Welcome to the 6th International Conference on Polymer Behaviour (ICPB6) at the University of Vienna, Austria. It is the sixth conference in a series of biannual meetings which started in Moscow 2004 followed by Strasbourg (2006), Marrakesh (2008), Lodz (2010), and Aveiro (2012).

The aim of the ICPB 6 is to report and discuss fundamentals, structures, properties and applications of all kinds of polymers both in academia and industry. In particular, the conference focuses on multiphysics approaches for the behaviour of polymers and polymer based nanomaterials.

The conference is focused on the following 9 sessions:

A: Fundamentals of structure and properties
B: Plasticity and mechanical properties
C: Modeling and simulations
D: Experiments on the nanoscale
E: Crystallization and phase transitions
F: Linkage between different length and time scales
G: Cellulose and other biopolymers
H: Functional polymers
I: Composites and fillers
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<td>9:00-10:30</td>
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<td>D1 Likos</td>
<td>E2 Negahban</td>
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<td>Deplancke</td>
<td>C1 Galeski</td>
<td>Woltzack-Michals</td>
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<td>12:30-14:00</td>
<td>Deplancke</td>
<td>Maccarone</td>
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<td>14:00-16:00</td>
<td>Deplancke</td>
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<td>15:50-16:10</td>
<td>Coffee Break</td>
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<td>18:00-21:00</td>
<td>Welcome</td>
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**Event Key:**
- **Registration**
- **Lunches & Breaks**
- **Poster Session**
- **Oral Talk**
- **Invited Talk**
- **Coffee Break**
- **Lunch**
- **Excursion**
- **Conference Dinner**
- **Closing Address**
- **ExCURSION 14:30 – 16:30**
- **Poster Session 15:50-18:00**
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- **Invited Talk 18:00-20:00**
- **Welcome Reception & Registration 18:00-21:00**
- **Coffee Break**
- **Conference Dinner 18:30**
# 6th International Conference on Polymer Behaviour

**Sunday 21 September 2014**

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<td><em>Mechanical behaviour of PA66 close to Tg; Modelling viscoelasticity</em></td>
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<td>9:30 – 9:50</td>
<td>Deplancke Tiana</td>
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<td><em>Mechanisms of chain re-entanglement during sintering of UHMWPE native powder: comparison of different molecular weights</em></td>
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<td>Gerets Britta, Wenzel Mirko, Bastian Martin, Schuster Tobias, Brüll Robert</td>
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<td><em>ß-Nucleation of PP-R: Correlation of Nucleation, Mechanical Behaviour and Morphology</em></td>
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<td>10:10 – 10:30</td>
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<td><em>The relaxation suppression mechanism in a polymer system above Tg</em></td>
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<td><em>Anisotropic plastic dilation for semi-crystalline polymers: experimental characterization and finite element modelling</em></td>
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<td><em>X-ray synchrotron radiation study of the structure evolution of polymeric material systems during deformation</em></td>
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<td>Längauer Manuel, Zitzenbacher Gernot, Kneidinger Christian, Liu Keyan</td>
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<td><em>Influence of Solid Bulk Properties and Frictional Behavior on Solids Conveying in Single Screw Extruders</em></td>
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Potential role of marine coral filled polymer composites for internal fixation application | 21   |
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<td><strong>Poier Peter, Matthews Richard, Likos Christos</strong>&lt;br&gt;<em>Effect of bending stiffness and confinement on a polymer chain under tension</em></td>
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<td><strong>Invited talk:</strong> Frontini Patricia, Rueda Federico, Machado Martin, Otegui José Luis, Major Zoltan&lt;br&gt;<em>External pressure induced buckling collapse of High Density Polyethylene (HDPE) liners: FEM modeling, predictions and experimental corroboration.</em></td>
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<td><strong>Längauer Manuel, Zitzenbacher Gernot, Keyan Liu, Kneidinger Christian</strong>&lt;br&gt;<em>Investigation of the melting behavior of different shaped polymeric bulk solids</em></td>
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<td><strong>Ovalle Cristian, Zaïri Fahmi, Naït-Abdelaziz Moussa</strong>&lt;br&gt;<em>Some insights about the modeling of self-heating in filled-rubbers</em></td>
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<td>Session C3: Modelling and Simulations</td>
<td><strong>Richter Tobias, Kosovan Peter, Holm Christian</strong>&lt;br&gt;<em>Modelling of ionization and conformations of star-like weak polyelectrolytes</em></td>
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<td><strong>Stepien Maja, Choong Gabriel Y.H., De Focatiis Davide S.A., Figiel Lukasz</strong>&lt;br&gt;<em>Elongational and shear rheological behaviour of polylactides: comparison of phenomenological (Giesekus) and molecularly-based (Rolie-Poly) models</em></td>
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<td><strong>Manik Gaurav, Singhvi Yash</strong>&lt;br&gt;<em>Molecular Simulation Study of Anti-Stain coatings</em></td>
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| 9:30 – 9:50  | **Wilhelm Harald, Spieckermann Florian, Polt Gerald, Zehetbauer Michael, Fischer Christopher**  
*Novel Creep Test Method for characterisation of strain bursts in semicrystalline polymers* | 27   |
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*Self-scrolled chitosane acetate fibres: a novel material for drug encapsulation and release.* | 27   |
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*On the difference in the molecular mobility at free or contacting polymer surfaces and in the polymer bulk* | 28   |
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*Cavitation mechanisms in high-density polyethylene during complex loading histories in tension revealed by time-resolved small-angle x-ray scattering* | 28   |
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<td><em>Laatar Fekri, Ben Romdhane Med Ramzi, Srasra Ezeddine</em>  &lt;br&gt;<em>Mechanical and Thermal Properties of Nanocomposite Based On Unsaturated Polyester Resin</em></td>
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<td><em>Sowinski Przemyslaw, Piorkowska-Galeska Ewa, Boyer Severine A.E., Haudin Jean-Marc, Zapala Kinga</em>  &lt;br&gt;<em>Nucleation of high pressure gamma form in isotactic polypropylene</em></td>
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<td><em>Candau Nicolas, Chazeau Laurent, Chenal Jean-Marc, Gauthier Catherine, Candau Nicolas, Munch Etien</em>  &lt;br&gt;<em>Contribution of chemical crosslinks and entanglements during strain induced crystallization of natural rubber at high strain rates</em></td>
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<td><em>Freire Lionel, Billon Noelle, Haudin Jean-Marc, Combeaud Christelle</em>  &lt;br&gt;<em>Crystallization of different grades of Polyamide 6-6 at high cooling rates</em></td>
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Jurczuk Kinga, Galeski Andrzej  
Roy Sunanda, Das Tanya, Tang Xiuzhi, Hu Xiao | **The Influence of Shape and Structures on the Properties of Polymer Nanocomposites**  
**Fabrication and Mechanical Characterization of Graphene-Epoxy Nano Composites**  
**Effect of Micro- as well as Nano-scaled Fillers on Rheological, Structural and Utility Properties of Polymer Composites**  
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<td>Session F1: Linkage between different length and time scales</td>
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Abstracts: Oral contributions
Session A1: Fundamentals of Structure and Properties

Invited talk:
Mechanical behaviour of PA66 close to Tg; Modelling viscoelasticity
Billon, Noëlle (Mines-Paristech, CEMEF, Sophia Antipolis, FRA)

Mechanical behaviour of injection moulded PA66 is explored together with local microstructure accounting for moisture. Microstructure is addressed combining POM, XRD, thermal expansion and DMA at a local level: in the thickness and throughout the entire molded plaque. Visco elasticity is proved and attempt to relate variation to local microstructure is made. Usual a priori decomposition of strain in first elastic then plastic is discussed. Novel Visco Hyper leastic model, based on a network theory, is used to model cyclic, uploading-unloading and relaxation experiments. Comparison with more usual approach demonstrated the advantage of this concept. Relative importance of moisture and microstructure are discussed.

Mechanisms of chain re-entanglement during sintering of UHMWPE native powder: comparison of different molecular weights
Deplancke, Tiana (Ingénierie et Sciences (MATEIS) - INSA de Lyon, Bât. B. Pascal, Villeurbanne, FRA)

One of the main issues of processing ultra-high-molecular-weight polyethylene (UHMWPE) is to overcome its very high viscosity that precludes injection or extrusion. As a consequence, sintering has been developed.

In particular, the diffusion of very long chains is generally described by reptation theory. However, studies have shown that another phenomenon permit a re-entanglement in less time than required for reptation: melting explosion. This can be explained by the high crystallinity and the high melting temperature of the UHMWPE native powder that have been assigned to non-equilibrium chain conformations.

In order to evaluate the influence of sintering parameters and chain lengths on mechanical properties, a device has been designed to perform sintering at various temperatures and duration. Four molecular weights were chosen, 0.6, 3.9, 6.8 and 10.5 Mg/mol.

Mechanical testing was carried out at 25°C and 150°C, to separate cocrystallization and re-entanglement in the interparticle reinforcement.

β-Nucleation of PP-R: Correlation of Nucleation, Mechanical Behaviour and Morphology
Gerets, Britta (SKZ - KFE gGmbH, Würzburg, GER); Wenzel, Mirko (SKZ - KFE gGmbH, Würzburg, GER); Bastian, Martin (SKZ - KFE gGmbH, Würzburg, GER); Schuster, Tobias (Fraunhofer LBF, Darmstadt, GER); Brüll, Robert (Fraunhofer LBF, Darmstadt, GER)

In PP-R N,N'-dicyclohexynaphtalene-2,6-dicarboxamide (NJSTAR®NU-100) works as β-nucleating agent. While the overall crystallinity is nearly independent of the nucleating agents’ content, morphology and mechanical behaviour are strongly influenced. For the used isotactic PP-R copolymer pipe grade ca. 1000 ppm were found as optimum regarding a preferably high β-crystallite content. As polarised light microscopy reveals there is a critical content of nucleating agent to start β-formation, but also a too high content causes problems due to agglomeration effects. Mechanical tests on samples cut of compression moulded sheets with a thickness of 4 mm show the highest values for yield stress and the best impact behaviour for 500-1000 ppm NU-100. As the optima match, a correlation between nucleation, morphology and mechanical behaviour can be deduced. This structure-property-relationship could be used to gain improved mechanical properties of components made of such grades, taking into account manufacturing conditions e.g. cooling rates.
The relaxation suppression mechanism in a polymer system above Tg

Arinstein, Arkadii (Department of Mechanical Engineering, Haifa, ISR)

Thermoplastic polyurethane (TPU), a multi-phase block-copolymer containing soft and hard segments, is referred to a class of shape memory materials. At the room temperature the hard segments can form hard domains, surrounded by 'liquid' matrix composed by soft segments (Tg=-50°C). If the fraction of the hard segments is enough high, the hard domains are forming an intercalated rigid structure providing the conserving of a deformed (non-equilibrium) sample state. Upon heating, the hard domains are being destroyed, and the sample starts to relax to equilibrium, recovering its permanent shape. In the case of low concentrations of the hard segments, no intercalated structure of the hard domains can be formed, and any non-equilibrium state of the system has to relax. Nevertheless, experimental observations demonstrate that in the TPU matrix the relaxation of non-equilibrium state can be suppressed. Based on the blob concept, a model is proposed to explain this phenomenon.

Session A2: Fundamentals of Structure and Properties

Invited talk:
Anisotropic plastic dilation for semi-crystalline polymers: experimental characterization and finite element modelling
Laiarinandrasana, Lucien (Mines ParisTech - Centre des Matériaux, Evry Cedex, FRA)

Semi-crystalline polymers exhibit cavitation phenomena during deformation. Micro-tomography has been used to characterize voiding resulting from a well controlled multiaxial stress state. These voids have been seen to be anisotropic and irreversible. They are therefore described as anisotropic plastic dilation. The evolution of cavities was inspected in terms of their 3D morphology, number and size.

The creation of voids was detected in the central part of the specimen before yielding. The mode of deformation was then seen to change depending on void position and the applied extension. During the post-yielding stress softening a pure volumetric deformation was observed whereas a uniaxial like deformation was observed during the stress plateau.

Finite element analysis, with a constitutive model accounting for porosity, was carried out so as to determine the local true stress and strain. The stress field which was determined was in good agreement with the porosity characteristic variables.

X-ray synchrotron radiation study of the structure evolution of polymeric material systems during deformation
Viana, Julio (IPC/i3N - Institute for Polymers and Composites, Guimaraes)

The understanding of the structure evolution during deformation of polymers is an essential route to establish the relationships between the morphology and the mechanical properties and to develop accurate constitutive models. This work reports a study on the structure evolution of polymers with different initial morphologies during stretching as assessed by x-ray synchrotron radiation (WAXS and SAXS). Amorphous and semi-crystalline PET and low and high degree of crystallinity PP samples were prepared by different thermomechanical conditions, resulting in different morphologies and, consequently, showing different mechanical responses. The evolution of the structural parameters (level of molecular orientation, phase fractions/degree of crystallinity, lamellar structure, voids) during deformation is discussed. The evolution of the structural parameters is related to the distinct regimes of the stress-strain curve (elastic, yielding, cold drawing, strain hardening). The global picture is not able of totally interpreting the observable mechanical responses and still open issues are highlighted.
Influence of Solid Bulk Properties and Frictional Behavior on Solids Conveying in Single Screw Extruders

Längauer, Manuel (Upper Austria University of Applied Sciences, Wels, AUT)
Zitzenbacher, Gernot (Upper Austria University of Applied Sciences, Wels, AUT)
Kneidinger, Christian (Upper Austria University of Applied Sciences, Wels, AUT)
Liu, Keyan (Upper Austria University of Applied Sciences, Wels, AUT)

The properties of solid bulk materials and their frictional behavior predefine the quality of solids conveying and the mass flow rate of single screw extruders. The apparent bulk density is strongly dependent on thermal and mechanical influences.

In this work, the apparent bulk density in dependence on temperature and pressure of two different polypropylene pellet shapes of the same grade is examined. The frictional behavior is studied at different velocities and pressures. Differences in the mass flow rate of the pellet geometries are evaluated on a laboratory-scale smooth barrel single screw extruder.

The experiments show a strong dependence of the bulk densities on temperature and pressure. In fact, long cylindrical pellets exhibit a low bulk density at standard conditions which increases above the values of spheroidal virgin pellets at elevated temperature and higher pressure. Furthermore the mass flow rate of the cylindrical pellets is significantly higher in the extrusion experiments.

Examination of the Influence of Processing Parameters on Morphology and Mechanical Properties of Uncompatibilized HDPE - PA-6 Blends

Riedl, Bernhard (University of Applied Sciences Upper Austria, Wels, AUT)

Processing mixed plastic waste is a challenging task for every recycling facility. Using compatibilizers is the most common way to treat those heterogenic materials. To choose the right compatibilizer type and its amount, it is necessary to understand which morphology is formed while processing uncompatibilized polymer blends.

In the scope of this research, compounds of polyamide 6 with different amounts and types of high density polyethylene were manufactured. These were used for a detailed examination of the effect of manufacturing parameters on the morphology of these blends and furthermore on the mechanical and rheological properties. For this reason, six different melt and mold temperature combinations were used for the injection moulding process.

