

CPP 7: Interfaces and Thin Films II

Time: Monday 14:00–17:30

Location: ZEU 114

CPP 7.1 Mon 14:00 ZEU 114

Cracking in thin polymer films promoted through physical ageing — ●MITHUN CHOWDHURY¹, CHRISTOPHE CALERS¹, ARNOLD CHANG-MOU YANG³, ULLRICH STEINER^{2,4}, and GÜNTER REITER^{1,2} — ¹Physikalisches Institut, Albert-Ludwigs-Universität Freiburg, 79104, Freiburg, Germany — ²Freiburg Institute for Advanced Studies (FRIAS) — ³Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan — ⁴Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK

Dynamics of polymers in ultrathin films is a long standing yet ever stimulating topic in the arena of polymer physics. Being inspired by occasionally observed cracking of such films during spin-coating, we performed systematic studies on the influence of film preparation and physical ageing at temperatures close but below the glass transition. We observed the growth of cracks after ageing and cooling the films to room temperature. Hierarchical patterns of interconnecting cracks were formed. AFM inspection showed nano/micro-structures of voids and fibrils within the cracks, indicating plastic deformation similar to crazing. We tentatively suggest that physical ageing of such films causes segmental relaxations of non-equilibrated polymer chains, introducing a gradient in lateral tension within the film in the direction normal to the film surface. Considering the possibility of generating strong mechanical tension at the film surface due to the formation of a 'crust' during film preparation, we may have to consider two antagonistic origins for crack growth: gradients in stresses induced by film preparation and amplification of such gradients during physical ageing.

CPP 7.2 Mon 14:15 ZEU 114

Free volume and aging in polymers of intrinsic microporosity (PIM) — ●STEPHAN HARMS¹, KLAUS RÄTZKE¹, FRANZ FAUPEL¹, WERNER EGGER², LUCA RAVELLI², NHAMO CHAUKURA³, and PETER BUDD³ — ¹Christian-Albrechts University at Kiel, Institute for Materials Science - Multicomponent Materials, 24143 Kiel — ²University of Armed Forces, 85577 Neubiberg — ³University of Manchester, Manchester M13 9PL, UK

Recently developed polymers of intrinsic microporosity (PIM) are suitable candidates as state-of-the-art gas separation membranes. However, as thin films, like other high free volume polymers, they can undergo aging which means that permeability and free volume become time-dependent and are reduced after prolonged storing and operation time. To investigate the time dependence of free volume, positron annihilation lifetime spectroscopy (PALS) at the pulsed low energy positron system (PLEPS) at FRM II has been performed. The PLEPS setup allows the measurement of depth profiles of the free volume for thin film samples. PIM films of different thickness and preparation method were investigated at two aging times. For all samples we could detect a time dependent decrease of the free volume compare to the bulk reference value. Samples with thickness ≥ 1300 nm do not show a homogeneous reduction of free volume but a steep gradient to the surface of the film. These experiments give valuable information for understanding aging phenomena in high free volume materials.

CPP 7.3 Mon 14:30 ZEU 114

The Young's Modulus of Polyelectrolyte Multilayer: Influence of Charge Density and Ambient Water Vapours — ●RALF KÖHLER^{1,2}, INGO DÖNCH³, PATRICK OTT⁴, ANDRÉ LASCHEWSKI⁴, and ANDREAS FERY⁵ — ¹TU Berlin, Dept. Applied Physical Chemistry, 10623 Berlin — ²HZB Berlin, Dept. Soft Matter, 14109 Berlin — ³Max Planck Institute of Colloids and Interfaces, Dept. Interfaces, 14424 Potsdam — ⁴University of Potsdam, Applied Polymer Chemistry, 14476 Potsdam — ⁵University of Bayreuth, Physical Chemistry II, 95440 Bayreuth: Germany

Polyelectrolyte Multilayers (PEM) are polymer films, self-assembled by consecutive adsorption of oppositely charged polyions. Our study addresses the impact of the internal interactions in the PEM on the macroscopic mechanical behavior. The strategy is to vary the ionic interactions by using polycations of different charge densities (ChD). Furthermore the internal interactions are modified by changing the water content in the PEM by a systematic variation of the ambient relative humidity (RH). PEM of sub-micrometer thickness are prepared in Layer-by-Layer spraying technique on flexible sheets of silicone-rubber.

The used polyions are PSS and PDADMAC-derivatives of different ChD. The E-modules are determined with the SIEBIMM-method. We obtained E-Moduli in the range from 0.3 to ca 1.5MPa. Basically for a higher-ChD PEM the E-Modulus is higher. But with increasing RH the PEMs soften until their E-Moduli coincide. Apparently the ionic interactions rule the mechanics in the first place but the incorporated water is able to moderate the E-Moduli over a wide range.

