CPP 29: Polymerphysics I

Time: Thursday 9:30–12:45 Location: C 130

CPP 29.1 Thu 9:30 C 130

The physical resolution limit for replica molding — •Ovidiu D. Gordan[1], Bo N. J. Persson[2], Claudia M. Cesa[1], Dirk Mayer[3], Bernd Hoffmann[1], Sabine Dieluweit[1], and Rudolf Merkel[1] — [1]IBN-4, FZ-Jülich, 52425, Jülich, Germany — [2]IFF, FZ-Jülich, 52425, Jülich, Germany — [3]IBN-2, FZ-Jülich, 52425, Jülich, Germany

The key element of the fast evolution in the information technology is the ability to replicate patterns at increasingly lower scales. Besides photolithography, in the last decade, soft lithography[1] developed as a cheaper microfabrication alternative. This technique also allows to imprint micro-structures in polymers. Therefore today micropatterned elastomer surfaces are widely used in micro-fluidics[2] and micro-contact printing. Moreover, it enables emerging techniques in biotechnology, where very soft microstructures are employed, to mimic physiological conditions for living cells. However, up to now the general understanding of pattern preservation during the molding process was limited to the rule of thumb "the harder the better".

This study shows the analytical dependence of the molding fidelity of the elastomer stiffness, surface tensions and dimensions of the topographic features.

[1] Y. Xia and G. M. Whitesides, Annu. Rev. Mater. Sci. 28, 153 (1998).

[2] G. M. Whitesides, Nature 442, 368 (2006)

CPP 29.2 Thu 9:45 C 130

Changing the fracture properties of Polypropylene by blending — •Stefan Fischer[1], Dirk Doser[1], Tobias Diesner[2], Bernhard Rieger[2], and Othmar Marti[1] — [1]Institute of Experimental Physics, Ulm University, Albert-Einstein-Allee 11, 89069 Ulm, Germany — [2]Wacker-Lehrstuhl für makromolekulare Chemie, TU München, Lichtenbergstraße 4, 85747 Garching, Germany

Isotactic Polypropylene is among the most widely used plastics. Still it suffers from brittleness at ambient conditions. By enhancing it's fracture properties it could substitute other structures stabilizing solids while introducing it's own advantages like low weight and ductility to high ranges. Therefore in industrial polymers different additives are used to soften the polymer, reducing the brittleness. Still the polymers tend to break easily.

Our research has shown, that blending commercially available Polypropylene with high molecular one we can access new ranges in mechanical stability under certain conditions. The high molecular weight iPP seems to facilitate and propagate the reorientation of crystalline material while suppressing the evolution of cracks. This prevents the fracture at low elongations and allows high stresses and elongations until failure.

We will show the results of tensile tests, SAXS (Small Angle X-Ray Scattering), WAXS (Wide Angle X-Ray Scattering), DSC (Differential Scanning Calorimetry) and AFM (Atomic Force Microscopy) measurements. The effect of high molecular Polypropylene will be discussed, the problems still appearing at ambient conditions will be addressed.

CPP 29.3 Thu 10:00 C 130

On the creation of dielectric interphases in composites containing nano- and micro- particles. — •Béatrice Hallouet[1], Pauline Desclaux[1], Bernd Wetzel[2], Alois K. Schlarb[2], and Rolf Pelster[1] — [1]Fachrichtung 7.2 Experimentalphysik, Universität des Saarlandes Campus E 2.6 D-66 123 Saarbrücken Germany — [2]Institut für Verbundswerkstoffe GmbH (IVW) Erwin-Schrödinger-Straße, Geb. 58 D-67 663 Kaiserslautern Germany

We investigate composites consisting of magnetic particles (Fe3O4) in a polymer matrix (an epoxy resin) using broadband dielectric spectroscopy in a frequency range between 50 Hz and 1 GHz. Especially, we compare systems containing nano-particles (mean diameter between 20 and 30 nm) and micro-particles (mean diameter about 5 μm). Temperature-dependent measurements allow us to characterize a molecular relaxation of the matrix material, that is modified by the presence of the dispersed particles. For a model-free and non ambiguous analysis of these effects we use the spectral representation of Bergman [1]. We discuss the results in terms of modified interactions at the interfaces of the particles and check whether they depend on the microstructure of the composites and/or on the surface-to-volume ratio of the particles.

