate natural skin, an electronic skin (E-skin) should be able to recognize both medium and low pressure perturbations. The former ranges from 10 to 100 kPa suitable for object manipulation while the latter is lower than 10 kPa for gentle touch. Herein, using a multiphase reaction, a polypyrrole (PPy) based hydrogel is fabricated as a pressure sensor for Eskin applications. Embedding different additives (i.e., carbon nanotubes and graphene nano platelets) and formulating different microstructures, a highly sensitive pressure sensor with tailored elastic properties is produced. The fabricated PPy based hydrogel can elastically deform and recover upon applying a mechanically induced compression load within the range of human skin detection. The intrinsic elasticity of these hydrogels originates from the hollow microspherical structure of the polymerized PPy forming a cross-linked network within the gel. Moreover, incorporation of PPy nanowires as the host matrix of these gels and its effect on the piezoresistive response of the sensor have been investigated. It is shown that due to the high surface area of the polymerized nanowires, the sensor exhibits a high sensitivity to the applied pressure while maintaining a good mechanical performance.

S19-61

Nakano Ryoko, Maeda Ai, Obuchi Hideaki, Tateishi Yukiko, Kanazawa Yuri, Sekiguchi Hiroshi, Yao Shigeru

Crystalline Supramolecular Interaction of crystalline side chain and its application.



In these days, we are investigating about the functions of side chain crystalline block co-polymer (SCCBC). The side chain crystalline unit (SCCU) of SCCBC shows very strong adhesive force to polyethylene (PE) crystalline surface. The origin of this force is van der Walls interaction. And the SCCU and PE are thought to be forming pseudo crystal. So, we can call this interaction as "Crystalline Supramolecular Interaction". By using this interaction, we can modify the surface properties of PE to any by choosing the other side of the block copolymer. We can also modify the inner surface properties of micro porous PE membrane. The hydrophilic modified membrane shows good separator function and also solid properties of Li electrolyte membrane ion secondary battery. Recently, we found that by using a monomer that has a tetrafluoroethylene structure side chain, we can modify the surface property of polytetrafluoroethylene to hydrophilic. In this time, we will discuss the mechanism of this Crystalline Supramolecular Interaction.

S19-693

Santos João Paulo Ferreira, Melo Guilherme Henrique França, Arjmand Mohammad, Sundararaj Uttandaraman , Bretas Rosario Elida Suman

Hybrid core shell electrospun nanofibers of poly(vinylidene fluoride)/polyaniline with barium titanate and nitrogen doped carbon nanotubes

Hybrid nanocomposites composed of two materials are usually designed to improve their performance over individual components. Here we report the incorporation of nitrogen doped carbon nanotubes (NCNTs) and barium titanate (BaTiO3) in core-shell nanofibers of poly (vinylidene fluoride)/polyaniline (PVDF/PANi) using the electrospinning technique. The core of the nanofibers was composed of PVDF/BaTiO3 and the shell a nanocomposite of PVDF/PANi/NCNT. Piezoelectric PVDF/BaTiO3 nanocomposites are capable of converting mechanical energy into electrical energy, which can be stored in energy storage devices. However PVDF/BaTiO3 is not conductive and thus, a conductive associate material is needed to transfer

accumulated static charges into the capacitor. NCNTs are n type conductor/semiconductors and, therefore could be a good choice. In this work NCNTs were synergically used with PANi, a semiconductive polymer, as a semiconductive shell. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the morphology of the nanofibers. Fourier Transform Infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) were carried out to study the crystalline beta-phase of PVDF. Four probe measurements were done in order to evaluate the electrical properties. The results showed that nanofibers with a core shell structure were succesfuly obtained; the nanofibers were semiconductive and there was an increase in the beta-phase in the electrospun PVDF nanofibers filled with NCNTs as compared with compression molded samples of neat PVDF.