It is shown that the formed morphology types and subsequently the mechanical properties are predominantly depending on the relation between the melt volume rate of the two blended polymers and on the processing parameters.
Session G1: Cellulose and other Biopolymers

Invited talk:
NANO-CELLULOSE: Renewable Resources for Advanced Applications
Mautner, Andreas (Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London | Institute of Materials Chemistry and Res, Vienna, AUT)
Bismarck, Alexander (Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London | Institute of Materials Chemistry and Res, Vienna, AUT)

Nano-celluloses – cellulose fibrils with diameters in the nanometer range – are materials from renewable resources with unique and potentially highly useful features. The nanodimensions of the structural elements result in a large surface area and hence powerful interaction of these materials with surrounding species, e.g. water, organic compounds, polymers, nanoparticles, or living cells. In addition, through appropriate modification of nano-cellulose or pre-treatments, various functional nanomaterials with outstanding properties or significantly improved physical, chemical, biological, as well as electronic properties can be developed. Thus, these materials open up the strongly expanding fields of nanocomposites and sustainable materials, as well as medical and life-science devices, to the natural polymer cellulose.

This talk intends to give an overview over different types of nano-celluloses and methodologies of how these materials are produced. Furthermore, recent developments and novel applications making use of nano-celluloses will be outlined. Eventually, two advanced applications, developed in the Polymer and Composite Engineering group at Imperial College London, are presented: on the one hand the application of nano-cellulose in renewable polymer-composites and on the other hand the production of nanopapers applicable for the treatment of wastewater by nanofiltration.

Investigation of the interaction between Microfibrillar Cellulose and different polymeric additives in aqueous suspensions
Agarwal, Deepa (School of Biosciences, Loughborough, GBR)
Foster, Tim (School of Biosciences, Loughborough, GBR)

This work aims to investigate the interaction between microfibrillar cellulose and different polymeric additives (e.g. Carboxyl methyl cellulose and Locust Bean Gum) in terms rheological properties of an aqueous suspension. Microfibrillar cellulose is a network of cellulose fibres and fibrils produced by subjecting pure cellulose pulp to either chemical or mechanical processes¹. In order to stabilize the network after drying, charged polymers like carboxymethylcellulose (CMC) and Locust bean gum (LBG) are added to avoid the hornification phenomena. Oscillatory measurements show that from suspension concentrations of 0.5% to 2% w/w show pseudo gel-like behaviour, where storage modulus (G’) is almost ten times greater than loss modulus (G”) with little dependency on frequency. All suspensions showed shear thinning behaviour (decrease in viscosity with increase in shear rate) independent of concentration. Relaxation NMR showed that the relaxation time (T₂) is dominated by elastic behaviour of suspensions and as the shear viscosity of suspension increases the spin-spin relaxation time decreases. Underlying principles for rheological control in correlation with relaxation NMR are investigated.

Acknowledgement: Sincere thanks Oslofjordfond, Norway for funding this study.

References:
Poly(lactide) (PLA) is a rigid biodegradable thermoplastic obtained from renewable sources that can be plasticized by reactive extrusion. In particular, plasticized PLA is obtained with the addition of poly(ethylene glycol) methyl ether acrylate (acrylPEG) during the extrusion. It exhibited an original morphology consisting of a slightly plasticized PLA-acrylPEG matrix in which was distributed elastomeric micro-domains of poly(acrylPEG). The tensile deformation mechanisms of plasticized PLA in terms of chain orientation, phase transformation, elastomeric phase transformation and matrix cavitation are not elucidated. Our research is focused on the identification of the tensile deformation mechanisms of plasticized PLA compared to neat PLA. By wide-angle X-ray scattering (WAXS), we noted that for plasticized PLA amorphous chain orientation is active and engender crystallization. Crystallization ability increased when decreasing strain rate or temperature. Scanning electron microscopy (SEM) illustrates stretching of elastomeric micro-domains in the tensile direction and may exhibit some internal cavitation depending on strain rate.

Correlations between physical properties of ternary cellulose acetate blends
Kabasci, S. (Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Oberhausen, GER)
Zepnik, S. (Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT / Center of Engineering Sciences, Martin Luther University Halle-Wittenbe, GER)
Erdmann, Rafael (Fraunhofer Institut UMSICHT, Oberhausen, GER)

Within the scope of the research presented, two different TPU’s from 0 to 30 wt.-% together with a constant plasticizer content of 15 wt.-% were blended with CA via melt compounding using a co-rotating twin-screw extruder. The blends were then injection moulded and analysed with respect to their mechanical properties and morphologies. Tensile and three-point-bending test were performed as well as instrumented charpy impact tests (notched and unnotched). It was revealed that the rigid CA can be softened with increasing TPU content. This is confirmed by the constant decrease of Young’s modulus and tensile strength of the blend. Furthermore, with TPU contents of up to 10 wt.-% the impact strength of the blends is increased, too. However, above that TPU content the impact strength decreases drastically with further increasing TPU concentration in the blend.

EFFECT OF PROCESSING CONDITIONS ON MECHANICAL PROPERTIES AND MORPHOLOGY OF POLY(LACTIC ACID) STAPLE FIBERS
Bruckmoser, Katharina (Otto Glöckel-Straße 2, Leoben, AUT)

Morphology and hence performance characteristics of poly (lactic acid) (PLA) are strongly dependent on processing parameters. Especially cooling conditions and draw ratio are expected to have a significant effect on the properties of extruded products. Thus, within the present study the effect of processing conditions on mechanical properties and morphology of PLA staple fibers was investigated in detail. Various PLA staple fibers were produced via melt spinning. Draw ratio as well as draw temperature were varied. Produced staple fibers were characterized as to tensile strength and elongation at break by tensile testing. Fiber morphology was analyzed applying differential scanning calorimetry (DSC) and Raman spectroscopy. Distinct correlations between processing parameters, mechanical characteristics, and fiber morphology were established, which allow for tuning performance characteristics. In general, an increase in draw ratio yielded an increase in tensile strength and a decrease in elongation at break along with an increase in crystallinity. However, draw temperature was found to have a minor effect on mechanical characteristics and morphology.
Session D1: Experiments on the Nanoscale

Invited talk:
Nanoindentation in polymer systems
Flores, Araceli (Institute for Structure of Matter, CSIC, Madrid, ESP)

Depth-sensing indentation (DSI), or nanoindentation, represents nowadays one of the leading techniques for mechanical testing. The attractiveness of DSI relies on the ability to extract mechanical properties from a small local deformation that progressively moves towards the nanometre range. In this presentation, the state-of-the-art on the application of nanoindentation to polymer-based materials will be offered, highlighting the challenges that still need to be approached. A few examples illustrating the validity of nanoindentation in providing information on the changes of mechanical properties with the polymer nanostructure will be presented. It will also be shown that DSI can readily detect filler content and filler dispersion in polymer composites. Finally, the capability of nanoindentation to spatially map the mechanical properties will be illustrated with an example on hierarchical (or multiscale) fibre-reinforced polymer composites in which the interphase properties have been successfully identified.

Dislocation generation in polymer crystals on the molecular scale
Speckermann, Florian (University of Vienna, Vienna, AUT)
Polt, Gerald (Physik Nanostrukturierter Materialien, AUT)
Wilhelm, Harald (LKT, Wien, AUT)
Zehetbauer, Michael (Physik Nanostrukturierter Materialien, Wien, AUT)
Zare Ghomsheh, Mohammad (University of Vienna, Vienna, AUT)

The dominant plastic deformations mechanism in polymer crystals is crystallographic slip. Still the question of the involved strain carriers is not fully solved. Recent investigations using X-ray line profiles analysis confirm the importance of dislocations for many semicrystalline polymers but twinning and martensitic phase transformations were also reported. Adiabatic melting as suggested by Flory seems to play a minor role in quasi-static conditions.

While the presence and multiplication of dislocations has been shown, the molecular mechanism involved in their formation is not yet fully clarified. The generation of monolithic screw dislocations was suggested as well as the formation of soliton like twist defects. Both models lead to considerably different activation energies potentially observable by the experiment.

Recently strain bursts in nanoindentation creep experiments in polyethylene also attributed to a dislocation mechanism were discovered. The related energy hints at the soliton like process. The alpha relaxation in mechanical spectroscopic measurements could also be explained by a twist defect and its intercrystalline mobility. With MXPA, nanoindentation and mechanical spectroscopy, powerful experimental tools are at hand to understand the molecular and atomistic mechanisms related to dislocation formation.

Effect of compatibilizer on the mechanical properties of biodegradable triplet polymer LLDPE / HDPE/ Starch
Tabashi, Sara (no. 8 khorasavani street vaziripur street mohseni square mirdamad street, Tehran, IRN)
Oromiehie, Abdulrasoul (khatam polymer Co, tehran, IRN)

Recently, the use of biodegradable polymers in the production of packaging materials has received much attention by manufacturers. Biodegradable packaging materials are composites based on biopolymers and synthetic polymers. Typically, starch and polyolefins were used to produce such packaging materials. In this study a novel composite based on Corn Starch /High density polyethylene (HDPE) / Linear low density polyethylene(LLDPE) were prepared by melt mixing. Three kind of compolymers such as: ethylene-vinyl alcohol (EVOH), ethylene vinyl acetate (EVA) and polyethylene grafted maleic anhydride (PE-g-MA)were used as a compatibilizers in HDPE/LLDPE/Starch composites. In comparing the effect of the above compatibilizers, the mechanical properties of the biocomposites showed that the tensile strength, Young’s modulus and elongation at break increase when a polyethylene-g-maleic anhydride(PE-g-MA) copolymer was used as compatibilizer.
**Influence of Hybrid Fillers and Functional Polymers on Performance and Thermal Behavior of Polypropylene/Calcium Carbonate Composite**

*Sastry, Pendyala (TASNEE Plastics Research Centre (NIPRAS), Al-Jubail, SAU)*

Polypropylene is a versatile polymer that is adaptable to various applications. Its performance is found to be improved significantly in the presence of CaCO$_3$/talc hybrid fillers and functional polymer viz. PP-g-MAH/PP-g-AA compared to CaCO$_3$ alone. The influence of particle size (CaCO$_3$ 6-12 microns; talc 1-10 microns), nature of filler surface and concentration are involved towards the 'synergistic effect' in the composite's mechanical and thermal properties. The property enhancement of the composite is attributed to the increased favorable interfacial interactions among the matrix, hybrid fillers and the functional polymer. The effect of hybrid fillers and the functional polymers on the composite's (a) crystallization behavior, (b) thermal stability, and (c) the activation energy, is presented. The cost-effective hybrid composite exhibited enhanced performance by approximately 30% compared to a competitor material; and found to be suitable for garden furniture application.

**Shape and Size effects on the phase behavior of polymer-nanorod composites**

*Tripathy, Mukta (Department of Chemical Engineering, Mumbai, IND)*

*Shankar, Uma K. (Department of Chemical Engineering, Indian Institute of Technology Bombay, Mumbai, IND)*

We present a detailed study of polymer-nanorod composites using integral equation theory. Entropy-driven depletion phase separation is predicted between polymer and rods of nearly all aspect ratios. Miscibility is achieved by introducing a small amount of attractive interaction between polymer and nanoparticles. At large polymer-nanoparticle attraction strengths a few polymer molecules bridge several nanoparticles giving rise to another phase separated regime. This creates a finite miscibility window that narrows with rod aspect ratio. Our work confirms previous experimental findings indicating that depletion-driven phase separation is enhanced with increasing size of nanospheres. However, we predict that nanorods display a subtle, and non-monotonic dependence of the depletion line on the rod thickness. In the bridging regime, larger nanospheres show enhanced bridging while nanorods display a non-monotonic behavior. Further, at large nanorod diameters, telebridging (nanoparticles bridged by more than one polymer layer) is predicted.

**Potential role of marine coral filled polymer composites for internal fixation applications**

*Periasamy, Kamalbabu (Department of Mechanical Engineering, Mangalore, IND)*

*G C, Mohankumar (Department of Mechanical Engineering, Mangalore, IND)*

Utilization of marine skeletons as reinforcing filler in polymer composites for bone fixation applications gained an immense attraction in the material development domain. In this study, raw cuttlebone particles in aragonite polymorphic form and calcined cuttlebone particles in calcite form were used as fillers in epoxy matrix. Both polymorphic forms of cuttlebone particles were characterized by XRD and FT-IR. Mechanical properties of the composites were evaluated and the results showed that the addition of cuttlebone particles increased the flexural strength (~27%), flexural modulus (~22%) and impact strength (~31%) over the neat epoxy. 'In-vitro' cytotoxicity and hemocompatibility tests for the composites revealed that cuttlebone with aragonite structure filled composites were more biocompatible than the calcite filled composites.

Keywords: Cuttlebone; coralline CaCO$_3$; composite; bone fixation
Session C1: Modelling and Simulations

Invited talk:
Depletion interactions beyond the Asakura-Oosawa model
Likos, Christos (Computergestützte Physik, Wien, AUT)

Since publication of the legendary paper by Sho Asakura and Fumio Oosawa 60 years ago, the Asakura-Oosawa (AO) model has served as the prototype for the understanding and the quantitative analysis of entropically induced attractions between large colloids, brought about by nonadsorbing polymer in the solution. In the AO-prototype, colloids are hard and unpenetrable both to one another and to the dissolved polymer. Advances in theoretical and simulational techniques, as well as in macromolecular chemistry, have brought about, in the last decade or so, novel elements into this picture. Colloids can be made to have arbitrary softness; polymers can be made to have tunable penetrability to the colloids; and the role of depleted and depletant agents can be reversed. In this talk, I will discuss how these factors influence, and dramatically change, the AO-view on depletion, bringing about a host of unusual and unexpected features for the depletion interaction. The AO-model, therefore, although still providing the correct fundamental physical picture of depletion, proves to be quantitatively inaccurate in many cases.

Crystallising Clusters
Blaak, Ronald (Computergestützte Physik, Wien, AUT)

In a coarse grained approach one can describe soft particles, such as polymer chains, under appropriate conditions by means of an effective pair-interaction. The centres of mass of such macromolecules can get arbitrary close without violating any steric constraints. Hence the divergent behaviour in the interaction found for atoms disappears within this type of description. Consequently, soft-particle systems allow in principle for the formation of multi-occupancy crystals, where at each crystal position several particles are found. An example of this behavior is found in the GEM-4 model [1] based on a density independent pair-interaction. The fact that the effective interaction between macromolecules in this model is not affected by the high density required to form multi-occupancy crystals, is however a major approximation of which it is not obvious that it remains valid in realistic systems.

Here we will show by computer simulations that amphiphilic dendrimers treated on the monomeric level are more realistic macromolecules that spontaneously form clusters in the fluid phase. On increasing the density these self-assembled clusters of multiple overlapping macromolecules can arrange themselves in crystalline structures. Free energy calculation prove the thermodynamic stability of these crystals, in which the lattice distance and number of molecules per lattice site are density dependent [2]. This demonstrates the existence of thermodynamically stable multi-occupancy crystals formed by soft particles and paves the road to the realization of experimental cluster solids.


