CPP 28: (Hydro) Gels and Elastomers

Time: Wednesday 9:30–12:30 Location: ZEU 222

Invited Talk CPP 28.1 Wed 9:30 ZEU 222

Rheo-imaging of Polymer Networks — •Norbert Willenbacher — Karlsruhe Institute of Technology, Germany

Combining mechanical rheometry and multi-particle tracking (MPT) optical microrheology provides insight into polymer network structure.

High absolute values but weak concentration dependence of shear moduli are generic features of Intermediate filament networks, which play a crucial role in metazoan cell mechanics. MPT experiments reveal uniform mesh sizes (0.1-1μm), but modulus values obtained from MPT are orders of magnitude lower than those from bulk rheometry. This discrepancy is attributed to a strong entropic contribution of stretched filament strands since attractive interactions at filament contact points prevent thermal equilibration. Addition of surfactant does not affect network mesh size, but allows filament strand equilibration, and the discrepancy between MPT and bulk rheometry vanishes.

Acrylate microgels, which are used as thickeners in a broad variety of commercial products, with similar chemical composition, but different molecular architecture have been investigated. Emulsion polymerization products form uniform networks (mesh size below 100nm). In contrast, the microgel system from solution polymerization is extremely inhomogeneous. Tracer particle mobility varies by orders of magnitude. Tracers diffuse freely within microgel particles, but are elastically trapped in overlap regions. A heterogeneous microstructure with a characteristic length scale of about 10μm can be directly visualized based on spatial distribution of tracer particle mobility.

CPP 28.2 Wed 10:00 ZEU 222

Nonlinear rheology and self-healing kinetics of supramolecular polymer network — •Tingzi Yan[1], Klaus Schröter[1], Florian Herbst[2], Wolfgang Binder[2], and Thomas Thurn-Albrecht[1] — [1]Institute of Physics, Martin-Luther University Halle-Wittenberg, Halle 06120, Germany — [2]Institute of Chemistry, Martin-Luther University Halle-Wittenberg, Halle 06120, Germany

A series of supramolecular polyisobutylenes melt samples showing self-healing properties was investigated by small angle x-ray scattering and rheological experiments in order to get a microscopic understanding of special mechanical properties. All samples were end functionalized with barbituric acids groups but had different molecular weights. Analysis of the SAXS data and linear rheology showed that the samples form a reversible network of interconnected micelles in which barbituric acids clusters act as physical cross-linking points. Startup shear experiments with large shear strain and high shear rate led to shear yielding accompanied by a fast stress relaxation, indicating failure of the cross-linked network. Small amplitude oscillatory shear measurements after shear yielding were performed to measure the recovery of network. Based on the results, we propose a two-step model for the self-healing process.

CPP 28.3 Wed 10:15 ZEU 222

Electron irradiation of gelatin hydrogels to tailor the material properties — •Emilia I. Wisotzki[1], Marcel Hennes[1], Carsten Schuldt[2], Wolfgang Knolle[1], Ulrich Decker[1], Josef A. Käs[2], Mareike Zink[2], and Stefan G. Mayr[1,2,3] — [1]Leibniz Insitute of Surface Modification (IOM), Leipzig, Germany — [2]Faculty of Physics and Earth Science, Leipzig University, Leipzig, Germany — [3]Translational Centre for Regenerative Medicine, Leipzig University, Germany

Gelatin is a derivative of the natural and prevalent substance collagen, making it a highly interesting biomaterial for application in a wide range of areas from biomedicine to bioengineering. Reagent-free treatment methods to tune the properties of hydrogels such as gelatin are highly desirable in order to preserve existing biocompatibility and biodegradability of the material. Gelatin hydrogels have been synthesized and subsequently electron irradiated by a 10 MeV linear accelerator, in order to alter the material properties through crosslinking. Quantification of the physical crosslinking was carried out by rheological measurements and investigation of swelling behaviour to observe hydrogel strengthening and elasticity. From this data, rubber elasticity theory and the Flory-Rehner equation for isotropically swollen elastomers were used to estimate the crosslinking densities and polymer mesh size. Fourier transform infrared spectroscopy and scanning electron microscopy were used to analyze changes of the gelatin structure with respect to the irradiation dose. Systematic approaches to precisely tune these material properties for desired applications were demonstrated with respect to irradiation dose and gelatin concentration.

CPP 28.4 Wed 10:30 ZEU 222

Mechanical properties of magneto-sensitive elastomers with the finite shape and different particle distributions — •Dmytro Ivaneyko[1,2], Vladimir Toshchevikov[1], Marina Saphiannikova[1], and Gert Heinrich[1,2] — [1]Technische Universität Dresden — [2]Leibniz-Institut für Polymerforschung Dresden e.V.