S19-63

Claracq Jerome, Bashir Mubasher, de Graaf Michael, Joo Jake

Silver Miniwires Grids Made by co-Electrospinning for Transparent Conductive Applications

Transparent conductive applications such as touch enabled displays require transparent electrodes to have minimal sheet resistance (Rs) and high optical clarity. Traditionally, indium tin oxide (ITO) is used as the standard transparent conductive material make the electrode (TCM) to of many optoelectronic devices. However ITO is struggling to deliver the combination of a very high clarity and very low Rs necessary for large surface panels. Among the candidates to replace ITO, silver miniwires meshes are closer to industrial scale production. However traditional printing techniques to make metal meshes currently suffer from a low production rate and large feature size. communication, In the present we are demonstrating the making of high performance transparent electrodes from a conductive grid of silver miniwires with co-electrospinning (co-ES) process. We spun, directly on a flexible PET film, bi-component fibers with low viscosity silver



32nd PPS International Conference 2016, Lyon, France nanoparticle ink in the fiber core and a polymeric outer sheath. We achieved fiber alignment by means of a high speed rotary collector drum. A mesh was then obtained by turning 90° the PET sheet between two co-ES passes. In a postprocessing step, the silver fibers were exposed to high photonic energy. The heat generated was sufficient to sinter the silver nanoparticles. We were successful in producing conductive PET films with low Rs=19 Ohm/sq and high clarity (T=89.4%, H=3.1%). The wires were hardly visible because of the small size (3 µm) and low moiré effect due to the co-ES overcoat. It is possible to reduce the haze further with smaller fiber size or using glass substrate. In that case such conductive layer would have a very low haze of 1.2% and a transparency higher than 97%. Therefore this fabrication method looked as a competitive approach to incumbent and coming TCM technologies. Keywords: microprocessing, rheology, nanoparticle suspension, electrospinning, metal nanofibers, transparent electrodes, touch screen.



Poster

S19-381

Nakamura Keisuke, Nishitani Yosuke, Kitano Takeshi

Frictional Properties of Plants-Derived Polyamide against Surface Microstructures of Metal Counterpart Fabricated by Femtosecond Laser

In recent years, laser surface texturing using femtosecond laser has been a great attention due to its versatility and precision for surface texturing technique in order to control the tribological properties of various engineering materials. In our previous works, we investigated the fabrication of microstructured surface of various polymeric materials and their frictional properties, and also the frictional properties of the polymeric materials against surface microstructures on the metal counterpart fabricated by femtosecond laser. Most polymeric materials are derived from nonrenewable petroleum supply resources, therefore there is a demand to replace them to biopolymer such as plants-derived polymer because of the problems of uncertainty of the petroleum supply and global warming. The purpose of this study is to investigate the frictional properties of the plantsderived polymeric materials against microstructures on the metal counterpart fabricated by femtosecond laser in order to control the tribological properties of polymeric materials. This study discusses the frictional properties in terms of various factors: microstructure pattern, sliding direction, sliding speed and so on. The material used in this study was plants-derived polyamide (PA). Plants-derived PA was extruded by a twin screw extruder and injection-molded. Surface microstructures on SUS304 were fabricated by femtosecond laser. This SUS304 with microstructures using femtosecond laser was used as counterparts. Tribological properties were measured by a pin-on-plate type reciprocatingsliding wear tester under oil lubrication conditions. It was found that the frictional coefficients of plants-derived PA against microstructures on SUS304 are lower than those of non-textured SUS304. This is attributed that the surface microstructure on the metal counterpart fabricated by femtosecond laser plays an important role to control the tribological properties of polymeric materials.

S19-544

Liu Qing, Capsal Jean-Fabien, Richard Claude

Solvent Effects on the Molecular Dynamics of Relaxor Ferroelectric P(VDF-TrFE-CTFE) and Electrostrictive Behaviors Thereof

Inkjet printing has been wide-spread recognized as a drop-on-demand printing technologies capable of depositing quantities of material accurately. With technique, automatic processing this and electroactive polymeric components design seems practical. However the physico-chemical properties of printed electroactive polymer highly depend upon the solution comprising because the defined post-printing area must undergo both volatilization and crystallization process. In current studies two solvent with quite different volatility, methyl ethyl ketone (MEK, b.p. 79.64°C) and triethyl phosphate (TEP, b.p. 215°C) for inkjet printing ink solvent for poly(vinylidene-fluoride solubilizing trifluoroethylene chlorotrifluoroethylene)[P(VDF-TrFE-CTFE)] relaxor ferroelectric powders were compared by analyzing resultant polymers. Pristine polymers of both solvents were prepared by depositing solution on PET substrate and annealed at given temperature. Curie and melting regimes were firstly monitored by differential scanning calorimetry and TEP polymers showed higher crystallinity over MEK counterparts but decreasing Curie enthalpy and transition points. Effects of solvent parameters on molecular dynamics were investigated by broadband dielectric spectroscopy, showing that TEP polymer exhibited the slowing down of segmental dynamics with increased Vogel temperature in amorphous and higher curie transition activation energy in crystal phase. Additional, due to presence of large Maxwell-Wagner-Sillars polarization, enhanced dielectric permittivity was observed at low frequency for TEP