Computer simulation of long-chain branching and branching indexes
Netopilik, Milos (Institute of Macromolecular Chemistry, Prague 6, AUT)

We modeled randomly branched Gaussian chains by repeated random movement of the end-point in a cubic grid. The radius-of-gyration- and viscosity-volume branching indexes, \( g \) and \( g' \), were calculated for randomly branched molecules and compared with data from the literature. It has been shown that a linear relation between the calculated values of the indexes, as well as values reported in literature and some experimental data in good solvents, fall close to a straight line. The points for data reported in theta-solvents show high scatter but do not show any systematic deviation. This findings supports the value of the branching exponent of \( \varepsilon = 1 \), relating \( g \) and \( g' \), proposed by other authors. (The project 13-02938S was financed by GACR.)
Effect of bending stiffness and confinement on a polymer chain under tension
Poier, Peter (University of Vienna, Vienna, AUT)
Matthews, Richard (University of Vienna, Vienna, AUT)
Likos, Christos N. (University of Vienna, Vienna, AUT)

Type II topoisomerase are enzymes that (un)knot DNA. There is experimental evidence that a certain type II topoisomerase preferentially cleaves adenine (A) and thymine (T) rich regions of the DNA. It is believed that AT-rich sequences are more flexible than random ones. This raises the question of whether the flexibility of the preferred cleavage sites of topoisomerase II could play a role in the regulation of knotting. With this motivation we study the effect of the bending stiffness and confinement on the free-energy cost of a knot in a polymer chain under tension. Via thermodynamic-integration we calculate the change of the free-energy cost of a knot due to modifications of the bending stiffness. The free-energy cost exhibits a minimum at a non-zero value for the bending stiffness [1]. This minimum is related to a suppression of the bending at the points where the strands of the polymer cross in the knotted region. We study how the minimum of the free-energy cost is affected by changing the knot type and introducing a two dimensional confinement for the polymer chain [2].


Session C2: Modelling and Simulations

Invited talk
External pressure induced buckling collapse of High Density Polyethylene (HDPE) liners: FEM modeling, predictions and experimental corroboration
Frontini, Patricia (INTEMA, Mar del Plata, ARG)
Rueda, Federico (INTEMA, Mar del Plata, ARG)
Rueda, Juan Pablo (INTEMA, Mar del Plata, ARG)
Machado, Martín (Johannes Kepler University Linz, Institute of Polymer Product Engineering, Linz, AUT)
Otegui, José Luis (INTEMA, Mar del Plata, ARG)
Major, Zoltan (Johannes Kepler University Linz, Institute of Polymer Product Engineering, Linz, AUT)

Polymers as protective lining materials in pipelines is currently much diffused. These components may fail by radial buckling induced by external pressure.

Through this work we evaluate the suitability of Three Network Model for the simulation of the mechanical response of HDPE liners undergoing buckling collapse. The input parameters for the model were evaluated from a series of tensile and compressive uniaxial tests. Simulations were performed using FEM analysis. The complex strain rate, temperature and pressure dependent mechanical response of HDPE was analyzed by modeling the dynamic event as an increasing volume of fluid entering the gap cavity between liner and host pipe. In addition a specific testing device consisting in a plastic pipe confined into a steel host pipe was designed and constructed to experimentally corroborate FEM simulation predictions.

The model predictions allowed establishing a mathematical relationship between the depressurization velocity of the tubes and the resulting collapse pressure.
Numerical implementation of an elastic-viscoplastic constitutive model to simulate the mechanical behaviour during polymer forming processes

Bernard, Chrystelle A. (ICube Laboratory, Strasbourg, FRA)
Correia, João Pedro M. (ICube Laboratory, Strasbourg, FRA)
Ahzi, Saïd (ICube Laboratory, Strasbourg, FRA)
Bahlouli, Nadia (ICube Laboratory, Strasbourg, FRA)

Polymers are commonly shaped at different temperatures and strain rates in order to obtain structural parts. Although easy to form, polymers exhibit a complex behaviour with strain rate, temperature and pressure dependence. Nowadays, Finite Element (FE) simulations are widely used to develop and/or to optimize forming processes such as thermoforming. However, to obtain accurate FE predictions with polymers, the constitutive model must take into account their complex mechanical behaviour (strain rate, temperature and pressure dependencies). In the present work, a constitutive model issued from the literature was implemented in the commercial FE software ABAQUS/Explicit via a user material subroutine VUMAT. Next, simulations of compressive test were performed in order to verify the implementation of the constitutive model. After these tests, a perforation test and a forming process were simulated for polycarbonate. The FE predictions are in agreement with experimental results from the literature.

Investigation of the melting behavior of different shaped polymeric bulk solids

Längauer, Manuel (FH OOE Forschungs und Entwicklungs GmbH, Wels, AUT)
Zitzenbacher, Gernot (FH OOE Forschungs und Entwicklungs GmbH, Wels, AUT)
Keyan, Liu (FH OOE Forschungs und Entwicklungs GmbH, Wels, AUT)
Kneidinger, Christian (FH OOE Forschungs und Entwicklungs GmbH, Wels, AUT)

The melting behavior of polymeric materials in single screw plasticizing units is a crucial factor for the further process steps. A new method to characterize the melting behavior of polymer bulk solids in a single screw extruder using a model experiment with an optical measurement system was introduced in 2013. Polymer granules or solid samples are pressed onto a heated, rotating shaft while the thickness distribution of the melt film is measured according to the principle of optical triangulation (light intersection).

In this work, the melting behavior of different shaped polymeric bulk solids is examined under processing conditions, considering different velocities, pressures and temperatures.

The measured results are compared to theoretical values which are calculated according to Tadmor’s “Drag Induced Melt Removal” Model, which is the basis for the calculation of the melting in a single screw plasticizing unit.

Some insights about the modeling of self-heating in filled-rubbers

OVALLE, Cristian (Laboratoire de Mécanique de Lille, Villeneuve d'Ascq, FRA)
Zaïri, Fahmi (Laboratoire de Mécanique de Lille, Villeneuve d'Ascq, FRA)
Naït-Abdelaziz, Moussa (Laboratoire de Mécanique de Lille, Villeneuve d'Ascq, FRA)

Extensively used in the transport-related industries due to their damping properties, filled-rubber components are submitted to cyclic loading under common operating conditions. Due to the thermo-mechanical coupling, in connection with the viscous-related rubber behavior, the material heats up.

Using a finite-strain thermo-viscoelastic constitutive model, the self-heating distribution on a Diabolo sample under fatigue is analyzed. The mechanical behavior is described by a Zener rheological representation in which the strain response is decomposed into two components: the first component captures the relaxed state and the second one brings the time-dependence deviation with regard to the relaxed response. The thermodynamic irreversibility is taken into account by means of the Clausius-Duhem inequality. The thermo-mechanical coupling is defined by postulating the existence of a dissipation pseudo-potential, function of the viscous dilatation tensor. The constitutive model was implemented into a finite element code. The capability of the thermo-viscoelastic model to describe the self-heating is discussed.
Session C3: Modelling and Simulations

Modelling of ionization and conformations of star-like weak polyelectrolytes
Uhlik, Filip (Department of Physical and Macromolecular Chemistry, Prague, CZE)
Kosovan, Peter (Department of Physical and Macromolecular Chemistry, Prague, CZE)
Limpouchova, Zuzana (Department of Physical and Macromolecular Chemistry, Prague, CZE)
Prochazka, Karel (Department of Physical and Macromolecular Chemistry, Prague, CZE)
Borisov, Oleg (IPREM Î· Institut des Sciences Analytiques et de Physico-Chimie pour l¿Environnement et les Matériaux, Pau, FRA)
Leermakers, Frans (Department of Physical Chemistry and Colloid Science, Wageningen)

In this work we study conformational properties of star-like polyelectrolytes with pH-sensitive (annealed) dissociation in salt-free solutions. We confront hybrid Monte Carlo (HMC) simulations with computationally less expensive approximate numerical self-consistent field (SCF) calculations and with analytical theories. We demonstrate when the mean-field results are reliable and their advantage over MC in terms of efficiency can be exploited and when not. In the interior of the star, where inter-arm interactions dominate over intra-arm ones, the mean-field approximation works well and SCF agrees with the MC results. Intra-arm interactions dominate at star periphery, and their role is underestimated by the mean field. Here, conformations and dissociation resemble those of linear polyelectrolytes. Consequently, the dissociation profile along the chain contour is qualitatively different between MC and SCF. Comparison of the two methods and a distinction between intra-arm and inter-arm contributions to interactions enables us to understand the transition in behaviour from linear to star-like chain topology.

Frequency dependent Stress Relaxation in Nanofilled Elastomers
Mathieu, Tauban (LPMA / Solvay, Saint-FONS, FRA)
Long, Didier R. (LPMA (CNRS), Saint-FONS, FRA)
Delannoy, Jean-Yves (Solvay, R&I Centre Lyon, Saint-FONS, FRA)

Nanofilled elastomer composites are used in a very broad range of applications such as tires, damping materials and impact modifiers. The addition of rigid particles in a polymer matrix induces nonlinear effects that are not yet fully understood.

In the present work, we propose a model for the reinforcement of nanofilled elastomers based on the reduced mobility of the polymer confined between two filler particles. The morphology of the fillers is defined explicitly as spherical particles aggregated in the polymer matrix. The model is then solved by mesoscale numerical simulation. We study the response of filled rubbers to deformations of various amplitudes and frequencies in the reinforcement regime. We show that relaxation mechanisms are related to the disorder (particle size and aggregation number) in the filler population.

Our model opens the path for the development of systems with tailored properties by adjusting the fillers morphology.

Elongational and shear rheological behaviour of polylactides: comparison of phenomenological (Giesekus) and molecularly-based (Rolie-Poly) models
Stepien, Maja (Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, Lodz, POL)
Choong, Gabriel Y.H. (Faculty of Engineering, University of Nottingham, Nottingham, GBR)
De Focatiis, Davide S.A. (Faculty of Engineering, University of Nottingham, Nottingham, GBR)
Figiel, Lukasz (Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, Lodz, POL)

Computer simulations used in the optimisation of polymer forming processes (e.g. film blowing) require accurate constitutive descriptions of polymer rheology under relevant processing conditions. This work aims at comparing the applicability of the Giesekus and Rolie-Poly models for the non-linear elongational and shear rheological responses across a wide strain-rate range. Thus, first a detailed experimental investigation was carried out on the linear rheology of a commercial polylactide in order to identify relevant model parameters. The nonlinear rheological tests across a range of strain rates from 0.05 s\(^{-1}\) to 10 s\(^{-1}\) set the benchmark for the experimental validation of models. It was found that both models can accurately capture the elongational and shear rheology up to strain rates of 1 s\(^{-1}\), but overpredict the response beyond this rate. Further work is on-going to identify the reasons for the overprediction, as well as in the application of the models to numerical simulations of realistic forming processes.
The processing phase has significant influence on final properties of polymer products. For example, creep failure varies substantially as a function of the processing parameters. Moreover, injection molding is an intrinsically heterogeneous process and results in differences in properties along a single polymer product. These variations in properties are a result of the differences in thermo-dynamic history the material experiences during the processing phase.

The objective of the present work is to determine property distribution along a single injection molded polymer product. An experimental-numerical approach is used which is based on the hypothesis that the polymer’s behavior is determined by both deformation kinetics and aging kinetics. These are directly related to the yield stress and its evolution in time. The methodology is validated by comparing experimental data with numerical results for polycarbonate. It is demonstrated that the simulations are able to satisfactorily describe the experimental results.

Molecular Simulation Study of Anti-Stain coatings

Manik, Gaurav (Department of Polymer & Process Engg., Saharanpur, IND)
Singhvi, Yash (Department of Polymer & Process Engg, Saharanpur, IND)

Molecular Dynamics simulations have been used to understand the structure-property relationships of specialty polymers [1, 2]. Recent advancements in coatings formulations, have given rise to HFPO, Teflon, PVF, PVDF and other modified molecules, that provide significant oleophobicity to serve as stain-repellant industrially relevant coatings [3]. This work demonstrates usefulness of molecular simulations as a tool to understand and compare the performance of some selected formulations based on such fluorine based moieties. Material Studio software available from Accelrys™ has been employed for running Molecular Dynamics (MD) simulations to estimate useful properties with polymer specific force fields (COMPASS and PCFF). A comparison of simulation results is made among such molecules to finally screen and propose a potentially better anti-stain formulation. References

Invited talk:

All-polymer nanocomposites by plastic deformation of single polymer crystals
Galeski, Andrzej (Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, POL)
Jurczuk, Kinga (Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz, POL)

Deformation of polymer was long used as mean to obtain thin and strong fibers. However, large stretching is restricted by entanglements of macromolecules, fibers are thick. Nanofibers are easily obtained from liquid crystalline polymers because of lack of entanglements. Some nascent polymers with flexible chains exhibit low entanglement. However, classical fiber spinning cannot be applied to produce nanofibers because melting leads to immediate chain entanglement. Process comprises: manufacturing fine crystalline polymer powder with unentangled macromolecules, dispersing polymer powder particles into another molten polymer and then thermally activated plastic deformation of crystals into nanofibers. Deformation into nanofibers is realized by shearing via viscous media. Nanofibers were generated during shearing of unentangled powders: polytetrafluoroethylene, polyethylene and polypropylene. The larger and longer the shear the thinner and stronger nanofibers. Shearing during compounding results in generation of nanofibers and thus, forming all-polymer nanocomposite. Several polymer matrices were used for the generation of all-polymer nanocomposites.

Novel creep-test method for characterization of strain bursts in semi-crystalline polymers
Wilhem, Harald (University of Vienna, Vienna, AUT)
Speckermann, Florian (Physik Nanostrukturierter Materialien, AUT)
Polt, Gerald (Physik Nanostrukturierter Materialien, AUT)
Zehetbauer, Michael (Physik Nanostrukturierter Materialien, Wien, AUT)
Fischer, Ch. (Laboratory of Polymer Engineering LKT-TGM / University of Applied Science Upper Austria, Vienna, AUT)

Recent nanoindentation experiments have shown that in semi-crystalline polymers, strain bursts emerge during creep experiments. A major disadvantage of nanoindentation is that due to the inhomogeneous stress field, a critical stress for the onset of strain bursts cannot be determined easily, and that for evaluating the activation energy some assumptions must be made.

Since the strain bursts in polymers are in the nm range, an extremely high resolution in deformation measurement is necessary. Modern solid state rheometers have a resolution <10⁻⁶ rad. Thus the deformation at the sample’s edges with 2.5 mm radius can be measured with a resolution of about 1 nm being sufficient to resolve individual strain bursts. With such a facility, single strain bursts in HDPE have been investigated in creep mode at stresses as low as <0.5 MPa. As the strain bursts only occur rarely, hundreds of creep experiments had to be carried out and evaluated statistically. By varying the temperature and the stress, the activation energy for the strain burst could be determined as 0.28 eV. To sum up, it could be shown that this new measurement method represents a powerful tool for characterization of strain bursts in semi-crystalline polymers.