A new theoretical formalism is developed for the studies of the mechanical behaviour of magneto-sensitive elastomers (MSEs) under a uniform external magnetic field [1]. This formalism allows to combine macroscopic continuum-mechanics and microscopic approaches for complex analysis of MSEs with different shapes and with different particle distributions. It is shown that starting from a model based on an explicit discrete particle distribution one can separate the magnetic field inside the MSE into two contributions: one which depends on the shape of the sample with finite size and the other, which depends on the local spatial particle distribution. The magneto-induced deformation and the change of elastic modulus are found to be either positive or negative, their dependences on the magnetic field being determined by a non-trivial interplay between these two contributions. Mechanical properties are studied for two opposite types of coupling between the particle distribution and the magneto-induced deformation: absence of elastic coupling and presence of strong affine coupling. Predictions of a new formalism are in a qualitative agreement with existing experimental data.

[1] D. Ivaneyko, V. Toshchevikov, M. Saphiannikova and G. Heinrich, Soft Matter, submitted.

CPP 28.5 Wed 10:45 ZEU 222

Poly(ethylene glycol) based microgel particles — •Kornelia Gawlitza, Stefan Wellert, and Regine von Klitzing — Stranski-Laboratorium, Institut für Chemie, Technische Universität Berlin

Due to their reversible temperature induced volume phase transition (VPT), microgels made of poly-N-Isopropylacrylamide (p-NIPAM) served as model systems for basic research and have been intensively studied, e.g. their swelling behavior and internal structure.[1],[2] The polymer p-NIPAM show cytotoxicity above the VPT temperature (VPTT) when exposed to living cells longer than 3 hours.[3] This makes them inapplicable for long-time medical applications. The problem of cytotoxicity can be overcome by the synthesis of Poly(ethylene glycol) (PEG) based microgels which are both, non-cytotoxic and thermoresponsive. In this study the size, VPTT as well as the mesh size were controlled by the amount of comonomer (OEGMA), cross-linker (EGDMA) and sugar surfactant (Glucopon 220) during the synthesis.[4] The polymer particles in bulk and at surfaces were characterized by scattering and imaging techniques. The swelling behavior at surfaces in dependence from the coverage was investigated by Atomic Force Microscopy (AFM) and ellipsometry. - [1] K. Kratz, A. Lapp, W. Eimer and T. Hellweg, Colloids and Surfaces A: Physiochemical and Engineering Aspects, 2002, 197, 55 [2] K. Gawlitza, S. Turner, F. Polzer, S. Wellert, M. Karg, P. Mulvaney and R. v. Klitzing, Physical Chemistry Chemical Physics, 2013, 15, 15623 [3] H. Vihola, A. Laukkanen, L. Valtola, H. Tenhu and J. Hirvonen, Biomaterials, 2005, 26, 3055 [4] J. Lutz, Journal of Polymer Science: Part A, 2008, 46, 3459

15 min break

CPP 28.6 Wed 11:15 ZEU 222

Reversibly crosslinked polymer networks - A self-consistent field theory study — •Thomas Gruhn and Heike Emmerich — Material and Process Simulation MPS, Universität Bayreuth, Germany

Reversibly crosslinked hydrogels are of great technological relevance for sensors, drug delivery and other applications. The connectivity of these polymer network may depend on external parameters like the temperature or the composition of the solvent. A large variety of microstructures can be formed if the netowork includes block copolymers. A system of particular interest consists of AB diblock copolymers and A and B homopolymers. We have studied the structure of this system, using an extended version of self-consistent field theory. We consider crosslink strengths weighted by the type of monomers involved. Varying the crosslink parameters the system shows a first order phase transition from a lamellar to a hexagonal microphase. We have calculated a phase diagram and compare the structure and free energy contributions as a function of the parameters [1-3].

[1] T. Gruhn, H. Emmerich, J. Mater. Res., 28, 3079, 2013.

[2] T. Gruhn, H. Emmerich, Chemosensors 1, 43, 2013.

[3] D. Li, T. Gruhn, H. Emmerich, J. Chem. Phys. (2012), 137, 024906.

CPP 28.7 Wed 11:30 ZEU 222

Collapse and swelling of bulk polymers and polymer brushes studied by solid-state NMR — Ute Böhme and •Ulrich Scheler — Leibniz-Institut für Polymerforschung Dresden e.V.

