CPP 25: Poster: Stress Relaxation in Polymers - From single molecules to biological cells (joint focus with BP)

Time: Wednesday 11:00–13:00 Location: Poster A

CPP 25.1 Wed 11:00 Poster A

Influence of the microstructure on the viscoelastic behavior of thin films of polypropylenes — •Martin Neumann, Toni Hille, and Robert Magerle — Chemische Physik, TU Chemnitz, D-09107 Chemnitz

With a microtensile testing setup that allows for simultaneous imaging with atomic force microscopy (AFM) we correlate the changes of the microstructure occurring during aging and deformation processes with the viscoelastic behavior of thin films of semicrystalline polymers. We study elastomeric polypropylenes (ePP) with different degrees of crystallinity (12% to 40%) and different molecular weights polymerized with metallocene catalysis. The films were annealed for several hours at different temperatures, which results in different microstructures and in turn different types of stress strain behavior and stress relaxation phenomena. For ePP films the elastic moduli are in the range between 0.2 and 10 MPa and the relaxation times between 2 s and 100 s. Cyclic loading experiments show changes of viscoelastic properties that are attributed to aging and crystallization processes. Series of AFM images measured at increasing strain show the deformation of individual lamella in spherulites in thin films of polypropylene with ultra-high molecular weight and 99% tacticity. At large deformations fractures and crazing between spherulites are observed.

CPP 25.2 Wed 11:00 Poster A

Characterization of conformational changes of single-chain, thin film and bulk polymers — •Frank Zocholl[1], Massimiliano Labardi[2], Daniele Prevosto[2], Kirsten Dammertz[1], Masoud Amirkhani[1], and Othmar Marti[1] — [1]Institute of Experimental Physics, University of Ulm, 89069 Ulm, Germany — [2]Dipartimento di Fisica Enrico Fermi, Università di Pisa, Largo Pontecorvo 3, 56127 Pisa, Italy

The possibility to induce conformational changes in Poly(4-Vinylpyridine) (P4VP) by application of ambient gas or electric fields is investigated. Characterization of dielectric properties both in bulk and thin films of P4VP are carried out by dielectric spectroscopy techniques, to find information about glass transition temperature and relaxation processes. Broadband Dielectric Spectroscopy (BDS) is a well established technique for dielectric study of bulk samples. Local Dielectric Spectroscopy (LDS) is a new approach based on Atomic Force Microscopy (AFM), applicable to ultra-thin films and capable of high spatial resolution, by sensing electric forces between the sample and the AFM tip. By means of a customized setup, shifts in instantaneous resonance frequency of the force sensor due to an ac applied voltage are measured, and provide information on the dielectric function of the material. By measuring dielectric relaxation dynamics for various thicknesses it is possible to evidence the effects of both spatial confinement and presence of interfaces.

CPP 25.3 Wed 11:00 Poster A

Synthesis and spectroscopic characterization of BODIPY dyes with aliphatic substituents in polymer matrices — •Melanie Bibrach, Stefan Krause, Christian von Borczyskowski, and Robert Magerle — TU Chemnitz, Fakultät für Naturwissenschaften, D-09126 Chemnitz

Boron dipyrrin (BODIPY) derivates are popular dyes for single molecule spectroscopy because of their high photoefficency and photostability. We aim at using BODIPY labelled polymers as fluorescent probes for the macromolecular dynamics in polypropylene and other semicrystalline polymers that is caused by relaxation of mechanical stress. To this end we synthesized BODIPY derivates with aliphatic substituents of different length from precursor molecules via the Heck reaction. Here we report on their spectroscopic characterization on the ensemble level. The fluorescent probes were embedded in thin films of different polymers (polypropylenes, block copolymers). Fluorescence spectra and fluorescence lifetime were measured in the temperature range from -50 °C to 160 °C. We discuss our results with respect to structural and dynamic changes of the polymers, such as glass transition and cystallisation.