Self-scrolled chitosane acetate fibres: a novel material for drug encapsulation and release
Luchnikov, Valeriy (Institut de Science des Matériaux de Mulhouse, Mulhouse, FRA)
Saito, Yukie (The University of Tokyo, Department of Global Agricultural Sciences, Tokyo, JPN)

Hollow-core multi-shell fibres are produced by self-scrolling of chitosane acetate (CA) films, in which a gradient of physico-chemical characteristics is induced either by ionic cross-linking with the use of sodium triply phosphor pentabasic (TPP), or via thermal treatment. This gradient is at the origin of different degree of swelling of the top and the bottom layers of the CA films, immersed in water, leading to the bending moment and scrolling. The structural inhomogeneity of the films in the normal direction is proven by ATR-FTIR spectroscopy. Due to biocompatibility of chitosane and its derivatives, CA fibres are perspective media for encapsulation and controlled release of macromolecular drugs.
On the difference in the molecular mobility at free or contacting polymer surfaces and in the polymer bulk
Boiko, Yuri (Laboratory of Physics of Strength, Ioffe Physical-Technical Institute, St. Petersburg, RUS)
Myasnikova, Liubov (Laboratory of Physics of Strength, Ioffe Physical-Technical Institute, St. Petersburg, RUS)
Lebedev, Dmitri (Laboratory of Physics of Strength, Ioffe Physical-Technical Institute, St. Petersburg, RUS)
Marikhin, Vyacheslav (Laboratory of Physics of Strength, Ioffe Physical-Technical Institute, St. Petersburg, RUS)

The molecular mobility at free and contacting near-surface polymer nano-layers has been investigated by employing the adhesion and plasma-induced thermoluminescence techniques, and compared with that in the polymer bulk. It has been shown that the segmental motion at the free surfaces of linear thermoplastic polymers having various chains architectures is enhanced with respect to that in the polymer bulk. Moreover, it has been found that the chain segments can diffuse across a polymer-polymer interface below the bulk glass transition temperature, indicating that the presence of the free surface is not the only reason due to which the observed increased molecular mobility takes place. The physical nature of this phenomenon will be discussed.

The financial support from the Russian Foundation for Basic Research is greatly acknowledged (Project 13-03-00634/14).

Session B1: Plasticity and Mechanical Properties

Invited talk:
Effects of some confinement mechanisms on segmental relaxation in polymers
Pieruccini, Marco (CNR Istituto Nanoscienze, Modena, ITA)

Local segmental rearrangements in a metastable polymer melt (α-process) can be viewed as transitions between basins of attraction in the phase space. The dynamics of these rearrangements is significantly affected by upper limits to the wavelengths of their Fourier components (e.g. due to crystals or crosslinks).

A "minimum coupling model" is proposed for the α-relaxation, whereby an increase of conformational entropy is locally triggered by the regression of energy fluctuations involving a certain number of monomers in the metastable phase. The connection between size of the rearranging regions and presence of dynamical constraints is highlighted.

Model confined systems such as semicrystalline, crosslinked and nanopore confined polymers are discussed to some extent. Open issues to be considered concern:

1. extending the model to the description of yield stress experiments
2. pointing out key aspects characterizing both the α-relaxation dynamics and the plastic deformation of polymeric materials near or below Tg.

Cavitation mechanisms in high-density polyethylene during complex loading histories in tension revealed by time-resolved small-angle x-ray scattering
Addiego, Frédéric (Centre de Recherche Public Henri Tudor, Hautcharage)
Patlazhan, Stanislav (Semenov Institute of Chemical Physics, Moscow, RUS)
André, Stephane (INPL-University of Lorraine, Vandoeuvre-lès-Nancy, FRA)
Bernstorff, Sigrid (Sincrotrone Elettra, Trieste, ITA)
Toniazzo, Valerie (CRP Henri Tudor-AMS, Hautcharage)
Ruch, David (CRP Henri Tudor - AMS, Hautcharage)

Cavitation mechanisms occurring in HDPE subjected to complex loading histories, including cyclic tension / compression, strain unloading, and stress recovery were investigated. Tensile/compressive testing was performed along with the SAXS beamline of the synchrotron of Trieste. An analysis methodology was based on quantification of cavitation information in terms of nanovoid cloud volume fraction fcl extracted from SAXS patterns. During stress loading, fcl progressively increased with the strain level, starting from the well-defined onset strain prior the yield point reaching at maximum 8.75 vol% for a strain of 12.5%. Stress unloading and strain recovery procedures caused healing of nanovoids which resulted in a decrease of fcl compared to the state prior unloading. fcl was divided into permanent and non-permanent components. For cyclic tension/compression testing, the maximum fcl was found to gradually increase with the cycle number, while each compression stage reduced fcl to zero.
Dynamic fracture analysis of PMMA by the optical method of caustics
Gao, Guiyun (Peking University, Beijing, CHN)
Li, Zheng (Peking University, Beijing, CHN)
Zhou, Jie (Peking University, Beijing, CHN)

Polymethyl methacrylate (PMMA) as a good transparent and tough engineering material has widely applied in commercial products. In order to study the dynamic fracture behavior of PMMA, Semi-Circular Bending (SCB) specimens are introduced in fracture analysis of mode I and mode II fracture. Here SCB specimens of PMMA with different pre-crack directions and positions were employed. An optical method of caustics was applied to calculate the crack initiation, crack propagation, stress intensity factor and fracture toughness, etc. Results shows that the fracture mode and behavior of PMMA can be adjusted by pre-crack position and direction. Moreover, the interaction between cracks or crack and damage was also investigated by using this optical method. Finally, the dynamic fracture behavior of PMMA under complicated situations can be concluded.

The Stepped Isothermal Method for accelerated creep testing of polymers
Achereiner, Frédéric (SKZ - KFE gGmbH, Würzburg, GER)
Engelsing, Kurt (SKZ - KFE gGmbH, Würzburg, GER)
Bastian, Martin (SKZ - KFE gGmbH, Würzburg, GER)

The increasing use of polymers in engineering applications requires suitable accelerated test methods for predicting their long-term behaviour. The Stepped Isothermal Method (SIM), originally developed for product testing of geosynthetics, was successfully applied to characterize the long-term creep behaviour of polymers. Based on the time-temperature superposition principle, this method can be described as a short-term creep experiment during which the temperature is elevated stepwise. It is shown that the temperature steps can be rescaled and shifted to generate a master curve matching the prediction of long-term creep resulting from the conventional approach of the time-temperature superposition principle (TTSP). This compliance with established test methods and its good reproducibility suggests that SIM is a useful tool for accelerated testing of long-term creep behaviour, especially for comparative purposes such as quick screening of material formulations during the early development stages, or the at-line assessment of resins as part of quality assurance.
Invited talk:
**Polyurea Networks and Nanocomposites**

Sanchez-Ferrer, Antoni (ETH Zurich, D-HEST, Zurich, CHE)
Reinecker, Marius (University of Vienna, Vienna, AUT)
Soprunyuk, Viktor (University of Vienna, Vienna, AUT)
Fally, Martin (University of Vienna, Vienna, AUT)
Schranz, Wilfried (University of Vienna, 1090, AUT)
Roge, Daniel (Institute Charles Sadron, Strasbourg Cedex, FRA)
Martinoty, Philippe (Institute Charles Sadron, Strasbourg Cedex, FRA)

Polyurea networks are covalently crosslinked polymeric systems which exhibit microphase-separation between the urea-rich hard domains and the soft crosslinked polymer backbones domains. These materials have the advantages of organic polymers, and the capability of dispersing inorganic nanoparticles which enhance the thermal, mechanical, optical and electrical properties of the matrix. Applications for these nanocomposites will be materials for heat and electrostatic dissipation, protection materials, photovoltaic elements, and artificial muscles.

The elastomeric matrix is obtained through a relatively new synthetic process, similar to that used for the synthesis of polyurethanes, but with no need for a catalyst to accelerate the chemical reaction. The reaction between a polyisocyanate and a poly-amine leads towards the formation of urea groups that can interact by hydrogen bonding. The microphase-separation and hydrogen bonding formation are responsible for the two glass transitions and a transient network below 100 °C, respectively, below the conventional rubber-like behaviour.

Fracture prediction of rubbers: effects of thermal ageing

Ben Hassine, Mouna (EDF, Moret sur Loing, FRA)
Naït Abdelaziz, Moussa (Polytech’Lille, Cité Scientifique, Villenueve d’Ascq, FRA)
Zairi, Fahmi (Polytech’Lille, Cité Scientifique, Villenueve d’Ascq, FRA)
Colin, Xvier (PIM, Paris, FRA)
Tourcher, Christophe (EDF, Moret sur Loing, FRA)
Marque, Gregory (EDF, Moret sur Loing, FRA)

In this work, we attempt to derive a new original approach allowing the prediction of the stretch ratio at failure in rubber components subjected to thermal ageing. To achieve this goal, the main idea is to combine fracture mechanics and the intrinsic defect concept.

Accelerated ageing tests for an Ethylene-Propylene-Diene Monomer (EPDM) show that the average molar mass of the elastically active chains seems to be the main indicator of the macromolecular network degradation. By introducing the time-temperature equivalence principle, master curves are derived for the average molar mass and for the ultimate mechanical properties. Fracture mechanics tests allow to point out the square root dependence of the fracture energy with the average molar mass. Moreover, it is shown that the mechanical response could be approximated by the phantom network theory, which allows to relate the strain energy density function to the average molar mass. Assuming that the fracture of a smooth specimen is the consequence of a virtual intrinsic defect the stretch ratio at break can be therefore computed for any ageing condition. The estimated values are found in a very nice agreement with EPDM experimental data.
**Thermal stability of deformation induced dislocations in Polypropylene**

**Polt, Gerald** (University of Vienna, Vienna, AUT)

**Spieckermann, Florian** (Physik Nanostrukturierter Materialien, AUT)

**Wilhelm, Harald** (LKT, Wien, AUT)

**Kerber, Michael** (Physik Nanostrukturierter Materialien, AUT)

**Schäfer, Erhard** (Physik Nanostrukturierter Materialien, Wien, AUT);

**Bernstorff, Sigrid** (Sincrotrone Elettra, Trieste, ITA)

**Zehetbauer, Michael** (Physik Nanostrukturierter Materialien, Wien, AUT)

Crystallographic slip is a basic deformation mechanism in polymer crystals, operating over a wide range of strains [1]. Preceding investigations showed that in some semicrystalline polymers this slip is guided by a dislocation based deformation mechanism [2,3].

In the present work, the thermal stability of deformation induced dislocations is investigated. In-situ X-ray diffraction experiments during stepwise annealing of pre-deformed a-phase Polypropylene (a-iPP) were performed. The diffraction patterns were analyzed by the Multi-reflection X-ray Profile Analysis (MXPA) method [4], which allows for determining the presence and density of dislocations, and the lamellae thickness. The development of the dislocation density obtained as a function of annealing temperature allows to identify the critical temperatures where the dislocations are being mobilized in a-iPP. By combining data from MXPA with those from dynamic thermo-mechanical analysis, it is possible to attribute the thermal stability of dislocations to various relaxation processes within the crystalline and amorphous phase.


**Rate mechanism and dislocation generation in high density polyethylene and other semicrystalline polymers**

**Zehetbauer, Michael** (University of Vienna, Vienna, AUT)

**Wilhelm, Harald** (LKT, Wien, AUT)

**Polt, Gerald** (Physik Nanostrukturierter Materialien, AUT)

**Ahzi, Saïd** (ICube Laboratory, Strasbourg, FRA)

**Spieckermann, Florian** (Physik Nanostrukturierter Materialien, AUT)

Strain rate jump tests of high density polyethylene (PE) have been carried out which provide activation volumes of about 300b^3 being typical of a process governed by dislocation generation [1]. It is thus reasonable to model both the temperature and the strain rate dependence of the yielding of PE as a superposition of two thermally activated processes, one originating from the amorphous fraction, and one from the crystalline phase representing the thermally activated generation of dislocations. Then, experimental parameters such as the lamella thickness, the shear modulus, and the dislocation density can be correlated with the yield stress. It is found that the use of a dislocation based model is able to model and simulate the strain rate and temperature dependence of the yield stress of PE-HD, PP and E/MAA co-polymers reasonably well. This successful introduction of the dislocation density as a model parameter and its impact on the yield stress show that the number and generation of dislocations can play an important role for the strength of semicrystalline polymers [2].

Martensitic transformation behavior of polyethylene investigated by in situ SAXS and WAXS at elevated temperature

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LAME, Olivier (Laboratoire MATEIS INSA Lyon, Villeurbanne, FRA)
Chenal, Jean-Marc (Laboratoire MATEIS INSA Lyon, Villeurbanne, FRA)
Chenal, Cyrille (CERMAV - CNRS UPR 5301, Grenoble, FRA)
Seguela, Roland (Laboratoire MATEIS INSA Lyon, Villeurbanne, FRA)
Vigier, Gerard (Laboratoire MATEIS INSA Lyon, Villeurbanne, FRA)

Martensitic transformation (MT) of polyethylenes with various topologic structures was studied by in-situ WAXS and SAXS at different temperatures. The onset of MT was traced by the first appearance of the monoclinic plane (001) in scattering patterns. The monoclinic plane (001) appeared first in meridian region of the scattering patterns suggesting MT initially occurred in the lamella located in polar region of spherulite. Macroscopic strain for the onset of MT increased with increasing the thickness of the crystalline lamellar and with elevated drawing temperature. It was confirmed the monoclinic phase was generated before the yield point for 75 °C drawing temperature. The macroscopic stress for the onset of MT decreased with increasing stress transmitter content, [ST]. In equatorial region of spherulite, monoclinic phase appeared beyond crystal shearing via chain slip in (100)[001]. We have also compared the initial of crystal shearing in the equatorial region versus the appearance of MT.

Session B3: Experiments on the Nanoscale and Crystallization

Invited talk:
Plastic deformation of glassy polymers and oligomers
Berlin, Alexander (Kosygina str. 4, Moscow, RUS)

The following peculiarities were found in experimental studies of deformation behavior of amorphous solid polymers. Upon annealing, the yield peak appears and grows. It disappears during the secondary deformation applied after the significant plastic flow. However, the yield peak occurs again after annealing. The creep and stress relaxation slow down during annealing while they accelerated significantly after the preliminary plastic deformation. All the described features are confirmed by the molecular dynamic simulations. The phenomenological model of plastic deformation was proposed. This model is based on the assumption of development of certain structural elements (alike the growing shear cracks), which are responsible for plastic deformation. It is suggested that decrease in shear resistance is caused by the decrease of local material density within the structural elements.