Dynamic NMR, relaxation NMR and measurements of residual dipolar couplings via double quantum NMR gives acces to molecular mobility over a wide range of corellation times. Combined with the detection under high-resolution solid-state NMR applying CRAMPS signals of different functional groups and in particular the solvent can be separated. The separation of solvent dynamics from thepolymer is key to this investigation. Slow polymer chain dynamics clearly shows in proton transverse relaxation. The chains of collapsed poly(acrylic acid) brushes are significantly more mobile than in the bulk polymer. Upon the addition of water this dynamic difference becomes stronger and an even more mobile component appears in the brush. The temperature-dependent collapse of PNIPAM has been followed by various techniques. The combination of relaxation NMR with CRAMPS shows the polymer dynamics in the collapsed state as well. There is a continous variation of the chain dynamics over a wide temperature range around the transition temperature as shown inproton T1rho, which is very selective for motions in the kilohertz range.

CPP 28.8 Wed 11:45 ZEU 222

Molecular modeling approach to the prediction of mechanical properties of silica-reinforced rubbers — Reinhard Hentschke[1], •Jonathan Hager[1] und Nils W. Hojdis[2] — [1]Fachbereich Mathematik und Naturwissenschaften Bergische Universität D-42097 Wuppertal, Germany — [2]Material Development, Advanced Tire Materials, Continental Reifen Deutschland GmbH D-30419 Hannover, Germany

Recently we have suggested a nano-mechanical model for dissipative loss in filled elastomer networks in the context of the Payne effect. The mechanism is based on a total inter-filler particle force exhibiting an intermittent loop, due to the combination of short-range repulsion and dispersion forces with a long-range elastic attraction. The sum of these forces leads, under external strain, to a spontaneous instability of 'bonds' between the aggregates in a filler network and attendant energy dissipation due to the 'jolt-like' motion of the aggregates involved. In this work we use molecular dynamics simulations to obtain the microscopic interactions forces between surface modified silica particles. The latter are combined with the above model to estimate both the loss modulus and the low strain storage modulus in elastomers containing the aforementioned filler-compatibilizer systems. The model is compared to experimental dynamic moduli of silica filled rubbers using different compatibilizers. We find good agreement between the model predictions and the experimental moduli as function of the compatibilizer concentration.

CPP 28.9 Wed 12:00 ZEU 222

Effect and Evolution of Nanostructural Complexity in Sensitive Polymer Gels — •Sebastian Seiffert — Helmholtz-Zentrum Berlin — Freie Universität Berlin

Sensitive gels consist of polymer networks that can react to changes in their environment. This is achieved by two different ways. One way is to use polymers that exhibit sensitive interactions with the surrounding solvent, leading to selective gel swelling and deswelling. Another way is to use gels that consist of polymers crosslinked by non-covalent bonds that can be broken and re-associated. Both classes of sensitive gels are established and used in applications. However, to make this truly useful, it is necessary to understand the relations between the gel structure, dynamics, and function.

Our group studies such relations by two complementary approaches. In one approach, we use droplet-based microfluidics to fabricate microgel particles with exquisite control on their nm-scale homogeneity. This allows us to impart custom inhomogeneities to these gel particles, offering their impact to be studied, for example, in view of microgel volume phase transitions. We also use microgels as building blocks to assemble larger gel-type materials with determined inhomogeneity. In a second approach, we create and use modular toolboxes of supramolecular polymer gels, allowing for consistent variation of the type and strength of transient chain crosslinking. These networks are probed by micro- and macrorheology to challenge and develop models for supramolecular gel self healing.

CPP 28.10 Wed 12:15 ZEU 222

The Swelling of Olympic Gels — •Michael Lang[1], Jakob Fischer[1,2,3], Marco Werner[1,2], and Jens-Uwe Sommer[1,2] — [1]Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany. — [2]Institute of Theoretical Physics, Technische Universität Dresden, Zellescher Weg 17, 01062 Dresden, Germany. — [3]Current address: Bio Systems Analysis Group, Jena Centre for Bioinformatics (JCB) and Department for Mathematics and Computer Sciences, Friedrich Schiller University of Jena, 07743 Jena, Germany.

The swelling equilibrium of Olympic gels is studied by Monte Carlo Simulations. We observe that gels consisting of flexible cyclic molecules of a higher degree of polymerization N show a smaller equilibrium swelling degree $Q \propto N^{-0.28}\phi_0^{-0.72}$ for the same monomer volume fraction ϕ_0 at network preparation. This observation is explained by a disinterpenetration process of overlapping non-concatenated polymers upon swelling. In the limit of a sufficiently large number of concatenations per cyclic molecule we expect that the equilibrium degree of swelling becomes proportional to $\phi_0^{-1/2}$ independent of N. Our results challenge current textbook models for the equilibrium degree of swelling of entangled polymer networks.