polymer. Influences on electrostrictive behavior were finalized and verified by unimorph bending mode. TEP polymer behaved larger tip displacement but equivalent free mechanical energy density (Y*S31^2/2) was obtained due mostly to its relatively low transverse stain (S31) and high Young's modulus (Y). Such results intended to give contribution to the behaviors of drop-on-demand inkjet printing films.

S19-584

Sun Yu-Chen, Shi Hao Tian, Naguib Hani

Fabrication of polymer and carbon nanotubes based artificial muscles through controlled electrospinning processes

In recent years, carbon nanotubes (CNTs) based artificial muscles attract many research attentions due to their superior actuation forces and high work density. Previous research successfully demonstrated that bundles of CNTs joined by Van der Waal's forces can behave as actuators when submersed in electrolyte with external voltage applied to the CNTs. Such behavior can be explained by the rearrangement of atomic structure of the CNTs and Coulombic forces; which were both induced by ions exchange between the CNT bundles and the electrolyte. It was suggested that the performance of CNT based actuators can be further improved by enhancing the interfacial surface areas via fiber alignment. Currently, most of the CNT based actuators are fabricated via direct drawing of the "CNT forests". Although commonly practiced in laboratory, the growth of 'CNT forests' still requires expensive and challenging techniques such as chemical vapor deposition (CVD). In this study, we present the results of CNT/polymer composites actuator fabricated by electrospinning processes. Such methods utilized electrospinning for manipulating the alignment and connection between individual CNTs. Compared to the results of different fabrication techniques shown in the literature, similar actuation behavior is found and reported in this study.

S19-638

PPS[®]32

El Brahmi Nabil, El Kazzouli Said, Mignani Serge, Cresteil Thierry, Bousmina Mostapha, Majoral Jean Pierre

New Drug-Loaded Phosphorus Dendrimers: Their synthesis and anticancer activities

Dendrimers are monodisperse nanosized polymeric molecules composed of a large number of perfectly branched monomers. The versatile chemical composition of dendrimers offers a variety of applications in different area such as: chemistry, biology, and medicine. The potential of using dendrimers as carries for drug delivery is revolutionizing medicine by improving the efficiency and reducing the toxicity of various treatments(1). Dendrimers can form either covalent or noncovalent (encapsulation) bounds with bioactive molecules. In the case of covalent bound, drug can be attached to dendrimer directly or via a linker and the resulting drug-loaded dendrimer can act as a nanovehicle for drug transport and controlled release. In this communication we will present the synthesis and characterization of new phosphorus dendrimers(2) (generations Gc1 to Gc3) containing various functional groups on their peripheries(3). We will report also the synthesis of different biologically active small molecules and their attachment to phosphorus dendrimer surface using different linkers. All the new drug-dendrimer conjugates are evaluated for their biological activities and these results will be described in this communication. (1)a) R. K. Tekade, P. V. Kumar, N. K. Jain, Chem. Rev. 109, 2009, 49. b) S. H. Medina, M. E. H. El-Sayed, Chem. Rev. 109, 2009, 3141.(2)a) A. Perez-Anes, G. Spataro, Y. Coppel, C. Moog, M. Blanzat, C-O. Turrin, A-M. Caminade, Rico- I. Lattes, Majoral, J-P. Org. Biomol. Chem. 7, 2009, 3491. b) S. Fruchon, M. Poupot, L. Martinet, C-O Turrin, J-P. Majoral, J-J. Fournié, A-M. Caminade, R. Poupot. J. Leuko. Biol. 85, 2009, 553.(3)a) N. El Brahmi, S. El Kazzouli, S. Mignani, E. M. Essassi, G. Aubert, R. Laurent, A. M. Caminade, M. Bousmina, T. Cresteil, J-P. Majoral. Mol. Pharmaceutics. 10, 2013, 1459-1464. b) N. El Brahmi, S. Mignani, J. Caron, S. El Kazzouli, M. Bousmina, A. M. Caminade, T. Cresteil, J. P. Majoral. Nanoscale. 7(9), 2015, 3915-3922.