Mechanical and Thermal Properties of Nanocomposite Based On Unsaturated Polyester Resin
LAATAR, FEKRI (National Research Center of Materials Science, Gabes, TUN)
BEN ROMDHANE, Med RAMZI (National Research Center of Materials Science, KORBA, TUN)
SRASRA, EZEDDINE (National Research Center of Materials Science, BENAROUS, AUT)

Unsaturated polyester (UP) resin is widely used for the matrix of composites such as fiber reinforced plastic (FRP) and polymer composites. Consequently, inexpensive and high performance resins are important for the future of polymer composites.

One recent method for enhancing the performance of polymer composites is the manufacture of UP-MMT (montmorillonite) nanocomposite synthesized by dispersing the UP resin into the silicate layers of MMT. This study investigates the mechanical and thermal properties of UP-MMT nanocomposites.

Test results supported by mechanical testing, X-ray diffraction (XRD), Fourier transform infrared spectroscopy DSC analysis and TEM microscopy ; indicate that the mechanical properties and the thermal stability of UP-MMT nanocomposites are better than those of pure UP.
NUCLEATION OF HIGH PRESSURE GAMMA FORM IN ISOTACTIC POLYPROPYLENE

Sowinski, Przemyslaw (Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, Lodz, POL)
Plorkowska-Galeska, Ewa (Center of molecular and Macromolecular Studies PAS in Lodz, Lodz, POL)
Boyer, Severine A.E. (PRIME Institute, ISAE-ENSMA Department of Physics and Mechanics of Materials, Futuroscope Chasseneuil Cedex, FRA)
Haudin, Jean-Marc (MINES ParisTech, Centre for Material Forming, Sophia Antipolis, FRA)
Zapala, Kinga (Center of molecular and Macromolecular Studies PAS in Lodz, Lodz, POL)

Under atmospheric pressure isotactic polypropylene (iPP) crystallizes usually in the monoclinic alpha or trigonal beta phase, whereas under high pressure in the orthorhombic gamma form. Our study focused on nucleation of the gamma form in iPP under high pressure. Four nucleating agents were used: calcium salt of cis-1,2-cyclohexanedicarboxylic acid, 1,3,2,4-bis(3,4-dimethylbenzylidene sorbitol (Hyperform HPN-20E and Millad 3988i from Milliken Chemicals), and poly(tetrafluoroethylene) (PTFE) submicron particles (Dispersez 200W2 from Polysciences Inc.), which nucleate efficiently crystallization of iPP in the alpha form under atmospheric pressure, and also calcium pimelate, which is known to nucleate the beta form. All alpha-nucleating agents accelerated crystallization of iPP under high pressure in the gamma form whereas the beta-nucleating agent did not. The alpha-nucleating agents either could nucleate directly the gamma form or the alpha "seeds" facilitating further crystallization of the gamma crystals. The second mechanism is especially probable for PTFE, which is known to nucleate the iPP alpha phase through epitaxy involving (110) alpha plane, which does not apply for the gamma form. The results show the possibility to nucleate the gamma form of iPP under high pressure.

CONTRIBUTION OF CHEMICAL CROSSLINKS AND ENTANGLEMENTS DURING STRAIN INDUCED CRYSTALLIZATION OF NATURAL RUBBER AT HIGH STRAIN RATES

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Strain-Induced Crystallization (SIC) of Natural Rubbers (NR) with different network chain densities (ν) is studied at high strain rates, i.e. close to real conditions of solicitation of rubber in pneumatic tires (from 1s⁻¹ to 10²s⁻¹). This is done by the use of a new homemade device allowing in situ WAXS observation during dynamic cycles. For the rubber with the highest ν, crystallinity index (CI) developed during these cycles is strongly decreased compared to the one measured during cyclic test at slow strain rate (~10⁻³s⁻¹). This is mainly due to SIC delay at high strain rates. Inversely, for the sample with the lowest ν, CI is found much higher during dynamic cycles than the one measured during cyclic test at slow strain rate. This enhancement of SIC in weakly vulcanized rubber at high strain rates might be related to dynamics of its free entanglements, which act as supplementary crosslinks at high strain rates.
Crystallization of different grades of Polyamide 6-6 at high cooling rates
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Polyamide 6-6 is a good candidate to replace metallic automotive parts thermomechanically solicited, in order to decrease vehicle weight.

The microstructure obtained during the forming process plays an important role on final mechanical or barrier properties of polyamide parts. Cooling rate of polymer during forming process has an important influence on the final microstructure.

Dried polyamide 6-6 is very hygroscopic, then it’s important to control sample preparation from the pellets (treatment of glass slides, vacuum drying, and storage). Such a protocol has been established to fulfill these requirements.

The aim of this work was to study crystallization of different grades of polyamide 6-6 (different Molar weight, branching …) at high cooling rates. The use of “Hyper DSC” allowed us to study crystallization of our polymers at cooling rates up to 700 °C/min and particularly overall kinetic of solidification. Postmortem microstructure morphologies checked by observation of microtomed sections are discussed.

Session E2: Crystallization and Phase Transitions

Invited talk:
Modeling and simulation of the effects of crystallization on the thermo-mechanical response of rubbers during large deformations
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Polymers undergoing crystallization during deformation can show substantial volume reduction due to the phase transformation, accompanied by stress relaxation and substantial increase in modulus. This kinetic process is controlled by the conditions of crystallization and stops short of complete conversion. The phase transformation and change of properties are gradual and the extent depends on the thermo-mechanical process, which is controlled by the thermo-mechanical loading and confinements from the surroundings. Capturing the response during this transformation requires a thermodynamically consistent hereditary thermo-mechanical model that can capture the influence of past history in addition to the complex interactions between confinements, volume reduction, loading, deformation, and changing rigidity. A model capable of capturing these transformations and interactions for rubber is presented and discussed.

Simulation of the response of a part under thermo-mechanical loading requires satisfaction of the laws of balance of mass, momentum, and energy. The close to incompressibility of the rubber phase requires one to additionally consider constrained deformations. Examples are presented of non-homogenous response of rubber. These include comparisons with anomalous response observed a crystallizing rubber oscillator, and FEM simulation of crystallization around rigid fibers/inclusion, as shown here, for example, for plane strain extension followed by crystallization around an inclusion.
Poly lactide (PLA) is a main biobased and biodegradable candidate for replacement of petrochemical polymers. Its crystallizability depends on enantiomeric composition and decreases with decreasing optical purity. Our study concerned shear-induced crystallization of PLAs, with a focus on a role of enantiomeric composition. Molten PLA was cooled to selected temperature $T_s$, ranging from 146 to 160°C, and sheared at rates ranging from 10 to 300/s, for 5 or 30 min, and subsequently cooled to ambient temperature at 10 or 30°C/min. The overall crystallization kinetics was followed by a light depolarization method, whereas the cooled specimens were analyzed by DSC, WAXS, and SEM. Shear strongly enhanced crystallization of optically pure poly(L-lactide). The effect was much weaker in two commercial PLAs purchased from NatureWorks LLC, USA, with 1.5 and 2.4% of D-lactide, respectively. The effect of shear on crystallization was stronger in the case of commercial PLA with less D-lactide; the influence of D-lactide content prevailed over that of molar mass.

ALIPHATIC-AROMATIC COPOLYESTERS OF VARIOUS CHEMICAL COMPOSITION

The aim of our studies, was to produce aliphatic-aromatic copolyester (ACC), which would combine ability to biodegradation and good physical performance. Therefore, several copolysters of poly(butylene adipate-co-succinate-co-glutarate-co-terephthalate) (PBASGT) differing in composition have been synthesized and characterized.

A series of copolysters has been synthesized containing from 10 to 100% of aromatic units. The increase of aromatic units contents caused an increase in crystallization temperature but did not change the crystallographic structure, in contrary to the results obtained by Li et. Al1 for poly(butylene succinate-co-terephthalate). In all PBASGT only butylene terephthalate (BT) blocks are able to crystallize in the crystallographic form characteristic of a PBT homopolymer. There are slight differences in several diffraction peak positions of PBASGT and PBT that are connected with slight distortion of certain crystallographic unit cell walls caused by the vicinity of aliphatic units. The most promising composition (containing 40-45% of aromatic units) was compared with commercial poly(butylene adipate-co-terephthalate) (PBAT). It appeared that, in contrast to aliphatic part of PBAT, the aliphatic part of PBASGT is unable to crystallize, when annealed below the room temperature2.

References

Acknowledgements
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Effect of tensile drawing on crystal transformation and mechanical properties of poly(butylene adipate)

Stretch-induced crystal transformation can be found usually, while stretch-induced bidirectional polymorphic transformation is rarely observed in polymer materials. Here we will demonstrate that tensile deformation could lead to both occurrence of $\alpha$ to $\beta$ and $\beta$ to $\alpha$ crystal transition via solid–solid process in poly(butylene adipate). Experimental results shows that either $\alpha$ or $\beta$ form can be adopted as the stable phase for PBA crystal depending on the competition between tensile strain and temperature. Higher temperature favors $\beta$ to $\alpha$ crystal transformation, while larger strain would result in $\alpha$ to $\beta$ crystal transformation. Due to the conversion of crystal stability during stretching, a unique “$\beta$ to $\alpha$ to $\beta$” transformation phenomenon of PBA appears at appropriate temperature for original $\beta$ spline. This study provides evidence that both temperature and tensile strain can alter the relative stability of polymorphic crystals. Also the reversible crystal transformation can be used to improve PBA mechanical properties.
Session I3: Composites and Fillers

Invited talk:
Dielectric Change of Copper Phthalocyanine and Polyurethane Foam with High Elasticity as a Function of Pressure
Discussed in Terms of Conversion from Natural Mechanical Energy to Electric Energy
Matsuo, Masaru (Department of Polymer Material Science, Faculty of Chemical, Environment and Biological Science, Dalian, CHN)

Dielectric composite with high elasticity was investigated by preparing copper phthalocyanine (Cupc) and commercial polyurethane (PU) foam with high elasticity. The continuous fibrils forming PU foam with many voids were covered by Cupc perfectly. The measurements were carried out for two specimens: 1) a Cupc film prepared by high pressure to Cupc gains and 2) the Cupc-PU composite. The results indicated that high complex permittivity of the Cupc film at low frequency was attributed to the movement of polarized polarons within Cupc grains. The dielectric effect of the Cupc-PU composite was attributed to boundary effects between Cupc grains coated on PU fibrils and between the grains and electrode. The boundary effects were evaluated by tunneling effect theoretically. Electrical energy as a function of pressure was evaluated for Cupc-PU composite. As the results, the dielectric materials with high elasticity suggested the possibility about conversion from natural mechanical energy to electrical energy.

Flax fibre reinforced composites based on boron oxide oligomer polypropylene matrix
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The flammability properties of flax fibre reinforced composites produced using a novel polypropylene (PP) – oligomer of boron oxide (OBO) matrix was investigated.

Three samples of PP resin with an OBO content of 15%, 30% and 40%, respectively, and flax needle-punched nonwovens were used to produce composites samples by compression moulding. The composite samples had the fibre / matrix composition of 30% / 70% by weight.

Flammability properties were examined using a cone calorimeter. Light microscopy was used to examine residues.

It was found that increasing the OBO content delayed the ignition time by 29% - 54%. The peak heat release rate (PHRR) for the PP-OBO composites was reduced by up to 51%. PP- OBO composites produced a lower cumulative smoke release and higher char residue (19% – 34%) compared to a control sample.

It is concluded that the OBO promotes char formation and acts as an efficient flame retardant and smoke suppressant for the natural fibre composites.
Morphing Skins: Carbon Fibre Reinforced Composites with Variable Stiffness

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The contribution reports on high performance carbon fibre reinforced composites with controllable stiffness with potential applications in morphing wings or deployable structures. A significant challenge in that field is the development of a stiff skin material that can withstand aerodynamic loads but can still be deformed with acceptable actuation forces. Two designs of materials have been developed, those which contain either thermo-responsive (polymer) interphases, or interleaf layers. At elevated temperatures they undergo large reductions in flexural stiffness (up to 98%) and fully recover when cooled, with no discernible loss in properties, thus meeting the requirements for use as skin materials in morphing wings. In the first design, composites containing thermo-responsive interphases were manufactured by continuously coating polystyrene onto carbon fibres followed by infusion with an epoxy resin. Dynamic mechanical thermal analysis and flexural tests showed stiffness reductions of up to 30 % when heating the composites beyond $T_g$ of the interphase. Composites containing polyacrylamide interphases were also analysed by DMTA. These composites underwent reductions in storage modulus of up to 79 % when the polyacrylamide interphase was partially hydrated and heated above $T_g$. In an alternative design, interleaved laminates containing plies of polystyrene between carbon fibre reinforced laminae were also manufactured. When heating the composites 120 °C beyond the $T_g$ of polystyrene, they exhibited up to 98 % loss in flexural stiffness and could undergo large deformations. The process was reversible as the composites could be returned to their original configuration and their flexural stiffness restored to their full values with no damage observed.

Dynamics of composite droplets subjected to shear flow in a narrow channel

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We discuss numerical modeling of deformation behavior of 2D composite droplets comprised of single viscous core and shell immersed into liquid phase which is subjected to simple shear flow. This kind of droplets attracts significant attention due to possibility to improve impact viscosity of composites based on ternary polymer blends. It was shown that decrease in channel thickness leads to increase the steady state deformation of the composite droplet, whereas the orientation angle is basically sensitive to capillary number. At certain ratio of core and shell radii the "propping" effect was found to become apparent and the confinement has no influence on the droplet deformation at larger core sizes. It was concluded that channel thickness and droplet composition have a significant impact on its deformation behavior.
Beyond dispute nanotechnology is one of the technologies that has the potential to have a big impact in the future on our daily life and is supposed to cover all important applications like health, energy, transport or communication. Polymers on the other hand are regarded as the material of the 21st century since they are easy to adapt to various conditions and can be economically produced in mass production. So there are a lot of efforts to combine nanotechnology with polymers. One promising way are so called polymer nanocomposites where various nanoparticles are incorporated in polymers to enhance properties and add new functionalities like flame retardancy or barrier properties. These enhancements are linked not only to the concentration and size of the nanoparticles but also to the shape and the structure in which they are present in the nanocomposite and in the polymer part. The structure in the nanocomposites can be strongly influenced by the processing type and the chosen processing route.

This talk presents the fundamentals of a successful use of nanoparticles in polymers. Furthermore the achievable shapes and structures in the nanocomposites are presented as well as the possibilities to influence them.

Graphene, a monolayer of carbon atoms arranged in a two dimensional lattice, has attracted great attention in recent years due to its extraordinary properties and potential applications. One obvious application of graphene is in the field of nanocomposites. In this work, the graphene platelets are used as the reinforcement agent in epoxy matrix in two different ratios. Raman spectroscopy and Scanning electron microscopy (SEM) are used to characterize the graphene. The mechanical properties of epoxy and graphene-epoxy nanocomposites are determined using tensile tests and dynamic mechanical analysis (DMA) in three point bending mode.

