CPP 35: Activated and Glassy Dynamics of Soft Matter (joint session CPP/DY, organized by CPP)

Time: Wednesday 9:30–13:00 Location: H51

CPP 35.1 Wed 9:30 H51

On the dynamics of densely grafted polymer chains — •Michael Lang, Marco Werner, Ron Dockhorn, and Torsten Kreer — Leibniz Institut für Polymerforschung Dresden, Hohe Straße 6, 01069 Dresden, Germany.

Large scale Monte Carlo simulations of a dense layer of grafted polymer chains in good solvent conditions are used to explore the dynamics of a "polymer brush". Monomer displacements are analyzed resolving the directions parallel and perpendicular to the grafting plane. Autocorrelation functions of segment and partial chain end-to-end vectors are analyzed as function of time. We demonstrate that the terminal relaxation time τ of entangled chains with a degree of polymerization N in a brush is related to the entanglement degree of polymerization, N_e, via $\tau \propto N^3 \exp(N/N_e)$. The confining tube in the brush is similarly stretched as the chain conformations with tube diameters perpendicular and parallel to the grafting plane related by $a_\perp \approx a_\parallel \, (N_e/g)^{1/2}$, whereby g is the number of monomers per correlation volume of the brush. One specific effect of the confining potential is that the terminal part of the perpendicular component of the monomer position vector auto-correlation function decays simultaneously for all monomers.

CPP 35.2 Wed 9:45 H51

Transient Cooperative Process in Dewetting Polymer Melts — •Sivasurender Chandran and Günter Reiter — Institute of Physics, Albert–Ludwig University of Freiburg, Freiburg, Germany

Polymer melts exhibit a rich dynamic behavior when exposed to intense shear fields. For example, amorphous polymers display a shear thinning behavior, while crystallizable polymers form correlated segments within the flow induced oriented structures. However, the role of such correlations on the dynamic behavior of crystallizable polymer melts is highly unexplored.

To explore this crucial aspect, we have compared the high velocity dewetting (*shearing*) behavior of molten amorphous (atactic polystyrene, aPS) and crystallizable (isotactic polystyrene, iPS) polymer films, above the melting point. For aPS, the apparent viscosity of the films (η_f) derived from dewetting was less than zero shear bulk viscosity (η_bulk), displaying the expected shear thinning behavior. Surprisingly for iPS films, η_f was always larger than η_bulk, even at about 50 °C above the melting point, with $\eta_\mathrm{f}/\eta_\mathrm{bulk}$ following an Arrhenius behavior. The corresponding activation energy of $\sim 160 \pm 10$ kJ/mol for iPS films suggests a cooperative motion of segments which were aligned and agglomerated by fast dewetting. These observations were not anticipated by standard models and hence indicate to the need for a new concept in polymer physics.

CPP 35.3 Wed 10:00 H51

Picosecond Dynamics of Liquid Glycerol Above T$_g$ — •Sebastian Busch[1], Alessandro Vispa[2], Nicolas Giovambattista[3], and Luis Carlos Pardo[2] — [1]German Engineering Materials Science Centre (GEMS) at Heinz Maier-Leibnitz Zentrum (MLZ), Helmholtz-Zentrum Geesthacht GmbH, Lichtenbergstr. 1, 85747 Garching bei München, Germany — [2]Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Barcelona, Spain — [3]Physics Department, Brooklyn College of The City University of New York, Brooklyn, USA

An understanding of the dynamics of glass-forming liquids at temperatures significantly above the glass transition still represents a much-coveted goal. If any theory or explanation is to be extrapolated to understand the undercooled regime from knowledge of high-temperature equilibrium states, a consensus must first exist on the underlying physics of the liquid phase at temperatures above the glass transition.

The aim of this work is to provide a detailed and critical appraisal of two specific questions about the dynamics of liquid glycerol, a prototypical glass-forming liquid: The first one concerns how many distinct dynamical processes are present in glycerol in the sub-nanosecond regime. The second one concerns whether a homogeneous (dynamically driven) or heterogeneous (structurally driven) scenario better describes Quasielastic Neutron Scattering data and Molecular Dynamics simulations.