S19-787

Seo, Baek Beom, Kim Jeong Ho , Dao Trung Dung , Jeong Han Mo

Aluminum hydroxide–CNT hybrid material for synergizing the thermal conductivity of alumina sphere/thermoplastic polyurethane composite with minimal increase of electrical conductivity

Multi-walled carbon nanotube (CNT) was hybridized with aluminum hydroxide utilizing aluminum trichloride hexahydrate as a precursor to prepare a filler that can be utilized for a thermally conductive yet electrically insulative polymer composite. The thermal conductivity of an alumina sphere/ thermoplastic polyurethane (TPU) mixture (100 parts) was enhanced 2 to 3-fold when 5 parts of this hybrid material (Al-CNT hybrid) was added as а synergizer for thermal conduction. This enhancement was better than that by CNT. Moreover, the electrical conductivity increase due to the added Al-CNT hybrid was marginal, whereas the increase was striking when CNT itself was added instead. Keywords: Carbon nanotube, Aluminum hydroxide, Hybrid, Thermal conductivity, Electrical conductivity, Tensile properties.

S20- Biobased Plastics and Materials for Renewable Energy

Keynotes

S20-124

Tadjiev T, Ungar Goran

Unusual crystal phase in linear aliphatic polyesters

Aliphatic polyesters are classic biobased polymers, and their properties are significantly affected by their semicrystalline nature. With the exception of poly(glycolic acid), the simplest polyester of the [-(CH2)n-1-CO-O]x type with n=2, all other members of the series, starting with $poly(\beta propiolactone)$ (n=3) to $poly(\varepsilon$ -caprolactone) (n = 6), via poly(4)hydroxybutyrate) (n = 4) and poly(δ valerolactone) (n = 5), exhibit Xray fibre diffraction patterns reminiscent of that of polyethylene, and a basically polyethylene like structure has been proposed. However, in most studies the diffraction pattern did not allow the determination of the space group, hence limited information could be extracted. Here report а fibre diffraction study we poly(hydroxynonanoate, PHN) (n = 9), prepared from vegetable oil. [1] The diffraction pattern shows not only numerous sharp equatorial reflections, but also a series of well resolved reflections on what turns out to be the first layer line, although one could confuse it with the 5th layer line due to the presence of noncrystallographic meridional streaks of 12 Å periodicity. The structure is essentially that of polyethylene with the ester groups nearly randomly distributed throughout the lattice. The deviation from randomness, i.e. the constant distance between the ester groups along each individual chain gives rise to the subsidiary layer lines, the equivalents of diffuse scattering in single crystals with correlated fluctuations. Due to the quantized longitudinal disorder, the structure can be likened to a "nematic on a lattice". [1] Z. S.

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S20-525

Raquez Jean-Marie, Spinella Stephen, Gross Richard, Habibi Youssef, Dubois Philippe

Reinforcing polylactide with lactic acid modified Cellulose Nanocrystals via melt blending

Polylactide (PLA) is currently considered to be the most interesting bio-based polymers from shortterm to durable applications such as electronics and packaging due to its unique properties such as high strength, biocompatibility and biodegradability. Despite all of these advantages, PLA has both low glass transition temperature and heat deflection temperature. Therefore the mechanical properties of PLA-based materials are relatively poor at temperatures greater than 60°C, impeding its use as a green engineering thermoplastic. In this respect reinforcing PLA with nanofillers represents a promising method to address these issues. Cellulose nanocrystals (CNCs) possess many attractive features for making nano-composites abundance; non-toxicity, such as its large biodegradability, low density, and a very large surface area that can be further functionalized. However, their surface-functionalization is not environmentally-friendly straightforward and because the inevitable use of organic solvents (through numerous solvent-exchanges) is required before dispersion of CNCs into polymeric matrix. Direct surface-functionalization starting from aqueous CNCs suspensions seems to be the best way to alleviate these issues. Recently, a green onestep method based on both Fischer Esterification and acid hydrolysis to obtain functionalized and ready-to-use CNs has been reported by some us. The aim of the present communication was hence to investigate the reinforcing effect of CNCs on PLAbased materials. Direct melt-blending PLA with CNCs not or functionalized with both acetic acid CNCs and lactic acid (LA-CNCs) moieties in order to investigate their effects on the thermomechanical properties of the blend. The corresponding thermomechanical properties were investigated by DMTA and it was found that LA-CNCs possess the



32nd PPS International Conference 2016, Lyon, France highest storage modulus. This increase in materials properties can potentially expand the applications of PLA based materials towards, e.g., energy applications.