Development of tailor-made polymeric materials has been intensively studied in the last time as the new applications require tuning of different material properties to get specific property profile of the final product. Using micro-scaled fillers like calcium carbonate, glass fibers, cost-effective composites with improved mechanical properties (higher tensile strength, stiffness) can be obtained. However, in conventional composite systems, due to typically high concentration of the filler and large particle size, respectively, some material properties (in particular impact strength) are deteriorated because of low interfacial adhesion between the matrix and dispersed phase. On the other hand, nano-scaled fillers like layered silicates or carbon nanotubes can enhance the polymer matrix by including of specific functionalities which provides higher interfacial adhesion between filler and polymer matrix.

In this work, selected micro-scaled fillers (e.g. glass fibers, basalt fibers) as well as nanofillers (commercial layered silicates as well as layered silicates with new surface treatment) have been incorporated into polymer matrix. Their effect on rheology, structure and application properties of the final composite system has been investigated. In some cases, a G’ secondary plateau characteristic for “rubber-like” behavior has been observed. This indicates that a 3D-physical network of filler particles in polymer matrix can be achieved with both nano- as well as micro-scaled fillers depending on polymer/filler chemistry as well as processing conditions. Comparing to conventional polymer composites, preparation of nanocomposites is often associated with specific reaction mechanisms, which are also discussed in this contribution.
Thermoplastic elastomers reinforced with poly(tetrafluoroethylene) nanofibers
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Promising alternative to conventionally filled polymers with ready-made nanofibers is formation of all-polymer nanocomposites with nanofibrillar inclusions directly by compounding. Poly(tetrafluoroethylene) (PTFE) nanofibers can be generated in situ by shearing of crystalline PTFE inclusions during compounding with another molten polymer, in the form of entangled network, which in turn drastically changes rheological behavior of the materials. Entangled network of PTFE nanofibers induces strain-hardening effect in polymers, which exhibit no strain-hardening themselves and improves melt strength of studied polymers. We present here that approach to improve the rheological behavior and other selected properties of thermoplastic elastomers by incorporation of entangled network of PTFE nanofibers. Presence of PTFE nanofibers, dispersed in the form of entangled network in elastomeric matrix, improves both rheological properties (extensional viscosity, melt strength) and mechanical properties (elastic modulus, yield stress, tensile strength) of studied materials.

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Fabrication of Advanced Nanocomposites at Significantly Low loading of Modified reduced Graphene Oxide
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Graphene has recently attracted remarkable attention around the globe due to its incredible electrical, thermal and mechanical properties. As a result of such unique properties, graphene based materials become the centre of current research work. However, in the area of Polymer nanocomposites, development of advanced graphene based polymer nanocomposites still confronts with lot of challenges. This is due to the high surface area and strong van der Waals force between the graphene nano-sheets which assist them to re-aggregate and stack and thus inhibit to exert its actual potential in polymer nanocomposites. In the present study, we have demonstrated a chemical modification process to fabricate functionalized reduced graphene oxide with reactive amine groups which can tremendously improve the mechanical, dynamic mechanical and thermal properties of the Nylon composites. Addition of only 0.25 and 0.35 wt % of modified GO showed 40 % and 50 % improvement in the tensile strength along with 65% and 71% in the Young’s modulus, respectively as compared to the neat polymer. The dynamic mechanical analysis (DMA) test showed ~ 22% and 28% increment in the storage modulus of the nanocomposites with inclusion of the same amount. Moreover, the 0.35 wt % modified GO-nanocomposites exhibited significantly high thermal stability as compared to the neat polymer (~ 12 °C increment).
Session H1: Functional Polymers

Invited talk:

**Filler content on the dynamic behavior of recycled polypropylene-based composite**

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The impacts of reprocessing and filler content on the properties of polypropylene (PP) based composite were investigated in our previous studies. In these, we characterized the evolution of rheological, thermal, chemical, physical and quasi-static mechanical properties of materials with reprocessing cycles by a multiphysical approach. We found that the molecular weight of the recycled materials slightly decreased after six reprocessing passes. The decrease of molecular weight of materials can be attributed to the chain scissions mechanism. This decreased molecular weight resulted in a decreasing viscosity of the materials. However, the reduction of the length of PP chains increased their mobility and hence, facilitated their rearrangement during the crystallization. This higher mobility caused a small increase of crystallinity of the PP. In addition, due to the presence of the anti-oxidant in neat PP, no significant oxidation of the recycled materials was observed.

To the best of our knowledge, the influence of reprocessing and filler content on the dynamic behavior of PP-based composites is less investigated. In automotive industry, PP-based composites are generally used in the manufacturing of bumpers [3-7]. In such a case, a detailed study of high strain rate and temperature sensitivities of recycled PP-based composites is essential since the bumpers undergo compressive impact loading in a wide range of temperatures. In present work, to simulate the mechanical recycling, the composites were extruded and re-extruded after a mechanical grinding of the extrudates for up to six times. We studied the recycling number 0, 3 and 6. The considered fillers consisted of ethylene octane copolymer (EOC) and talc. The investigated filler content was 0 wt. %, 10 wt. % and 20 wt. %. The dynamic behavior was investigated by using split Hopkinson pressure bars, at different strain rates and at different temperatures.

**Clathrates of syndiotactic polystyrene (s-PS) and sulfonated s-PS with different guest molecules**

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s-PS forms different co-crystals (clathrates) with several guest molecules and so far different advanced materials[1] have been produced starting from s-PS co-crystalline films. Particularly, sulfonated s-PS (s-SPS) can be used as proton exchange membrane for fuel cells. The morphology of s-PS clathrates with guest molecules of different size and shape and the structural behaviour of s-SPS upon hydration can be more thoroughly understood by combining X-ray scattering and FT-IR with SANS[2]. Exploiting the neutron contrast variation between different hydrogenated and deuterated components of s-PS and s-SPS clathrates, additional and unique information about the distribution of guest molecules in the crystalline and amorphous region and about the hydrated domains can be obtained. A SANS investigation of morphological changes in s-PS films from their crystallization with guest molecules followed by subsequent sulfonation and hydration will be presented.

Internal Dynamics of sensitive polymer microgels
Maccarrone, Simona (Forschungszentrum Jülich GmbH, Garching, GER)
Holderer, Olaf (Forschungszentrum Jülich GmbH, Garching, GER)
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Microgels are nanosized, cross-linked polymer particles swollen by solvent, and the degree of swelling can be controlled by temperature, pH, ionic strength, solvent. The sensitivity of the swelling behavior to external stimuli makes microgels ideal candidates in a broad range of application such as drug delivery, separation and purification technologies and so on.

We present Neutron Spin Echo results about the internal dynamics of microgel particles at various degree of swelling. The dynamical behaviour is then comprehensively described within the theory of semidilute polymers in solutions. For partially collapsed microgels, Zimm segmental dynamics can be detected with enhanced apparent viscosity. The swollen microgel particles have a faster internal dynamics described by Zimm-like relaxations with a slightly higher viscosity than the solvent mixture and an additional diffusive contribution from the cross-linkers. The cross-over to a collective diffusive motion is found for the smallest q-values only for the collapsed microgels.

NOVEL WATER-SOLUBLE REGULAR POLYIMIDE BRUSHES AS NANOCONTAINERS FOR CYANOPORPHIRAZINE AGENTS OF PHOTODYNAMIC THERANOSTICS
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Meleshko, Tamara (Institute of Macromolecular Compounds, RAS, St. Petersburg, RUS)
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Klapshina, Larisa (Institute of Organometallic Chemistry, RAS, Nizhny Novgorod, RUS)
Balalaeva, Irina (Institute of Living Systems, NNSU, Nizhny Novgorod, RUS)
Douglas, William (CNRS UMR 5253, Universite Montpellier II, Montpellier, FRA)

An approach to the synthesis of new regular polyimide-graft-(polymethacrylic acid) brushes is elaborated, including 1) synthesis of multicenter polyimide macroinitiators, 2) controlled ATRP of tert-butylmethacrylate on the prepared macroinitiators, and 3) protonolysis of tert-butyl ester groups of side chains of thus obtained polyimide-graft-poly(tert-butylmethacrylate). Experimental conditions for attaining complete conversions of the first and the third stages of the process are determined by means of 1H NMR and FTIR-spectroscopy. Polymer products of the first and the second stages of the process, as well as poly(tert-butylmethacrylate) side chains cleaved from the polyimide-graft-poly(tert-butylmethacrylate) copolymers by complete decomposition of the polyimide backbone under alkaline hydrolysis conditions, are characterized by GPC. Kinetics of poly(tert-butylmethacrylate) chain growth on a polyimide macroinitiator under ATRP conditions is studied. The obtained results prove a controlled character of the ATRP process and regular structure of the synthesized graft-copolymers. A regular brush character of the synthesized polyimide-graft-(polymethacrylic acid) copolymers is proved by the data of TEM obtained for conjugates of these brushes with Yb(III)-cyanoporphirazine complexes.

Compared to other water-soluble polymers, e.g., polyethylene glycol, used for solubilization of hydrophobic molecules, the obtained polyimide-graft-(polymethacrylic acid) nanocontainers with cyanoporphirazines and their Yb(III)-complexes incorporated into the space between side chains of a molecular brush provide a much more efficient transport of the indicated photodynamic theranostics agents into tumor cells.

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**Session F1: Linkage between different length and time scales**

**Invited talk:**

Relation between macroscopic behaviour and local deformation mechanisms in semi-crystalline polymers

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Xiong, Bijin (INSA de LYON lab MATEIS, Villeurbanne, FRA)
Millot, Coraline (INSA de LYON lab MATEIS, Villeurbanne, FRA)
Chenal, Jean-Marc (INSA de LYON lab MATEIS, Villeurbanne, FRA)
Rochas, Cyrille (Cermav, Grenoble, FRA)
Vigier, Gérard (INSA de LYON lab MATEIS, Villeurbanne, FRA)

The mechanical behaviour of semi-crystalline polymer depends on the local properties and on the complex microstructure that transfers the stress from macroscopic scale to the local one. In situ SAXS and WAXS measurements allow obtaining new information concerning this transfer. It gives access to the changes of averaged local data such as intercrystalline long period or inter-atomic plane distance in the crystal during a tensile test. In this study, in-situ tensile test have been performed on several polyethylenes and few results on polyamide are also presented. In the pre-yield domain, SAXS measurements allow obtaining the local deformation that is linked with both the local modulus as well as the stress transfer. In situ WAXS measurements can be used to determine approximately the local stress which finally gives an estimation of the local modulus of the amorphous phase by combining these results with the SAXS data. These estimations have been found to be consistent with the initiation of cavitation.

**Polymeric flow in microcavities coated with nanocrystalline diamond**

Neto, Victor (Department of Mechanical Engineering, AVEIRO)

The increasing production demand of polymeric microparts has been leading microinjection moulding to a continuous growth. Nonetheless, downscaling the macro-injection process requires a thoughtful comprehension of the physics underlying microinjection moulding. High surface-to-volume ratios in microparts require higher injection pressure and injection speed to prevent premature solidification. In these conditions, the interaction between the melt and mould channels are critical, due to the increase of friction, wear, or even adhesion, leading to a deterioration of the quality of the micromouldings. Advanced moulding systems, making use of proper instrumentation and surface engineering, mas assist the microinjection moulding to attain better performance. In this presentation, the result of the polymeric flow in microcavities coated with nanocrystalline diamond is investigated. To better understand the polymeric flow in the microcavities, a grid of optical fibre Bragg grating (FBG) based sensors are used to measure online the temperature profile during the injection process.

**Molecular origin of the β relaxation in PB and SBR**

Souillard, chloé (7 avenue Jean capelle, VILLEURBANNE, FRA)

The most used elastomers for car tire fabrication are styrene-co-butadiene copolymers (SBR). Relaxation phenomena are of the main importance, as they result into energy dissipation within the rubber. Thus, it is essential to understand the origin of relaxations in SBR and we focus here on the β relaxation. We studied SBR and PB with different 1.2PB, 1.4PB and styrene ratio. Most of previous works were performed using dielectric spectroscopy (at high frequency) but because 1.4 trans groups are not polar, it is difficult to determine their role. Comparison between mechanical spectroscopy (DMA) and dielectric spectroscopy allows us to attribute the low temperature contribution of β relaxation to 1.4 groups motions and its high temperature contribution to 1.2 groups. Moreover, our data show that styrene acts as a solvent changing the amplitude of this secondary relaxation. Fitting data using two Havriliak-Negami functions permits to correlate percentages of 1.4 or 1.2 and the shape of the β relaxation SBR.

**Insights into craze growth in polymers through mesoscale simulations**

Venkatesan, Sudarkodi (Department of Mechanical Engineering, Kanpur, IND)
Basu, Sumit (Department of Mechanical Engineering, Kanpur, IND)

Crazes are deformation characteristics displayed typically by polymers. Mesoscale simulations of glassy amorphous polymers have been carried out using coarse grained molecular samples to study the phenomenon of craze growth. Coarse graining procedure involved a super coarse graining on an united atom model. The mechanism of craze growth is investigated. The nature of fibril formation and the role of the entanglement structure is analysed. The observations throw light on the complex physics of the process. The results from united atom model and the mesoscale model lead us into new insights into the phenomenon of craze growth observed at macroscale.
Abstracts: Poster presentations
1. Composites from Agricultural Animal Waste
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Luckham, Paul (Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, GBR)
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The demand of milk, meat and other livestock products increases every year due to population growth, urbanisation and increasing income in developing countries. This results in a significant increase in animal waste products and feed residues. In order to promote environmental sustainability, new uses of livestock wastes are pursued. Ruminants, such as cattle, sheep and goats, only convert about 50% of the consumed feed to energy and the remains are excreted. Therefore, the waste of these animals contains still a significant amount of fibrous materials originating from their feed. This study identifies the amount of usable fibres (cellulose, hemicellulose and lignin), proteins and nutrients existing in goat excrements. Parts, which are useful fertilisers, were separated from the waste while the remaining fibres were further reduced and refined to pulp suitable for papermaking. This study also investigates the production of animal waste polymer composites which follow closely to the papermaking process. The thermal and mechanical properties of the produced animal waste polymer composites will also be discussed.

2. Ratcheting Behavior of Ultra High Molecular Weight Polyethylene (UHMWPE)
Çolak, Özgen Ümit (Yıldız Teknik Üniversitesi, Basıktas, Istanbul, TUR)
Asmaz, Kerem (YTÜ, Basıktas, Istanbul, TUR)

In this work, biaxial ratcheting behavior of ultra-high molecular weight polyethylene (UHMWPE) has investigated experimentally. Strain symmetric axial cyclic tests with constant pressure have been performed on pressurized thin-walled tube specimens of UHMWPE.

Afterwards, a modeling study is performed using the viscoplasticity theory based on overstress (VBO) with the modified Chaboche kinematic hardening rule to improve the circumferential strain ratcheting response of UHMWPE. The proposed changes are designed to account for kinematic hardening and tangent modulus effects relevant to the modeling of ratcheting behavior of UHMWPE. The experimental and simulation results are compared to demonstrate the current state of the simulations.