A. Vispa et al., "A Robust Comparison of Dynamical Scenarios in a Glass-forming Liquid", PhysChemChemPhys, accepted.

CPP 35.4 Wed 10:15 H51

Mechanically induced ageing and compaction of porous polymer membranes — •Ulrich A. Handge — Helmholtz-Zentrum Geesthacht, Institut für Polymerforschung, Max-Planck-Strasse 1, 21502 Geesthacht

The permeability of porous polymer membranes often is reduced by mechanical compaction caused by the applied pressure. This process is strongly determined by the viscoelastic properties of the polymer and its plasticization caused by the feed medium. In this work, the time-dependent compaction of porous polymer membranes under pressure is modelled. We focus on the influence of viscoelastic and diffusion properties of the polymer material on compaction and on the decrease of membrane permeability with time. Different membrane morphologies are discussed. The life-time of a porous polymer membrane is associated with the time at which the glass transition is achieved in a creep experiment. We calculate the maximum life-time of polymer membranes based on compaction. The analysis of our model reveals that the diffusion coefficient, the average retardation time in creep, the magnitude of creep compliance and the time-temperature-pressure shift factor strongly influence the pressure induced compaction of microporous membranes. Generally, a larger tortuosity at constant porosity leads to a lower life-time of the membrane. Buckling of cell struts is the dominant failure mechanism in porous membranes with a very high porosity.

CPP 35.5 Wed 10:30 H51

Lifetime Prediction of Physical Ageing in Glassy Polymer Membranes — •Nils Müller[1], Ulrich Alexander Handge[1], and Volker Abetz[1,2] — [1]Helmholtz-Zentrum Geesthacht, Institute of Polymer Research, Geesthacht, Germany — [2]University of Hamburg, Institute of Physical Chemistry, Hamburg, Germany

The long-term performance stability of glassy polymer membranes is strongly affected by physical ageing. Therefore, we investigate the lifetime evolution of membrane properties through the application of the ageing model developed by Struik [1] and the statistical analysis thereof [2]. We propose several lifetime definitions suitable for membrane characterisation. The bootstrapping method is used in our analysis of the influence of a reduction of the data points used in model fitting on prediction quality. In this context we discuss the interdependency of experimental time expenditure and choice of model parameters with regard to lifetime prediction. A dimensional analysis of the Struik equation yields a master curve concerning the accelerated ageing behaviour of thin films. Our analysis of the master curve reveals a weak dependence of the membrane lifetime on initial conditioning. Dependent on the lifetime definition, we find a varying relationship between lifetime and relaxation time ranging from proportional to inverse proportional.

[1] L.C.E. Struik (1978). Physical aging in amorphous polymers and other materials.

[2] N. Müller, U.A. Handge, and V. Abetz (2015). Physical ageing and lifetime prediction of polymer membranes for gas separation processes. Submitted for publication.

15 min. break

Invited Talk CPP 35.6 Wed 11:00 H51

The extraordinary mechanical properties of spider silk and it's molecular foundation — •Friedrich Kremer[1], Markus Anton[1], Periklis Papadopoulos[2], Roxana Figuli[3], and Wilhelm Kossack[1] — [1]Universität Leipzig — [2]Max-Planck-Institut für Polymerforschung, Mainz — [3]Karlsruher Institut für Technologie (KIT), Karlsruhe

Spider silk is a high-performance fiber with unique mechanical properties which are currently not met by man-made materials. It consists essentially out of two proteins, major ampullate spidroin1 and spidroin2, having alanine-rich blocks interrupted by glycine-rich sequences. The former assembles to ß-sheeted nanocrystals which are embedded in the amorphous chains of the latter and which are interlinked by a ~ 10 % fraction of prestressed chains. This causes within the fiber a negative inner pressure which is counterbalanced by the matrix surrounding the fibrils and by the outer skin. Wetting of the fiber results in a spontaneous "supercontraction" into the equilibrated state. - In the talk a detailed description of this interplay between inner and outer constraints will be discussed based on a variety of complementary experimental methods like polarized, time-resolved FTIR-spectroscopy, measurements of the mechanical modulus and micro-X-ray scattering. It enables one to deduce a quantitative model describing the macroscopic response in the dependence on the microscopic parameters.