CPP 7.4 Mon 14:45 ZEU 114

Supported Polyelectrolyte Multilayer under Mechanical Stress: Sequential Change of the Internal Structure — ●JOHANNES FRÜH¹, ADRIAN RÜHM², HELMUTH MÖHWALD¹, RUMEN KRASTEVA³, and RALF KÖHLER^{4,5} — ¹MPI of Colloids and Interfaces, Dept. Interfaces, 14424 Potsdam — ²MPI for Metal Research at FRM-2, 85747 Garching — ³NMI at the University of Tübingen, 72770 Reutlingen — ⁴TU Berlin, Dept. Chemistry: Applied Physical Chemistry, 10623 Berlin — ⁵HZB Berlin, Dept. Soft Matter, 14109 Berlin. Germany

Polyelectrolyte Multilayer (PEM) are composite materials build-up of alternating layers of organic polyions of opposite charge. We study the changes of the internal structure of mechanically loaded PEM on molecular level. The PEM are prepared in layer-by-layer technique on solid substrates using PSS and PDADMAC as polyions. Small elongations ($\epsilon < 0.2\%$) are studied with neutron and X-ray reflectivity on deformed PEM-coated glass slides. We observe an increase of the film thickness upon stretching. This might be a result of a formation of *molecular cavities* in the PEM. Large elongations ($\epsilon \sim 10\%$) are investigated with fluorescence spectroscopy on Pyrene-labelled PEM on silicone-rubber substrates. An irreversible molecular decoiling is observed upon stretching. When the limit of plastic deformation is exceeded, i.e. almost full decoiling, macroscopic cracks appear, indicating the destruction limit of the PEM. Our Study on the molecular response on external mechanical stress allows for new insights into internal processes in PEM, e.g. molecular decoiling and the creation of defects.

CPP 7.5 Mon 15:00 ZEU 114

Interdiffusion in Polyelectrolyte Multilayers during Film Formation — ●OLAF SOLTWEDEL¹, OXANA IVANOVA¹, PETER NESTLER¹, RALF KÖHLER^{2,3}, and CHRISTIANE A. HELM¹ — ¹Inst. für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, D-17487 Greifswald — ²Helmholtz-Zentrum für Materialien und Energien, Hahn-Meitner-Platz 1, D-14109 Berlin — ³Stranski-Laboratorium für Physikalische und Theoretische Chemie, TU Berlin, Strasse des 17. Juni 112, D-10623 Berlin

Using neutron reflectivity, the internal structure of polyelectrolyte multilayers is described on the nanoscale. The polyanion is poly(styrenesulfonate) (PSS), and the polycation is poly(allylamine hydrochloride) (PAH) or poly(diallyldimethylammonium chloride) (PDADMAC). Each film consists of a protonated and a deuterated block, built from x protonated and y deuterated polycation/polyanion bilayers, respectively. The number of bilayers $N = x + y$ is kept constant; the position of the interface between the blocks is varied systematically. The internal roughness is smallest next to the film/air interface and increases with the number of bilayers away from the film/air interface until an equilibrium value is reached. For PDAMAC/PSS films, the diffusion constant increases with the PDADMAC polymer length, therefore the interdiffusion is attributed to stress relaxation during deposition. The equilibrium internal roughness increases with PDADMAC polymer length and the salt concentration in the deposition solution. However, the number of polyanion/polycation layer pairs necessary to achieve the equilibrium internal roughness depends nonmonotonically on the salt concentration.

CPP 7.6 Mon 15:15 ZEU 114

The structure of the liquid-liquid water-CO₂ interface during hydrate formation — ●JULIA NASE¹, FELIX LEHMKÜHLER², MICHAEL PAULUS¹, LARS BÖWER¹, SEBASTIAN TIEMEYER¹, SEBASTIAN HOLZ¹, and METIN TOLAN¹ — ¹Fakultät Physik/DELTA, TU Dortmund, 44221 Dortmund — ²DESY, Hasylab, 22607 Hamburg

Hydrates are ice-like inclusion compounds with gaseous guest molecules in water cages. In recent years, they have incited the interest

of researchers due to both their importance in oil industry (pipeline blockage) and as a promising possibility for CO₂ sequestration. Despite the increased interest, the formation process on a molecular level is still poorly understood. MD simulations predict the existence of different pre-structures, but an experimental proof is still pending. Hydrate formation is generally thought to be initiated at interfaces. We report on a x-ray reflectivity study of the liquid-liquid water-CO₂ interface. This technique was shown to be a reliable tool to determine the thickness and roughness of interfaces and thin layers.