3. Parameters affecting localization of multi-walled carbon nanotubes in PC/SAN blends
Bijani, Hasti (Dep. of Polymer Eng -amirkabir university of tech., tehran, IRN)
NAZOCKDAST, HOSSEIN (Dep. of Polymer Eng -amirkabir university of tech., tehran, IRN)

The main objective of the present work is to study the role of thermodynamic and kinetic parameter groups as two competitive driving forces in determining CNTs localization in PC/SAN blend system. The blend nanocomposites with the same MWNT content (1%wt) but varying in the PC/SAN blend ratios (20/80, 60/40, 80/20 wt.) all prepared by the melt mixing were considered. A combination of rheological technique, thermal analysis and electron microscopy were employed. It was shown that, due to close thermodynamically affinity of CNT to the blend’s constituents the kinetic parameters could play much stronger role in localization of CNT compared to thermodynamic parameters. Interestingly, the extent of CNT localization in the blend components were found to be significantly affected by the morphology of the blend samples (matrix-disperse and co-continuous) i.e. The extent of localization was more significant in the samples with matrix-disperse morphology compared to co-continuous.
4. **SEETechnology, a bridge between universities/research institutes and companies**  
*Coseri, Sergiu (Petru Poni Institute of Macromolecular Chemistry, Iasi, ROU)*

The SEETechnology project responds to three main challenges:

- SMEs in the South Eastern Europe are especially weak in terms of innovation and access to innovation
- There is a mismatch between the supply and demand of research products at local/regional/transnational level
- University conducted science park lack resources and knowledge and do not work closely with SMEs

In this presentation we will present some of the actions and achievements of the SEETechnology project directed toward improving the market potential, access to market potential of SMEs, and improve access of SMEs to research ideas and products and to services offered by universities and research institutes.

**Acknowledgement**

I would like to thank SEETechnology project, SEE/D/0224/1.2/X for the funding the participation at 6th International Conference of Polymer Behaviour.

5. **Matrix-Free Natural Fibre Composites**

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*Koon-Yang, Lee (Department of Chemical Engineering, University College London, Torrington Place, London, GBR)*
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Sustainable natural fibre composites are growing in demand due to the fact that they can be reused and/or recycled or be disposed of through composting (in the case of green natural fibre composites) or burned for energy recovery. One of the main problems with natural fibre composites is the adhesion between the fibres and the matrix, which is thought to be due to the fact that natural fibres are composites themselves (the cellulose fibrils are embedded in the lignin matrix) and, therefore, have different parallel and transverse linear thermal coefficients of expansion (LTCE). The difference in the LTCE makes the fibres shrink differently from the matrix, and therefore, the stress transfer is affected within the composite. These issues could be addressed by using only cellulosic materials within the composite. By doing so, the adhesion problem between the fibre and the matrix is considerably reduced.

Natural fibre composites without a matrix are produced by combining natural fibres with pulp, nanofibrillated cellulose or bacterial cellulose. Cellulosic materials of vastly different sizes are combined to utilize the space within the macro fibres and thus reduce the porosity of the composites and enhance their mechanical properties. These composites are manufactured in a simple way based on paper making processes. Cellulose hornification allows the formation of a cellulosic network which enables stress transfer between the fibres and holds them together and therefore a matrix is not required. The novelty of the matrix-free natural fibre composites lies in the fact that no dissolution and cellulose regeneration is needed and therefore no chemical waste is produced, which is one of the drawbacks of all-cellulose composites. The properties of the matrix-free natural fibre composites are discussed.

6. **Impact behavior of semi-crystalline polymers: experimental characterization and FEM simulations**

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*Torres, Juan Pablo (University of Mar del Plata, Mar del Plata, ARG)*
*Machado, Martín (Johannes Kepler University Linz, Linz, AUT)*
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In the past decades, there has been a continuously growing presence of thermoplastic polymers in highly demanding engineering applications in the aeronautic, automotive, electronics and biomedical fields. In addition, there is a special interest in accurately predicting how such polymeric components will perform under high impact conditions in safety-critical applications such as car-crashes, accidental drop, ballistic and blast loading. The objective of this work is to develop an overall experimental characterization programme and a FEM modeling routine that will allow for the accurate prediction of the high strain-rate mechanical response of two semi-crystalline polymers: HDPE (high density polyethylene) and PP (polypropylene). Tensile impact (uniaxial) tests were carried out together with optical 3D strain measurements and digital correlation image (DIC) processing. In addition, temperature evolution of the samples was assessed using infrared thermal measurements. The experimental data was used for the calibration on an advanced 3D constitutive model using an inverse method calibration technique. The model prediction capability was then validated performing biaxial falling-weight impact tests and contrasting the experimental results with finite element simulation predictions.
7. **ON THE RELATIONSHIP BETWEEN PHYSICAL CROSSLINKING DENSITY AND FRACTURE TOUGHNESS IN GELATIN GELS**

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Frontini, Patricia M (INTEMA, Universidad Nacional de Mar del Plata - CONICET, Mar del Plata, ARG)

Gelatin forms physical gels in which the crosslinking points (junction zones) are created by secondary ordered structures similar to the triple-helix arrangements in native collagen. It is well documented that stiffness is dominated by triple-helix concentration. This work explores whether fracture toughness is also governed by triple-helix concentration. Several gel samples differing in gelatin concentration, gelatin source (bovine or porcine) and solvent (water/water-glycerol/water-sorbitol) are studied. Fracture toughness is determined by the Wire Cutting method at 100mm/min and the triple-helix concentration through the number-average molecular weight between crosslinking points. Higher fracture toughness values are obtained by increasing gelatin concentration, adding glycerol and sorbitol as co-solvents and using porcine rather than bovine gelatin. All these observations are consistent with the development of a more physically crosslinked structure in the gels. Our results identify the relevance of triple helix-concentration as key parameter controlling fracture toughness of gelatin gels.

8. **Annealing of PP-R pipes: Influence on Crystallinity and Impact Performance**

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Wenzel, Mirko (SKZ - KFE gGmbH, Würzburg, GER)
Bastian, Martin (SKZ - KFE gGmbH, Würzburg, GER)
Schuster, Tobias (Fraunhofer LBF, Darmstadt, GER)
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Annealing of PP-R pipes lead to a significantly improved impact performance. This effect can be detected for unnucleated as well as for α- or β-nucleated PP-R. While morphological analysis only show a slight increase in crystallinity due to post-crystallisation, IR-mappings of the impact area reveal an improved homogeneity concerning transition and distribution of crystallinity. For this purpose the 998 cm⁻¹/974 cm⁻¹ ratio can be evaluated. The failure rate in impact tests with a constant drop height of 2.0 m and a falling weight of 1.00 kg performed on commercial β-nucleated PP-R pipes show that even temperatures in the range of typical application conditions e.g. in the field of hot water lead to an improvement of the mechanical behaviour after a few days. A discussion whether samples should be annealed before impact testing could be useful with regard to application conditions - the current practice provides additional safety.

9. **Infrared Microscopy: A Tool for Quantification of Oriented Additives**

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The rate of crystallization and the size of the resulting crystals have a strong impact on the mechanical and optical properties of plastic components, especially in polypropylene (PP). Therefore nucleating agents, such as the β-nucleating agent N,N'-dicyclohexyl-naphthalene-2,6-dicarboxamide (NJSTAR®NU-100) are used to control the crystallization process. The direction of crystallite growth is highly dependent on the orientation of the nucleating agent, which is forming fine needles in the polymer matrix. NU-100 exhibits an intense IR-absorption at 1628 cm⁻¹, which can be assigned to its two amide groups. In contrast to the band at 1747 cm⁻¹, caused by the carbonyl group of an antioxidant, the band at 1628 cm⁻¹ shows strong dichroism. The dichroic effect can be used to calculate the three dimensional orientation of nucleating agents and polymer chains of the processed material from IR-spectroscopic measurements.
10. Cross-linking effects in atomistic simulations of nanoparticle-polymer interfaces

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Lyulin, Alexey V. (Technische Universiteit Eindhoven, Eindhoven)

Adding fillers to polymer-matrix nanocomposites may enhance the resulting nanocomposite mechanical properties. However, understanding of how chemical constitution of their components influence macroscopic (structure and mechanical) properties of these components remains one of the main challenges in tire industry.

We carried out molecular-dynamics computer simulations of a crosslinked (1,4) cis-polyisoprene (PI) - silica films samples with realistic coupling and covering agents in order to quantify the role of molecular features on segmental dynamics. After a thorough equilibration we studied the PI film stratified structure (chain size, chain shape, local segmental ordering and density), polymer segmental dynamics (bond vector relaxation) and performed dynamical analysis under deformation for different filled systems varying the degree of cross-linking and thickness of the films. We considered the results in terms of “glassy” layers, and focused on stiffness loss, in particular on atomistic nature of Payne effect.

11. Hyaluronic acid gel characterization using classical rheology and passive microrheology technique

Hnyluchová, Zuzana (Brno University of Technology, Brno, CZE)

Passive microrheology is a novel approach determining viscoelastic properties of soft materials based on the Brownian motion of inserted probes. From the particle movement one can calculate viscosity in case of Newtonian fluids and viscoelastic parameters (G’, G”) in case of non-Newtonian fluids. In our work microrheology was utilized to investigate hyaluronic acid gels formed mixing hyaluronic acid solution with cetyltrimethylammonium bromide (CTAB). Four gels of different concentrations of hyaluronic acid and CTAB were prepared. Their microstructure was characterized via video based particle tracking microrheology using three sizes of inserted particles – 0.1, 0.5, and 1 um to study it’s microstructure. All data were compared to classical rheology results providing informations about the sample macrostructure. Each particle size shows different results corresponding to local microenvironment of the particle in response to the mesh size of the polymer structure and doesn’t respond to the classical rheology results characterizing macrostructure of the sample.

12. Superabsorbent Polymers for Agricultural Usage

Kolajová, Romana (Faculty of Chemistry, Brno, CZE)

The aim of our research is to develop agriculture preparations based on superabsorbent polymer which can be used as a delivery vehicle for the controlled-extended release of different types of fertilizers. A six series of polyacrylic acid gel derivatives has been prepared and NPK fertilizer was added as a main active ingredient. They differed in a content of lignohumate addition, acrylamide addition and in initial dosage of NPK. The mechanisms of phosphorus and potassium release from hydrogel carriers were observed together with their swelling properties. Both experiments were carried out together in an environment of demineralized water for a period of five days. Concentration of K+ ions in surrounding water was determined by potentiometric measurements every 24 hours. Total content of potassium and phosphorus were determined by ICP – OES technology every day as well.

13. Experimental and theoretical investigation of anisotropy of the mechanical properties of reinforced elastomeric nanocomposites

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The study of the mechanical properties of anisotropic elastomeric composites reinforced by nanoparticles of different types indicates that they differ in both the strength properties and the degree of softening. The samples were subjected to uniaxial loading acting in two orthogonally related directions. The anisotropic properties of composites appeared most vividly in the samples exhibiting a high degree of hysteresis in the first cycles of deformation. The results of numerical simulation obtained for the loaded fragment of a filled elastomer show that such difference becomes possible because of the elastoplastic behavior of an interfacial layer in which residual strains are accumulated differently under loading that acts in different directions. The study is supported by the RFBR (grants 13-01-96016-a and 14-08-96013-a) and the Ministry of Education of Perm Krai (agreement C-26/627).
14. Partitioning of salt between polyelectrolyte gels and solution
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Kosovan, Peter (Department of Physical and Macromolecular Chemistry, Prague, CZE)
Holm, Christian (Institute for Computational Physics, Stuttgart, GER)

In this work we employed grandcanonical hybrid molecular dynamics / Monte Carlo (MC/MD) simulations to study swelling equilibrium of polyelectrolyte gels in salt solution. We present simulation results at various polymer parameters (degree of charging, crosslinking density) and at various salt concentrations in the bulk solution. We obtained qualitative agreement with simple Donnan theory for the osmotic pressure of ions, combined with Gaussian model for the network elasticity. A quantitative comparison reveals systematic deviations especially at high charge fractions. They hint towards further improvements of the theoretical model by inclusion of inhomogeneous distribution of ions in the gel, with their preferential location near the polymer. In an augmented model, we account for this inhomogeneity, which leads to an improved agreement between the theory and the simulation data.

15. STUDY OF NANOPARTICLES FORMED BY NEGATIVELY CHARGED HYALURONAN AND CATIONIC SURFACTANTS USING LIGHT SCATTERING TECHNIQUES
Krutisova, Tereza (Brno University of Technology, Faculty of Chemistry, Brno, CZE)

Negatively charged hyaluronan binds to cationic surfactant via electrostatic interactions which result in self-assembly nanoparticles formation. These particles have a core-shell like structure and can be used in targeted drug delivery of hydrophobic active substances. The aim of our study was to prepare and study these systems using dynamic light scattering methods. Titration experiments (size distribution and zeta potential measurements) were utilized to explore the formation of aggregates. Hyaluronan or surfactant was used as titrant for comparison of two preparation methods of these systems. Effect of molecular weight and concentration of hyaluronan were investigated. Aggregates formation is influenced by preparation of systems. Different types of particles are formed if hyaluronan is added to surfactant solution or vice versa. If hyaluronan have a role of titrant, final particles are smaller than in the case of surfactant as titrant and can be more suitable for drug delivery applications.

16. Photoconductivity of semiconducting powders covered by polyaniline
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Light induced conductivity increase of a composite filling a test surface between two parallel golden electrodes has been studied. A group of hydrothermally prepared semiconducting binary oxides - along with reference materials: CdS and P25 TiO2 - served as base material of the composites. Spin coating has been used to deposit base on glass with previously deposited electrodes. Later polymer in solution has been deposited and dried to form composite connecting electrodes.

Experiment was preformed with high power sources of light varying from near UV to close IR. Effects of short light impulses and continuous illumination have been registered. Keithley 4200-SCS served as measurement and data collection tool.

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17. Study of polymer-based nanocomposites with intermetallic (Co-Sn, Ni-Sn) nanoparticles for anodes in lithium ion batteries
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Markova, Ivania (University of Chemical Technology and Metallurgy, Sofia, BGR)

Intermetallic (Ni-Sn, Co-Sn) nanoparticles are synthesized through a borohydride reduction with NaBH₄ in a mixture of aqueous solutions of the corresponding chloride salts at mass ratios Ni:Sn = 45:55 and Co:Sn = 35:65. The ratios are chosen in accordance with the Ni-Sn, Co-Sn binary systems phase diagrams. Subsequently, carbon polymer-based nanocomposites are obtained. A "template" technique which involves reductive precipitation of intermetallic nanoparticles on a support (fluorinated graphite - CF, beta cyclodextrin hydrate) is used. The content of the polymer in the obtained nanocomposites varies between the samples. The reductive precipitation is carried out at room temperature and atmospheric pressure. Samples are studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) analysis. The samples are electrochemically tested as electrode materials in Li-ion battery in argon filled glove box. A comparison between their characteristics (specific capacity, cyclability) is made. This study was conducted with a financial help from Project BG051PO001-3.3.06-0038 funded by OP Human Resources Development 2007-2013 of EU Structural Funds.