CPP 25.4 Wed 11:00 Poster A

Computer simulation study of viscoelastic properties of entangled polymers using a translationally invariant slip-spring model — •Veronica Chappa[1,2], David Morse[3], Annette Zippelius[2], and Marcus Müller[2] — [1]CONICET, Argentina — [2]Institut für Theoretische Physik, Georg-August-Universität, Göttingen, Germany — [3]Department of Chemical Engineering and Materials Science, University of Minnesota, USA

Different slip-spring models have been proposed and used to describe the behavior of entangled polymers in computer simulation. Some of them break translational invariance by anchoring slip-links to fixed points in space or alter the equilibrium properties of the polymeric chains. We introduce a slip-spring model that represents entanglements via pairwise, translationally and rotationally invariant interactions and exactly compensate for the additional interactions such that the presence of slip-springs does not modify the equilibrium statistics of the polymers. These slip-springs were implemented in computer simulations of a soft coarse-grained polymer model and we study the viscoelastic properties of entangled polymer systems. Each end of a slip-spring can move to a neighboring segment along the chain to which it is attached and renewal processes at chain ends simultaneously account for tube renewal and the effect of constraint release. We present results for the mean squared displacements, shear viscosity, stress relaxation, and diffusion of the slip-springs along the chains in equilibrium and under flow. Our simulation results are compared to theoretical models and experiments.

CPP 25.5 Wed 11:00 Poster A

Changes in Structural and Wetting Properties of Polyelectrolyte Multilayers upon Mechanical Load — Johannes Früh[1], Adrian Rühm[2], Helmuth Möhwald[1], Rumen Krastev[3], and •Ralf Köhler[4,5] — [1]MPIKG Potsdam, Interfaces, 14424 Potsdam/Golm — [2]MPIMR Stuttgart, ZWE FRM II, 85747 Garching — [3]NMI at the University of Tübingen, Biomaterials, 72770 Reutlingen — [4]TU Berlin, Stranski-Lab, 10623 Berlin — [5]HZB, Soft Matter (F-I2), 14109 Berlin; Germany

Polyelectrolyte Multilayers (PEM) are formed by alternating adsorption of oppositely charged organic macromolecules onto a charged template. Despite big attempts for understanding the complex interactions in PEM and their subsequent effects, several major features are still unclear. This study addresses the mechanical properties of thin PEM films, with focus on the molecular changes upon lateral stress. Internal and overall restructuring is investigated using neutron and X-ray reflectivity, and UV-vis spectroscopy. An transition from elastic to plastic deformation is observed at an elongation of ca 0.2%. (A very tiny value which resembles the behaviour of solid bodies.) The transition is attended by, either a reversible, or an irreversible uptake of water from the ambient atmosphere. A superstructure created by selective replacing of PSS with deuterated PSS in the PSS/PDADMAC-multilayer showed gradual and irreversible degradation of the layer structure upon elongation. Decoiling of entangled polymer chains which, in extra, are strongly interacting via ionic bonds is considered as the origin of the molecular intermixing upon mechanical load.

CPP 25.6 Wed 11:00 Poster A

"Stress relief" via embedding of cyclopropane derivatives in polymers — •Miriam Wollenhaupt and Dominik Marx — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum

Due to their special physical properties such as elasticity, breaking strength, chemical and thermal stability, polymers are widely used. But continuous strain causes weakening of the polymer strands and, therefore, leads to material failure. The embedding of mechanophores (stress-responsive chemical groups that undergo a chemical reaction when exposed to a mechanical force) in the single polymer chains can provide a "stress relief".

Under mechanical forces, gem-dichlorocyclopropanes incorporated along the backbone of cis-polybutadiene exhibit an electrocyclic ring opening accompanied with a chlorine migration[1].

Besides the practical aspects, theoretical investigations on cis- and trans-1,1-dichloro-2,3-dimethylcyclopropane unveil a field of striking features, such as a lack of selectivity at high forces or unexpected branching ratios[2]. We used static calculations to investigate the change of electronic properties along the reaction pathways under

different forces. The analysis of wavefunction and electron density was performed using Natural Bond Orbitals and Quantum Theory of Atoms In Molecules.