[1] B. Hallouet, B. Wetzel, and R. Pelster, "On the dielectric and magnetic properties of nanocomposites " , JNM in press.

CPP 29.4 Thu 10:15 C 130

Free volume in two untreated, presure-densified, and CO2 gas exposed polymers — Günter Dlubek[1], Jürgen Pionteck[2], •Muhammad Qasim Shaikh[3,4], Liane Häussler[2], Stefan Thränert[3], Essmat Sayd Hassan[3], and Reinhard Krause-Rehberg[3] — [1]ITA Institut für Innovative Technologien, Köthen/Halle, Wiesenring 4, D-06120 Lieskau (Halle/S.), Germany — [2]Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, D-01069 Dresden, Germany — [3]Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik, D-06099 Halle/S., Germany — [4]Technische Fakultät, Lehrstuhl für Materialverbunde, Christian-Albrecht Universität, Kaiser Str.2, D-24143, Kiel, Germany

Changes in the microstructure of the free volume and its temperature dependence in ethylene-norbornene copolymer and bisphenol-A polycarbonate due to densification under pressure and swelling with CO2 gas have been examined using positron annihilation lifetime spectroscopy (PALS) and were compared with pressure-volume-temperature (PVT) experiments from Dresden. From the PALS spectra analyzed with the new routine LT9.0 the size distribution of subnanometre holes and its mean and mean dispersion were calculated. Above Tg, the dispersion mirrors the thermal fluctuations in the free volume. PALS data show that the mean hole size and its dispersion in the glassy state is decreased due to densification and increased due to swelling.

CPP 29.5 Thu 10:30 C 130

Generalized mode-Grüneisen-parameters as a universal measure for the chemically induced glass transition in reactive systems — •Ulrich Müller[1], Martine Philipp[1], Jan Kristian Krüger[1], Roland Sanctuary[1], Wulff Possart[2], Bartosz Zielinski[1], Jörg Baller[1], Ravindrakumar Bactavatchalou[1], Patrick Alnot[3], and Christelle Vergnat[1] — [1]Université du Luxembourg, LPM, Campus Limpertsberg, L-1511 Luxembourg — [2]Universität des Saarlandes, ASPG, 66041 Saarbrücken — [3]Université Henri Poincaré - Nancy I, Nancy, France

A fundamental understanding of the glass transition is still lacking and so the controversy about the nature of the glass transition, being it a kinetic or intrinsic transition, is going on. The investigation of an isothermal cure of reactive systems by means of generalized mode-Grüneisen-parameters (gMGP) offers an alternative access to this problem. In contrast to the MGP known from solid state physics being sensitive to changes of elastic anharmonicity (3rd order elasticity), gMGP probe in addition 2nd order elasticity modified by structural changes during the curing process. Using epoxies and polyurethanes as model systems and combining Brillouin spectroscopy with high resolution refractometry the temporal evolution of the related gMGP indicate indeed the onset of chemical freezing. The comparison with caloric data suggests that there is a rough coincidence of the gGMP anomaly and the vanishing excess heat capacity with respect to the heat capacity of the glassy state.

break

CPP 29.6 Thu 11:00 C 130

MAO is a polymer! - Analysis of polymeric methylaluminoxane via small angle neutron scattering and neutron spin echo spectroscopy — Aizhen Niu[1], •Jörg Stellbrink[1], Jürgen Allgaier[1], Dieter Richter[1], Geoffrey W. Coates[2], and Lewis J. Fetters[2] — [1]IFF, Forschungszentrum Jülich, D-52425 Jülich — [2]Cornell University, Ithaca, New York 14853, USA

Since its discovery as a crucial co-catalyst in metallocene and post-metallocene olefin polymerizations methylaluminoxane (MAO) has retained commercial and academic status. In spite of continued interest the MAO structure remains until now ambiguously defined.

Here we present a combined SLS/DLS/SANS study on the structural properties of MAO in toluene solutions ($\phi/\phi^* \leq 0.6$). In dilute solution the main structure assayed is a linear polymer chain consisting of [-Al(CH$_3$)-O-] monomer units with a M$_w$ of 20 kg/mol, $R_g \approx 46\AA$ and a negative second virial coefficient A_2. The latter fortifies the recognized state of play that toluene is a poor MAO solvent. With increasing concentration SANS data reveal the (reversible) formation of interchain branching due to a change from 3 to 4 in the coordination number of the Al-atoms in the polymer backbone [1].