S20-564

Iozzino Valentina, Askanian Haroutioun, Leroux Fabrice, Verney Vincent , Pantani Roberto

Tuning the hydrolytic degradation rate of Poly-Lactic Acid (PLA) to more durable applications

The disposal of polymeric waste is increasingly becoming an issue of international concern. The use of biodegradable polymers is an possible strategy to face most of the problems related to the disposal of the durable (non-biodegradable) polymers. Among biodegradable polymers, PLA (obtained from renewable sources) is a very attractive one, due to its good processability, biocompatibility, interesting physical properties. Hydrolysis is the major depolymerisation mechanism and the ratecontrolling step of PLA biodegradation in compost. The propensity to degradation in the presence of significantly limit specific water industrial applications such as automobile, biomedical, electronic and electrical appliances, agriculture. Therefore the control of biodegradation rate is more important somewhat even than the characteristic of biodegradability itself. This is the reason why it is critical to find additives able to modulate the biodegradation rate of biodegradable polymers in relationship to the expected lifetime. Since the kinetics of hydrolysis strongly depend on the pH of the hydrolyzing medium, in this work some fillers able to control the pH of water when it diffuses inside the polymer were added to PLA. In particular, fumaric and succinic acid, both bio- and eco- friendly additives, were used as fillers. In order to control the release of these molecules and their dispersion inside the polymer, intercalation in biocompatible nanofillers like layered double hydroxides (LDH) is extremely promising. These fillers were added to the material using meltcompounding technique, suitable for industrial application. The preliminary results obtained are encouraging toward the possibility of effectively controlling the biodegradation rate.

S20-619

Singer Kenneth, Gross Richard, Dawson Nathan, Maiorana Anthony, Liu Fei , Spinella Stephen, McMaster Michael, Peters Kyle, Ibrahim Mohammad, Mekala Shekar

Biobased materials for optoelectronics

Biobased materials offer many advantages over synthetic materials including facile production and the replacement of non-sustainable materials and feedstocks. Imparting optical and electronic functionality could produce new classes of materials for energy and information technology. We are investigating several avenues for using biobased materials for a number of functions in both energy capture and storage through organic photovoltaic and related devices. Our investigations include biobased structural capacitors, cellulose nanocrystals as substrates for plasmonic nanoparticles for enhancing optical absorption, conducting bacterial cellulose films, and self-organizing semiconductor motifs. Α number of various structures of biobased epoxy resins have been produced for use as structural dielectric materials for capacitors. Dielectric spectra and electrical breakdown studies have been carried out to characterize structure-property relationships for a series of epoxy resins with varied unsaturated motifs. Cellulose nanocrystals have been decorated with silver nanoparticles using a facile water borne methodology where the cellulose nanocrystals acts as both the reductant and stabilizing ligand for the silver nanoparticles. This results easily in dispersible random arrays of plasmonic organic/inorganic nanoparticle conjugates. Experimental and theoretical studies indicate nearfield particles interactions among the to supplement field enhancement effects for concentrating light into photovoltaic devices. Ultrathin cellulosic bacterial mats have been produced using a novel low volume static fermentation technique. Several post-processing approaches are being investigated for producing transparent conducting "nano-wire" networks. Finally, porphyrin functionalized sophorolipids are being investigated as self-assembling semiconductors for photovoltaics.