[1] J. Am. Chem. Soc., 2009, 131, 10818–10819
[2] Angew. Chem. Int. Ed., 2011, 50, 7105–7108

CPP 25.7 Wed 11:00 Poster A

Güte der Abstandsmessungen von D-Banden in Kollagenfibrillen — •Christopher Robert Pech[1] und Robert Magerle[2] — [1]Fakultät für Mathematik, TU Chemnitz, D-09107 Chemnitz — [2]Fakultät für Naturwissenschaften, TU Chemnitz, D-09107 Chemnitz

Mittels Rasterkraftmikroskopie ist eine mikroskopische Untersuchung des lokalen Deformationsverhaltens von Kollagenfibrillen in Sehnen und Bänder möglich [1]. Noch gibt es aber keinen Algorithmus und eine dazugehörige umfassende Analyse, die den Abstand zwischen zwei benachbarten D-Banden und den dabei gemachten Fehler bestimmt. Bisher wird über die Gesamtheit mehrerer Abstände gemittelt [1]. Wir entwickeln daher einen Algorithmus, der über die einzelnen Pixel interpoliert und dann den Abstand zwischen benachbarten lokalen Extrema bestimmt. Dieser Algorithmus wird an verschiedenen Testproblemen erprobt, um die Genauigkeit sowie die Störanfälligkeit bei verschiedenen Arten von Rauschen zu bestimmen. Der Algorithmus soll eingesetzt werden, um Veränderungen des lokalen Deformationsverhaltens von Kollagenfibrillen in chemisch behandelten Sehnen zu untersuchen, die als Transplantate eingesetzt werden.

[1] S. Rigozzi et al., J. Struct. Biol. **176**, 9 (2011)

CPP 25.8 Wed 11:00 Poster A

Ultrastructure and the viscoelastic properties of anterior cruciate ligament studied with atomic force microscopy — •Mandy Göring[1], Eike-Christian Spitzner[1], Stephanie Röper[1], Anke Bernstein[2], and Robert Magerle[1] — [1]Chemische Physik, TU Chemnitz, D-09107 Chemnitz, Germany — [2]Department für Orthopädie und Unfallchirugie, Muskuloskelettales Forschungslabor, Universitätsklinikum Freiburg, D-79106 Freiburg, Germany

Tears of the anterior cruciate ligament (ACL) are one of the most common injuries in young and active humans. In today's surgical practice, it is common to use autologous graft tissue for ACL reconstruction. Allografts have recently gained popularity in orthopaedic sports medicine, especially in primary and revision reconstruction of ACL. However the allografts need to be sterilized either by freeze-drying, with peracetic acid or gamma radiation. Most current sterilization procedures have inherent disadvantages affecting biological properties and mechanical function of the graft. We investigate cryosections and collagen fibres isolated from bovine ACL. The samples are prepared like human grafts, adsorbed onto a silicon wafer and studied with atomic force microscopy (AFM) operating in tapping mode. The local viscoelastic properties of the specimen are determined by measuring the dissipated energy between the AFM tip and the collagen fibril as well as the local indentation of the tip into the surface. Changes of the ultrastructure and local viscoelastic properties are discussed with respect to the different types of chemical and physical treatment.

CPP 25.9 Wed 11:00 Poster A

Modeling the stretch and relaxation properties of cytoskeletal filament systems in neutrophil — •Othmar Marti[1], Michael Beil[2], and Stephan Paschke[3] — [1]Institute of Experimental Physics, Ulm University, D-89081 Ulm — [2]Department of Medicine, University Hospital Ulm, D-89081 Ulm — [3]Department of Surgery, University Hospital Ulm, D-89081 Ulm