CPP 35.7 Wed 11:30 H51

Tayloring the properties of polydiene elastomers via associating hydrogen bonding groups: A micro- and macroscopic approach — •Barbara J. Gold, Claas H. Hövelmann, Wim Pyckhout-Hintzen, Andreas Wischnewski, and Dieter Richter — Forschungszentrum Jülich, JCNS-1 & ICS-1, 52425 Jülich, Germany

Nature uses a combination of dynamic hydrogen and static covalent bonds e.g. in the muscle protein TITIN [Wojtecki et al., Nature Materials 2011] to achieve toughness in otherwise elastic materials. We transferred this mechanism into conventional elastomers by introducing associating hydrogen bonds into covalent crosslinked polydiene networks. Since the associating behaviour of these functional groups can be triggered by temperature or mechanical stimulation this new generation of elastomers serves as key actor for the design of novel knowledge-based materials.

The influence of the hydrogen bonding groups on the dynamics of linear polymer chains has been studied by oscillatory shear rheology, dielectric and neutron spin echo spectroscopy. We observe a clear influence on the relaxation time spectra resulting in a longer disentanglement time, higher segmental friction as well as a second relaxation process related to the lifetime of the associating groups. Furthermore the Gaussian chain structure, observed via small angle neutron scattering, remains unaffected which excludes phase separation within the material. Stress-strain investigations show a significant increase of the mechanical resistance due to the additional functional groups compared to conventional elastomers.

CPP 35.8 Wed 11:45 H51

Chain-level dynamics and relaxation in supramolecular self-healing networks — Anton Mordvinkin and •Kay Saalwächter — Institut f. Physik-NMR, Martin-Luther-Univ. Halle-Wittenberg, Betty-Heimann-Str. 7, 06120 Halle, Germany

We elucidate the relationship between the local "sticker lifetime" and the mechanical properties of different polyisobutylene (PIB) based supramolecular elastomers with self-healing capability [1,2]. The systems comprise linear PIB end-functionalized with hydrogen-bonding units [1] and randomly functionalized with ionic side groups [2]. In both cases, the supramolecular groups form clusters that correspond to high-functionality crosslinks, rendering the relationship between local bonding-debonding dynamics and the rheological behavior complex. We study the chain-level dynamics using an NMR-based molecular rheology approach [3]. Our results provide the microscopic underpinning of the rheological properties, and show the first direct evidence of "sticky reptation" [4] in the randomly functionalized ionomer case.

[1] T. Yan et al., *Macromolecules* **47**, 2122 (2014)
[2] A. Das et al., *ACS Appl. Mater. Interf.* **7**, 20623 (2015)
[3] F. Vaca Chavez, K. Saalwachter, *PRL* **104**, 198305 (2010)
[4] M. Rubinstein, A.N. Semenov, *Macromolecules* **34**, 1058 (2001)

CPP 35.9 Wed 12:00 H51

A novel approach to determine the cross-linking level of epoxy resins — •Lisa Maria Uiberlacker, Moritz Strobel, and Sabine Hild — Johannes Kepler University Linz, Institute of Polymer Science, 4040 Linz, Austria