S20-752

Habibi Youssef

Recent advances in nanocellulose-based materials

Since their first isolation in 1940s by Randy, nanocrystalline cellulose start attracting the attention of the material community. Later during 1980s, Turbark group's succeeded in extracting a new kind of nanocellulose, called at that time microfibrillated cellulose, stimulating further the interest toward these renewable building blocks. Nowadays with the emergence of the green portfolio, numerous efforts are being focused on the use of materials from renewable resources, and we are attesting a huge and unprecedented interest for nanocellulose. This interest is due to their renewability and biodegradability, in addition to their appealing intrinsic properties such as low density, outstanding mechanical properties. Moreover, nanocelluloses possess spectacular optical properties originating from their ability to self-organize into liquid crystalline arrangements. All these impressive properties allow their use in wide range of applications ranging from high performances composites, optical devises, and energy harvesting. This presentation will provide an overview on nanocellulose, their chemical modification and processing using various techniques to access useful nanomaterials for different applications.

Oral

S20-173

Singha Amar Singh

Chemically modified natural fiber reinforced corn starch matrix based green composites – Evaluation of thermal, morphological and mechanical properties

Chemically modified natural fiber reinforced corn starch matrix based green composites - Evaluation of thermal, morphological and mechanical properties Ashish Guleria1, Amar Singh Singha2*, 1Faculty of Science and Technology, ICFAI University, Baddi (H.P.) 174103 2Department of Chemistry, National Institute of Technology, Hamirpur (H.P.) 177005 Tel. +91 1972-254120 Fax: +91 1972-222584 Email: amarchemnit@gmail.com Abstract: Plastic materials produced from petrochemicals are widely used in packaging, automotive, healthcare application, and communication or electronic industries. As these conventional synthetic polymers are not easily degraded because of their high molecular mass and hydrophobic character, they may accumulate in the environment and represent a significant source of environmental pollution potentially harming wildlife. The environmental pollution caused by the widespread consumption of petroleum based polymers and plastics have spurred a thrust into the development of biodegradable or environmentally acceptable materials. Biodegradable polymeric materials derived from renewable sources, are considered as the most promising materials because their easy availability and cost effectiveness. In recent years, new materials, usually called biocomposites composed of plant fibers and biodegradable polymers, have become verv attractive materials. New biocomposite were prepared from a mixed suspension of modified okra cellulose micro particles and corn starch matrix by compression molding method. The urea-formaldehyde polymer

318

was used as cross-linking agent for preparation of biocomposites. The morphology, thermal behavior, and mechanical properties of biocomposites were investigated. The biocomposites exhibited significant increases in the tensile strength, compressive strength, and flexural strength from 11.26 MPa to 17.2 MPa, 21.93 MPa to 37.64 MPa and 35.51 to 67.5 MPa respectively as compared to corn starch matrix. Further, biocomposites prepared with 15wt% fiber reinforcement shown maximum increase in mechanical properties.

S20-44

Yue Liang, Maiorana Anthony, Patel Ammar, Gross Richard A., Manas-Zloczower Ica

Processability and Mechanical Properties of Biobased Epoxy Resin Systems for Wind Turbine Blades

Lightweight polymer composites are in high demand for applications such as wind turbine blades and structural automotive parts. Epoxy thermosets are ideal matrices for vacuum infusion molding of continuous fiber mats at room temperature. Our work is aimed at the replacement of diglycidyl ether of bisphenol A (DGEBA) with a bio-based resin utilizing diphenolic acid derivatives known as diglycidyl ethers of diphenolates (DGEDP). DGEDP resins have shown good properties thermomechanical when directly compared to DGEBA, however, their viscosities are still too high for infusion molding. Two types of DGEDP epoxy monomers with an ethyl and pentyl ester side chain respectively, were formulated with a eugenol based reactive diluent in order to tune the initial viscosity and gelation time allowing for resin formulations suitable for vacuum infusion molding of continuous glass fiber mats. The processing window for such systems was determined through chemorheology studies and compared with commercially available infusion resins. Engineering-glass fiber mats were infused with the different biobased resins and compared with a commercial epoxy resin system and a DGEBA resin mixed with the biobased reactive diluent. The mechanical properties of the prepared composites such as flexural strength, fatigue life,



and fracture toughness were determined and against a commercially benchmarked viable infusion system. The bio-based DGEDP-ethyl resin system shows overall better mechanical properties with respect to fatigue life and fracture toughness and competitive properties in terms of flexural and glass transition temperature. The results demonstrate a feasible biobased alternative to the industrial standards and this work gives further insight into processing parameters required for vacuum infusion molding. Keywords: Polymer composites; Biobased epoxy; Vacuum infusion molding; Chemorheology; Mechanical properties