18. Glassy dynamics and multiscale behaviour in polyurea elastomers
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Fally, Martin (University of Vienna, Wien, AUT)
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Schranz, Wilfried (University of Vienna, Wien, AUT)

The elastomere polyurea exhibits a phase separated mesoscopic structure with hard nanodomains embedded in a soft (compliant) matrix. This system shows two glass transitions at T_{g1}<T_{g2}, which are related to the freezing of motion of molecular segments in the soft domains (usual polymer glass transition at T_{g1}) and to regions of restricted mobility near the hard nanodomains at T_{g2}, respectively. We present detailed dynamic mechanical analysis (DMA) measurements [1] for polyureas with different molecular weight of the polyetheramines (soft domains), i.e. with varying segmental chain lengths l_ and volume fractions phi_x of the hard domains. It is found, that T_{g1} increases drastically with increasing phi_x, whereas T_{g2} remains almost constant. Around phi_x=0.25 the two curves cross, i.e. T_{g1}=T_{g2}, which corresponds to the percolation threshold of the hard nanodomains. It means, that below phi_{x_c} the system consists of hard spheres embedded in a soft matrix and above phi_{x_c} vice versa. Adding MoS₂ - nanotubes into the matrix leads to a reinforcement of polyureas and an increase of T_{g1}, whereas T_{g2} remains unaffected [2].

In conclusion, the properties (i.e. glass transition temperature, hardness, Young’s modulus, etc.) of polyurea networks can be easily tuned by varying their segmental chain length’s l_ and/or by adding inorganic nanoparticles.

Acknowledgements

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19. Toughening Poly (ethylene terephthalate) (PET) by modified Polypropylene (PP) with Glycidyl Methacrylate (GMA) Through Reactive Mixing

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Composites are useful for upper properties than root elements. Polyethylene terephthalate (PET) is more useful if its mechanical properties can be improved to higher toughness. Blends of PET and modified Polypropylene (PP) with Glycidyl Methacrylate (GMA) were prepared through reactive mixing. Afterward, effects of dicumylperoxide (DCP) as grafting reaction initiator, grafting monomer concentration and presence of styrene as co-monomer were examined on grafting. Morphological and mechanical properties of blends and extent of compatibilization were studied using Scanning Electron Microscopy (SEM), Dynamical Mechanical Analysis (DMA), tensile and impact tests. Impact strength of blends is compared with virgin and waste PET. Optimum grafting results were obtained at the GMA concentration of 5 phr and DCP concentration of 0.5 phr and [St]/[GMA]=1.5. Also, the best blend composition was achieved at 20 phr of PP and [St]/[GMA]=1.5.

Acknowledgment. Technical help from Polymer engineering group, chemical engineering department of university of Tehran is gratefully acknowledged.

20. Liquid-Crystalline Elastomer Micropillar Array for Haptic Actuation

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A new LCE micropillar array with two-dimensional prolate polydomain conformation of the polymer backbone and the mesogens has been successfully synthesized. This new concept of the orientation of silicone-based LCE systems by uniaxial compression (biaxial orientation) allows for the obtaining of micropushers, with actuation temperatures around 55 ºC.

The resulting LCE micropillars show an expansion factor of $e_z = 21\%$ along the axial direction and a contraction factor of $e_r = 15\%$ in the radial direction upon isotropization of the sample. These changes in the dimensions, together with the actuation force of $F = 20 \text{ mN (s_t = 5.6 kPa)}$, and the possibility of obtaining different shapes on demand – besides the common LCE strip –, make the LCE materials very suitable candidates for haptic applications, as well as for their integration in Microsystem Technology, in the development of complex devices through a batch process.

21. Dynamics of loop closure in a chemically active polymer

SARKAR, DEBARATI (INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH, BHOPAL, IND)

Looping dynamics of polymer in which two monomers along the chain approach each other within a small distance, is a very active research topics because of some real life examples like the cyclization in DNA which is important in gene expression, RNA and protein folding etc. Large amount of experimental as well as theoretical literature is available for the closure time calculations in sticky ended polymers. However, not much has been done so far for a more general situation of polymer with long-range interactions. The knowledge of chain closure dynamics in presence of long-range interaction may provide some hint about the factors behind the protein folding. In our work we investigate the loop closure dynamics of a chemically active polymer having long-range attractive interaction between two ends. The origin of the attractive interaction in our case is diffusiophoretic in nature, which is due to the chemical activity on one part of the polymer. We have investigated the loop formation in both flexible and semi-flexible polymer with the end, which attract each other due to diffusiophoretic forces. We employ the hybrid MD-MPCD model to study the polymer dynamics.
22. Study on Crystallization Behavior of Polypropylene/Ethylene Octene Copolymer Blends in Presence of Nanoclay
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The aim of the present work was to study the Effect of EOC and nanoclay on crystallization of PP matrix in PP/EOC blends. The blends and hybrid samples were compounded by using an internal mixer. The microstructure characterizations of the melt compounded samples were performed by using Rheology in combination with DSC and POM. The isothermal crystallization results showed presence of EOC in PP matrix decreased crystallization rate and also decreased spherulites number based on POM results. The addition of nanoclay was found to have an increasing effect on crystallization rate at low concentration and decreasing effect at high concentration in PP80/EOC20 blend that this corresponding to rheological peculation. But nanoclay in PP50/EOC50 blend was increased crystallization rate in all of the concentration; the results which related to effect of nanoclay on morphology beside nanoclay nucleation at low concentration and 3D physical network formation at high concentration of nanoclay.

23. Stability of humic acids in aqueous solutions
Velníková, Katerina (Purkynova, Brno, CZE)

The aim of this study has been to define stability of humic acids (HA) in aqueous solutions. Three concentration series in different mediums were used to study HA: NaOH and NaCl (prepared either by neutralization of NaOH by HCl or direct dissolution of NaCl solution). Several analytical methods have been used to characterize HA: density measurement with oscillatory U-tube, high resonance ultrasonic spectroscopy and dynamic light scattering.

24. High-pressure crystallization in various semicrystalline polymers and compounds
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Polt, Gerald (Physik Nanostrukturierter Materialien, AUT)
Wilhelm, Harald (LKT, Wien, AUT)
Spieckermann, Florian (Physik Nanostrukturierter Materialien, AUT)
Zehetbauer, Michael (Physik Nanostrukturierter Materialien, Wien, AUT)

In this work, different polymer systems (PP-GF, PB, PEEK, PEEK-CF, PPS-CF) were crystallized under high pressure in order to find out whether and which new phases are going to form. The resulting structures were analyzed by means of DSC, XRD, and also of compression tests for mechanical characterization. For realization of high pressure structures, a crystallisation device equipped with an in-situ heating system was set up for pressures till 1000 MPa. For the actual crystallization experiments, various pressures up to 500 MPa have been applied within a temperature range of 95 – 300°C. Various crystallinities could be reached with all temperatures, provided the crystallization time was chosen properly.

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H-shaped polymers in dilute solution were studied by dissipative particle dynamics (DPD). Simulations of homopolymers with the same backbone length and several combinations of arm lengths in a good solvent were performed to study the effect of architecture and total chain length on the hydrodynamic (relaxation time, diffusion coefficient, viscosity) and conformational behavior (gyration radius, segment densities from the mass center). The contraction factors g (ratio of squared gyration radius of H-shaped and linear polymer with the same total length) and g’ (the ratio of intrinsic viscosities), which are important for chromatographic separation of mixture of samples differing in architecture and length dispersity, were calculated.
26. Self-assembly Behavior of PLA-b-PAAb-b-PLA Triblock Copolymers and Their Applications in Sustainable-Controlled-Release Drug System

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Well-defined pH-sensitive amphiphilic triblock copolymers poly(D(L)-lactide)-b-poly(acrylic acid)-b-poly(D(L)-lactide) (PD(L)LA-b-PAA-b-PD(L)LA) were successfully synthesized and their self-assembly micelles were developed for oral delivery of hydrophobic drugs. The precursors poly(D(L)-lactide)-b-poly(tert-butyl acrylate)-b-poly(D(L)-lactide) (PD(L)LA-b-PtBA-b-PD(L)LA) were first synthesized by combination of SET-LRP and ROP techniques, and following hydrolysis provided the targeted amphiphilic copolymers PD(L)LA-b-PAA-b-PD(L)LA. The study showed that critical micelle concentration (CMC) values of the mixture of PD(L)LA-b-PAA-b-PD(L)LA and PLLA-b-PAA-b-PLLA is lower apparently than that of PD(L)LA-b-PAA-b-PD(L)LA or PLLA-b-PAA-b-PLLA, due to the effect of stereocomplex. Doxorubicin was selected as model drug and wrapped into the core of micelles via micro-emulsion method. The in-vitro release behavior of Doxorubicin from the micelles was pH-dependent, and the release showed a sustainable release behavior under high pH condition. All the results showed that the pH-sensitive PLA-b-PAA-b-PLA and its complex micelles can work as prospective candidates of oral drug delivery carrier for hydrophobic drugs with controlled release behavior.

27. DEGRADATION OF POLYETHYLENES CONTAINING OXO-ACCELERATING ADDITIVES

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Polyethylene (PE) has achieved a very important position in several sectors due to its low cost, high versatility, acceptable mechanical properties, high thermal stability and light-weight. Nevertheless, PE waste persists for many years after disposal causing a serious environmental problem. An approach to increase PE degradation is the addition of pro-oxidants.

In the present studies thermo-oxidative degradation was carried out by placing commercially available films in an oven maintained at 70°C for extended period of time and sampling the material at regular time intervals to monitor the degradation. The oxygen and water was delivered in the control manner to the oven chamber during the whole degradation process. The humidity was kept on the level of 50%.

Changes of PE at different stages of degradation were examined using scanning electron microscope (SEM), X-ray diffraction and scattering and Fourier transform infrared spectroscopy (FTIR). The extend of thermo-oxidative degradation of LDPE and HDPE in the presence of pro-oxidants was compared. The results indicate that the rate of degradation depends on the material density, i.e on the degree of crystallinity. Moreover, the crystal structure remains intact during the degradation process while the amorphous phase escapes from the material. It is concluded that oxo-degradation is concentrated on the amorphous phase because during solidification the pro-oxidants are rejected from crystals into amorphous material. The remnants after oxo-degradation are polyethylene isolated nanocrystals that are resistant to further degradation. Then they are released to the environment.

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A closed cell foam structure of unfilled polylactic acid (PLA), plasticized PLA/epoxidized soybean oil (ESO) and nanocomposite (PLA/ESO/organoclay) were successfully fabricated with the aim of achieving suitable properties while maintaining PLA biodegradability. For each formulation a fixed content of azodicarbonamide was used as a chemical foaming agent and the foamed samples were prepared by compression molding technique. The results of thermal analysis (DSC and DMA) and scanning electron microscopy (SEM) showed partial miscibility for the PLA/ESO foam sample. However, plasticized nanocomposite foam sample showed interfacial enhancement. X-ray diffraction analysis results revealed that intercalation of organoclay has been occurred in plasticized nanocomposite and foaming led to more increased interlayer spacing of organoclay as compared to unfoamed sample. SEM micrographs also showed organoclay acted as a nucleating agent and increased cell density and reduced cell size of plasticized PLA foam.

29. Plastic deformation by dislocations in HDPE by high-resolution nanoindentation creep experiments

Zare Ghomsheh, Mohammad (Fakultät für Physik, Universität Wien, Vienna, AUT)
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Polt, Gerald (Physik Nanostrukturierter Materialien, AUT)
Wilhelm, Harald (LKT, Wien, AUT)
Zehetbauer, Michael (Physik Nanostrukturierter Materialien, Wien, AUT)

There are only few investigations which provide a reliable proof of the participation of dislocations in the plastic deformation of semicrystalline polymers, i.e. (in-situ) deformation synchrotron by the X-Ray Line Profile Analysis.

A new method of investigation has been recently applied by Li and Ngan (Li, J. Ngan, A. H. W. Scripta Mater., 62 (2010) 488) showing the occurrence of dislocation avalanches during nanoindentation creep tests of polyethylene, and another one by Wilhelm (Wilhelm, H., PhD thesis, University of Vienna, in progress) performing high-resolution torsion creep tests in PE, exhibiting marked strain bursts being another evidence for the occurrence of dislocation avalanches during plastic deformation.

The experiments performed uniquely identify strain bursts to arise from avalanches of dislocations as the defects governing the plastic deformation during creep. This has been shown by nanoindentation creep studies done by the applicant on as-received PE samples where strain bursts were observed which were in the order of the lamella thickness. Studies with variations of the loading rate as well as force in nanoindentation creep test are presented. The influence on the occurrence and height of the strain bursts is presented and discussed.
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<td>Schmidgasse 18, 1080 Vienna</td>
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<tr>
<td>Heurigen Evening at Winery „10er Marie“, Sept. 25 at 18:30</td>
<td>Ottakringer Straße 222, 1160 Vienna</td>
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<tr>
<td>Globe Museum of the Austrian National Library, Sept. 26 at 15:00</td>
<td>Herrengasse 9, 1010 Vienna</td>
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- Faculty of Physics
  - Strudlhofgasse 4 / Boltzmanngasse 5, 1090 Vienna
Social Programme

Welcome Reception

The Welcome Reception will take place on Sunday, September 21, 2014, from 6 p.m. to 9 p.m. in the Berchtold Saal of Seminarhotel Strudlhof (entry via Strudlhofgasse 10, close to the conference site) where a registration desk will be prepared.

Heurigen Evening: Invitation by the Lord Mayor of City of Vienna

The conference dinner will be held as a Heurigen Evening (Wine of the Year) on September 25, 2014, at 18:30 at the Heurigen (Winery) 10er Marie (Ottakringer Straße 222, 1160 Vienna) by invitation of the Mayor of Vienna City.

Heuriger is the name given to Eastern-Austrian wine-taverns in which wine-growers serve the most recent year's wines and where the guests can experience Gemütlichkeit. These taverns need a special licence. Heurig means this year's (as an adjective) in Austrian German; thus, a Heuriger.

To access the site, a historic tramway will leave at 17:30 from the tramway station Bauernfeldplatz close to the conference site. After a guided tour around the famous Ringstrasse it will arrive at the Heurigen Restaurant at about 18:30.
**Cultural Events: Classical Concert / National Library**

On Tuesday, Sept. 23, 2014, evening we invite you to a Classical Music Concert in a traditional Viennese Concert Hall. On Friday, Sept. 26, 2014, afternoon we visit the Austrian National Library with the prestigious State Hall and the world unique Globe Museum. As the number of participants is limited for each of these events (80 for Concert, 50 for National Library), lists will be available at the conference site for signing-up (by first come - first choice principle).

Classical Music Concert with Duo Piano/Cello in Concert Hall of Bezirksmuseum Josefstadt (=District Museum of 8th Vienna district), 1080 Wien, Schmidgasse 18. Open doors: 18:30 h, Begin: 19:00 h (maximum 80 persons)

Globe Museum of the Austrian National Library, 15:00 h -16:30 h (maximum 50 persons)

For general touristic information on Vienna visit:  
http://www.wien.info/en
We cordially thank our sponsors of the ICP6 conference:

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