The individual contribution of cytoskeletal filament systems to the regulation of cell deformation remains to be elucidated in detail. We investigated the mechanical behavior of differentiated NB4 cells which are a model for neutrophil granulocytes [1]. Cellular deformability was studied by optical stretching [2] before and after cells were exposed to cytochalasine D and colchicine to disassemble the actin cytoskeleton and microtubules, respectively. The mechanical response of the cells in the stretcher was modeled by a mechanical model consisting of parallel and series connections of elastic and viscous elements. We found that the salient features of the deformation curves can be described adequately. Microtubules were discovered to mainly contribute to cell elasticity, whereas filamentous actin was in control of cell viscosity in this model system. This link between the cytoskeleton and cell mechanics might point to novel options for the pharmacological modulation of the cell migration.

[1] Bruel, A., Paschke, S., Jainta, S., Zhang, Y., Vassy, J., Rigaut, J.P. and Beil, M., Anticancer. Res. 21, 3973-80 (2001) [2] Guck, J., Ananthakrishnan, R., Mahmood, H., Moon, T.J., Cunningham, C.C. and Käs, J. , Biophys. J. 81, 767-84 (2001).

CPP 25.10 Wed 11:00 Poster A

Conformational properties of stretched and unstretched semiflexible polymer chains — •Hsiao-Ping Hsu[1], Wolfgang Paul[2], and Kurt Binder[1] — [1]Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, D-55099 Mainz, Germany — [2]Theoretische Physik, Martin Luther Universität Halle-Wittenberg, von Seckendorffplatz 1, 06120 Halle, Germany

Semiflexible polymer chains under good solvent conditions are described by self-avoiding walks on the square and simple cubic lattices in $d = 2$ and $d = 3$ dimensions, respectively, and the stiffness of chains is controlled by the bending energy ϵ_b. With the pruned-enriched Rosenbluth method (PERM), we observe a double crossover behavior, rigid-rod-like to (almost) Gaussian random coils, then to self-avoiding walks, for the chain length up to $N = 50000$ in $d = 3$, but only a single crossover from rigid-rod-like to self-avoiding walks for the chain length up to $N = 25600$. in $d = 2$. Testing the applicability of the Kratky-Porod model, we also check whether the chain conformation is dominated by the excluded volume effects or not as the chain length and its flexibility vary. We extend our study to the problem of stretching semiflexible chains. Varying the strength of the force, the flexibility of the chain, and the chain length, the theoretical predictions of the force-extension relationship at different length scale regimes (linear response - Pincus blob - Kratky-Porod model - freely joined chain) are checked. Our large scale Monte Carlo simulations give clear evidence for the importance of excluded volume effects on the stretching behavior of semiflexible polymer chains.

CPP 25.11 Wed 11:00 Poster A

The effect of moisture on mechanical deformation of PETG — •masoud amirkhani[1], Andrew Boryor[2], Juliana Kurniadi[3], Martin Geiger[2], Thanapon Panchapongsaphak[2], Othmar Marti[1], and Bernd Lapatki[2] — [1]Institute of Experimental Physics, University of Ulm, Germany — [2]Department of Orthodontics, University of Ulm, Germany — [3]DWI at RWTH Aachen e.V. and ITMC / TexMC, RWTH Aachen University, Germany

In this work, we studied the deformation properties of polymer systems in the presence of the water molecules. Depending on the type of polymer network, water molecule may cause softening or hardening of the network. This study shows that polyethylene terephthalate (PETG) immersed in water initially swells whereby its stiffness decreases but after a certain time its stiffness increased to almost its initial point as shown in Figure 1. We applied three-point bending experiments on several stripes (10mm x 55mm) of PETG immersed in water for 14 days. The experiments showed that the elastic modulus of the tested PETG material decreases until 30 hours, after which a gradual increase in the elastic modulus was experienced until 14 days where the E-module almost reached that of the dry material. The reduction of the elastic modules is due to plasticiser effect, which is caused by dispersing water molecules in the network. The increase in stiffness after 30 hours can be attributed to the rearrangement of the polymer chain which also causes a repelling of the water molecules from the polymer network.