Moreover, preliminary analysis of neutron spin echo (NSE) experiments reveals a dynamical stiffness of MAO chains. Zimm dynamics typical for polymer solutions in a good solvents are crucially retarded indicating a large internal rotational barrier of MAO chains.

[1] J. Stellbrink et al., *Macromolecules*, **40**, 4972, 2007.

CPP 29.7 Thu 11:15 C 130

Tomographic Techniques in Small-Angle X-Ray Scattering (SAXS) and Grazing-Incidence SAXS (GISAXS) — •Jan M. Feldkamp[1], Christian G. Schroer[1], Marion Kuhlmann[2], Stephan V. Roth[2], Andreas Timmann[2], Rainer Gehrke[2], Norbert Stribeck[3], and Armando Almendarez-Camarillo[3] — [1]Institute for Structural Physics, TU Dresden, D-01062 Dresden, Germany — [2]HASYLAB at DESY, Notkestr. 85, D-22607 Hamburg, Germany — [3]Institute of Technical and Molecular Chemistry, Hamburg University, Bundesstrasse 45, D-20146 Hamburg, Germany

Small-Angle X-Ray Scattering (SAXS) has become a standard technique for the investigation of nano-structured materials. The emerging technique of Grazing Incidence Small-Angle X-Ray Scattering (GISAXS) enables one to study the nano-structure at the surface of materials and in thin films. These measurements provide valuable information to scientists from various fields, including material science, chemistry, polymer science, and biology.

In many cases the structure of a specimen is not homogeneous on a macroscopic scale. For these kinds of samples, scanning tomography provides additional real-space information. Using SAXS-tomography, the distribution of the nano-structure can be studied at each location on a virtual section through the sample. GISAXS-tomography allows one to map the distribution of the nano-structure on surfaces and in thin films.

In this presentation, these tomographic techniques are used to determine the structure of inhomogeneous polymer samples.

CPP 29.8 Thu 11:30 C 130

SANS observation of the relaxation of a hyperbranched polymer in a linear matrix after a large step strain deformation — •Louisa Dahbi[1], Wim Pyckhout-Hintzen[1], Juergen Allgaier[1], Dieter Richter[1], Ekkehard Straube[2], Nikos Hadjichristidis[3], Hermis Iatrou[3], and Melissa Sharp[4] — [1]Forschungszentrum Juelich, IFF, D-52425 Jülich, Germany — [2]M-L University Halle, D-0 6122 Halle, Germany — [3]University of Athens, Polymer Group, Greece — [4]GKSS, IMR, D-21502 Geesthacht, Germany

The feasibility of well defined branched model polymer and the recent advances in the tube model theory gave rise to a better understanding of the dynamic and rheology of branched polymers. Our study aims to focus on the relaxation of a non-linearly stretched hyperbranched polymer blended with linear chains of different length, constituting the matrix, so as to study the effects of this latter on the time dependence of the relaxation process of the hyperbranched arms. The relaxation was investigated with quenched SANS experiments using our elongational stretching rheometer which decouples microscopic and laboratory time scales. Hyperbranched as well as linear polymers used for this study are constituted by polyisoprene. Both systems (short and long matrix) were submitted to identical relaxation times so as to quantify and conclude on the influence of the matrix length on the time dependence of the relaxation process of the hyperbranched arms. The relaxation of the short matrix taking place concurrently is expected to accelerate the relaxation of the hyperbranched itself. A link to a former work on linear polymer and well entangled H-shaped is presented.

CPP 29.9 Thu 11:45 C 130

Characterisation of structural changes during deformation and relaxation of semi-crystalline polymers by simultaneous online SAXS and WAXS measurements — •Konrad Schneider[1], Andreas Schöne[1], Andreas Timmann[2], and Manfred Stamm[1] — [1]Leibniz Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany — [2]DESY, Hasylab, Notkestr. 85, 22607 Hamburg, Germany

Time resolved small and wide angle x-ray scattering using synchrotron radiation allows to follow up structural changes during deformation and relaxation of semi-crystalline polymers. On the example of polyolefins the changes of the structure in the crystalline and in the amorphous domains were followed during the three characteristic stages of the load-displacement curves: The elastic stage and the plastic range composed of the stage of the lowering load in the force-displacement-curve (yielding) and the strain hardening.