The cross-linking density of epoxy resins is a crucial parameter that determines its mechanical properties and characteristic data such as the glass transition temperature. Typically, the glass transition temperature increases with increasing cross-linking level of the epoxy system. A direct measurement of glass transition temperature is possible with DSC, but the cross-linking level has to be calculated from the remaining enthalpy compared to a completely cured sample. Raman spectroscopy is often used for the determination of the cross-linking density of epoxy resins. The decrease of the epoxide vibration peak is compared to the vibration peak of the phenyl ring peak, which is not affected by the curing of the epoxy system. Our approach is to determine the glass transition temperature of the resin with various crosslinking levels using an AFM equipped with a heatable cantilever. Performing local thermal analysis is based on a temperature calibration with known polymer standards to correlate the tip temperature with the applied voltage on the tip. AFM has a high spatial resolution which allows the determination of local differences in the glass transition temperature. The local thermal analysis with AFM is compared with conventional methods like Raman spectroscopy and DSC.

CPP 35.10 Wed 12:15 H51

Supramolecular association in transiently branched polymer systems — •Mariapaola Staropoli, Claas Hoevelmann, Juergen Allgaier, Andreas Raba, Wim Pyckhout-Hintzen, Andreas Wischnewski, and Dieter Richter — JCNS-1 Forschungzentrum Juelich

In this contribution, the investigation of hydrogen bonding mechanism in a transiently branched comb-like polymer system, is presented. The system under investigation consists of a polybutylene oxide (PBO) based backbone, randomly functionalized with thymine (Thy) groups, in combination with shorter PBO chains, end functionalized with Diaminotriazine (Dat) groups. The functional groups are able to associate through hydrogen bonds. The complementary association of these groups leads to the formation of a transiently branched comb-like polymer system. The interaction of hydrogen bonding groups in the melt state has been studied on microscopic level by Small Angle Neutron Scattering technique (SANS), by mean of the selective labeling scheme.A peak observed in the scattering function, reveals the formation of a block copolymer, due to the complementary association of the hydrogen bonding groups. The scattering profile of a block copolymer is described by mean of RPA formalism through which it is possible to obtain an average aggregation number in the melt and thus, the association constant. Rheological measurements in the melt have been performed in order to study the influence of the transient bonds on the macroscopic properties of the polymer system and to analyze the effect of the reversible interaction on the dynamic.

CPP 35.11 Wed 12:30 H51

ReaxFF+ I - a new reactive force field method for the accurate description of ionic systems — •Oliver Böhm[1], Stephan Pfadenhauer[1], Roman Leitsmann[1], Philipp Plänitz[1], and Michael Schreiber[2] — [1]AQcomputare GmbH, Annabergerstr. 240, 09125 Chemnitz — [2]Institut für Physik, Technische Universität Chemnitz, 09107 Chemnitz

We present a powerful extension of the reactive force field method ReaxFF which we call ReaxFF+ . We have implemented a new charge equilibrium scheme which takes into account different bond types yielding different screening factors. The main advantage of this procedure is the correct distinction and description of covalent and ionic bonds. Therefore, it is the only force field that allows reactive molecular dynamic simulations in ionic gases and liquids.

CPP 35.12 Wed 12:45 H51

ReaxFF+ II - highly efficient parametrization methods for the ReaxFF+ at the example of the hydrolysation of aluminosilicates — Oliver Böhm[1], Stephan Pfadenhauer[1], •Roman Leitsmann[1], Philipp Plänitz[1], and Michael Schreiber[2] — [1]AQcomputare GmbH, Annabergerstr. 240, 09125 Chemnitz — [2]Institut für Physik, Technische Universität Chemnitz, 09107 Chemnitz

One of the biggest challenges for using force fields is to find a suitable parametrization according to the chemical or physical problem. Especially in the ReaxFF+ method several hundred parameters have to be fitted. Therefore, the development of efficient optimization methods is the key for a successful application of reactive force fields in general and of the ReaxFF+ method in particular. We present a fast multidimensional optimization method which is parallelized using OpenMP. Moreover, we introduce an automatic training scheme which allows a continuous improvement of the training set as well as the identification of critical properties and non fittable properties. The method will be demonstrated by the example of the hydrolisation of aluminosilicates.