S20-756

Bellani C. F., Morelli C. L., Ferrand A., Benkirane-Jessel N., Bretas R. E. S., Branciforti Marcia-Cristina

Cell Viability Of Cnc And Pbat/Cnc Bionanocomposite

Biocompatible polymers play an important role in the formation of functional new tissue from transplanted cells. They provide a temporary scaffolding to guide new tissue growth and organization until the newly formed tissues are structurally stabilized. Poly(butylene adipate-coterephthalate) (PBAT) is a biocompatible polymer and has been studied for medical devices [1]. Mechanical and thermal properties of PBAT can be improved through the addition of nano-sized fillers, as cellulose nanocristals (CNC) [2,3] for biomaterial application. CNC are biocompatible, biodegradable and show excellent chemical and thermomechanical properties, making them suitable candidates as polymer reinforcements [4]. Recent studies reported by our research group demonstrated elastic modulus and tensile strength PBAT increasing with the addition of of unmodified CNC, confirming the obtation of bionanocomposites with good CNC dispersion and interfacial interaction between PBAT and CNC by casting process [2] or by melt extrusion [3]. A biomaterial must have biocompatible surfaces to be used in tissue regeneration. Therefore biocompatibility essays related to pure CNC and bionanocomposites of PBAT and CNC should be evaluated prior to their production as scaffolds for

applications in tissue engineering. In this work, we evaluated cell proliferation/viability of these materials particularly interesting for further applications in bone tissue engineering 1. B-S. Kim; D. J. MooneyTrends Biotechnol. 1998, 16, 224. 2. C. L. Morelli; M. N. Belgacem; M. C. Branciforti; R. E. S. Bretas; A. Crisci; J. Bras Comp.Part A accepted 2015. 3. C. L. Morelli ; M. N. Belgacem ; M. C. Branciforti ; M. C. B. Salon ; J. Bras, R. E. S. Bretas Eur. Polym. J. submitted 2015.



Poster

S20-665

Hui Bing, Ye Lin

Synthesis and Structure of Polyvinyl alcohol-gacrylic acid -2-acrylamido-2-methyl-1propanesulfonic acid Hydrogel for Advanced Pb(II) Removal

The polyvinyl alcohol-g-acrylic acid -2-acrylamido-2-methyl-1-propanesulfonic acid hydrogel (PVA-g-AA-AMPS) with varying AMPS/AA molar ratio was synthesized through free radical polymerization method. The shear storage modulus (G') and effective network density (ve) of the hydrogel increased with the increase of AMPS dosage, and the more uniform and dense porous network structure formed. Pb2+ adsorption capacity of the hydrogel increased with increasing AMPS/AA molar ratio, reaching as high as 200.7mg/g under 60% neutralization degree and 400 mg/L of the initial Pb2+ concentration. A bidentate chelate formed between the carboxyl group of the hydrogel and Pb2+. The adsorption kinetics of the PVA-g-AA-AMPS hydrogel was mainly controlled by the intraparticle diffusion, and belonged to the second-order kinetic model, indicating that the ratelimiting step for Pb2+ removal might be chemical adsorption. The Langmuir isotherm fitted well with the experimental data, indicating the homogeneous nature of the monolayer adsorption of Pb2+ on the hydrogel, while the irreversible adsorption can be achieved at high initial Pb2+ concentration. A relatively good reusability of the hydrogel for Pb2+removal can be achieved.

S20-796

Khedim A. *, Feddag A., Bengueddach A.

Wastewater Treatment By Synthetic Zeolite

The use of heavy metals is essential in many branches and applications of industry. This practice

poses a problem because of their sometimes high toxicity it human being and the animals, of the extremely strict limits must be observed for the concentration of heavy metals in polluted water, an experimental study was undertaken for the elimination of heavy metals Cadmium and Zinc snuffs separately and mixes some for synthetic solutions by a crystalline aluminosilicate (NaX zeolite synthesized at the pure laboratory starting from the products by the method of direct synthesis and which shows a rate of crystallization

and which shows a rate of crystallization 92,64%).The experiment is carried out in discontinuous and continuous system for various masses of zeolite, a temperature of 25°C and 30°C, a follow-up of the evolution of pH before and after elimination







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