It is found that most rigorous changes are observed during yielding. There are found changes on a scale of seconds during relaxation, while the structural changes during relaxation in the other regions are much less pronounced.

CPP 29.10 Thu 12:00 C 130

Structure investigations of thermo-sensitive triblock copolymers — •Amit Kulkarni[1], Kordelia Troll[1], Charles Darko[1], Christine M. Papadakis[1], Weinan Wang[1], Peter Müller-Buschbaum[1], Achille M. Bivigou Koumba[2], and André Laschewsky[2] — [1]Physikdepartment E13, TU München — [2]Institute für Chemie, Universität Potsdam

Thermo-sensitive triblock copolymers consisting of a hydrophilic block, poly(N-isopropylacrylamide) (PNIPAM), and hydrophobic polystyrene end blocks, are expected to form physically cross-linked micellar gels in aqueous solution, which are swollen below the lower critical solution temperature (LCST) and collapsed above. They are of interest for a number of applications. We focus on the conformational change of the micellar shell as a function of temperature and the PNIPAM volume fraction. Three triblock copolymers with different PNIPAM volume fractions and three triblock copolymers having deuterated polystyrene blocks were studied by small angle X-ray scattering, small angle neutron scattering and dynamic light scattering with respect to the core-shell structure and swelling-deswelling of the shell. The non-deuterated triblock copolymers show the LCST at 31°C with micelles size of around 22 nm below collapse temperature and 17nm above.

CPP 29.11 Thu 12:15 C 130

The relation between craze structure and molecular weight in PS as revealed by μSAXS experiments — •Nikolaos E. Zafeiropoulos[1], Richard J. Davies[2], and Manfred Stamm[1] — [1]Leibniz Institut für Polymerforschung Dresden, Hohe strasse 6, 01069 Dresden — [2]European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble Cedex, France

The phenomenon of crazing in polymers has received considerable attention in the past as it plays a pivotal role in determining the performance of polymers under load. One aspect of particular interest has been the interconnection between molecular structure, craze characteristics and macromechanical properties. It is generally accepted that the mean craze fibril diameter, the mean craze fibril spacing and the orientation of the craze fibril with respect to the tensile load direction control the craze stability. The fibril volume fraction is independent of molecular weight (MW) under test conditions at temperatures significantly below the glass transition temperature. In addition, little changes in crazing are expected for MWs above the critical molecular weight of entanglement. Three different grades of polystyrene (PS) with different molecular weights have been systematically investigated in situ with synchrotron radiation microfocus SAXS. The results suggest that there are different mechanisms operating in PS samples with low and very high molecular weights, compared to those of medium-high molecular weight. Previously it was thought that, above the critical molecular weight of entanglement, the effect of molecular weight on PS's mechanical behaviour at room temperature was negligible.

CPP 29.12 Thu 12:30 C 130

Structural levels of organization in spider silk as studied by time-resolved polarized Rheo-FTIR spectroscopy — •Periklis Papadopoulos, Jan Sölter, Immanuel Weidner, and Friedrich Kremer — Universität Leipzig, Germany

The employment of polarized FTIR spectroscopy in combination with mechanical measurements is unique in unraveling the effects of external fields on the different moieties of spider silk under both equilibrium and non-equilibrium conditions. This allows us to construct quantitative structural models for the major (dragline) and minor ampullate spider silk and explain the differences between their respective mechanical properties. Both silks are semi-crystalline with β-sheeted crystals interconnected by pre-strained amorphous chains. The frequency shift of several absorption bands, in combination with a simple quantum mechanical model, allows tracing the microscopic force on the crystals and its distribution[1]. Thus, the structural model delivers the experimentally observed stress-strain dependence for both major and minor ampullate silk[2]. The former has a significantly higher degree of pre-strain, explaining its higher modulus, the lower extensibility and the effect of supercontraction, whereas the latter exhibits some degree of strain-induced crystallization. The very high toughness in both cases is attributed to the breaking of hydrogen bonds in the crystals.

[1] Papadopoulos, P.; Sölter, J. and Kremer, F. *Eur. Phys. J. E: Soft Matter* (2007) *in press*

[2] Papadopoulos, P.; Sölter, J. and Kremer, F. *Biophys. J.* (2007) *submitted*