Previous studies on the liquid-gas interface in the theoretical hydrate stability region could not confirm the existence of precursor structures, however, a macroscopic hydrate phase did not occur. In our present study, the high offer in CO₂ molecules at the liquid-liquid interface resulted in a macroscopic hydrate formation. Results on the roughness of this interface beyond the stability region, an information that has been lacking so far, and on structural changes just before the appearance of a macroscopic hydrate phase are presented in this talk.

15 min. break

CPP 7.7 Mon 15:45 ZEU 114

Dynamics of complex systems in the proximity of a solid interface — ●SULIVAN D.B. VIANNA¹, MARKUS A. PLUM¹, HATICE DURAN^{1,2}, HANS-JÜRGEN BUTT¹, and WERNER STEFFEN¹ — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — ²TOBB Economy and Technology University 43, 06560 Ankara, Turkey

An experimental investigation of the effect of solid surfaces (e.g Au) on the motion of colloids and dynamics of polymers is reported. The novel experimental approach for probing the interphase in a system close to the solid interface is the use of surface plasmons or optical waveguide modes as incident fields in resonance enhanced dynamic light scattering (REDLS) or waveguide enhanced dynamic light scattering (WEDLS). Our incident fields are localized at the surface. For surface plasmons the penetration depth is typically 200 nm and for the waveguides the penetration depth can be tuned typically from 100 to 1000 nm. The influence of a nearby interface on translational and rotational diffusion of colloids in solution is explored. Due to the localization and hence strong enhancement of the field in the surface plasmon or the evanescent part of the waveguides utilized, we are able to study ultrathin polymer films, i.e. dynamic processes above the glass transition.

CPP 7.8 Mon 16:00 ZEU 114

Characterization of spectral diffusion and its application to probe thin polymer films — ●DANIELA TÄUBER¹, STEFAN KRAUSE¹, BEATRIZ ARÁOZ², PEDRO F. ARAMENDÍA², and CHRISTIAN VON BORCZYKOWSKI¹ — ¹nanoMA, TU-Chemnitz, Institut für Physik, Germany — ²FCEN, Universidad Buenos Aires, Argentina

Dye molecules with a large solvent shift are used to probe local properties in thin polymer films. Upon excitation with the 488 nm line of an Argon-ion-laser, the emission spectra show spectral diffusion: small temporal fluctuations and larger jumps. In analogy to anomalous spatial diffusion we use a newly developed tool[1] to characterize this spectral diffusion: Probability distributions of spectral diffusivities [2].

This method is applied to analyze different thin poly-n-alkyl methacrylate films on Si wafers with 100 nm SiO_x.

[1] M. Bauer, M. Heidernätsch, D. Täuber, C. von Borczykowski, and G. Radons, *Diffusion Fundamentals*, 11, 2009, 104.

[2] S. Krause, P.F. Aramendía, D. Täuber, C. von Borczykowski, *Freezing Single Molecule Dynamics on Interfaces and in Polymers*, PCCP, accepted.

CPP 7.9 Mon 16:15 ZEU 114

Measuring the Elasticity of Polymer Films with AFM Nanoindentation — ●CAGRI ÜZÜM, ANNA BURMISTROVA, MARCEL RICHTER, JOHANNES HELMWIG, DMITRY VOLODKIN, and REGINE V. KLITZING — Stranski-Laboratorium, Institut für Chemie, TU Berlin, Strasse des 17.Juni 124, 10623 Berlin, Germany

Mechanical properties of polymeric films and microparticles have to be revealed once they are to be used in biological applications [1]. For submicron structures, the (visco)elasticity can be measured by means of AFM nanoindentation. Together with its nanoscale imaging ability, this makes the AFM a unique technique in the relevant area.

In this contribution, elastic properties (Young's modulus) of poly(L-lysine)/hyaluronan (PLL/HA) thin films as well as other hydrogel

films/particles were investigated. Young's modulus was observed to depend strongly on the temperature and the cross-linker density while the film thickness itself had only a minor effect. Either colloidal probes or blunt tips were used as nanoindenters. The well-known problem of determining the exact indenter-sample contact point was tried to be overcome by various data handling processes [2].

[1] Picart, C., Senger, B., Sengupta, K., Dubreuil, F., Fery, A. *Colloids Surf., A* 303, 30-36 (2007)

[2] Dimitriadis, E.K., Horkay, F., Maresca, J., Kachar, B., Chadwick, R.S. *Biophys. J.* 82, 2798 (2002)

CPP 7.10 Mon 16:30 ZEU 114

Microcantilever sensors for monitoring microdrop evaporation of pure liquids and binary mixtures — ●ELMAR BONACCURSO¹ and CHUANJUN LIU^{1,2} — ¹Center of Smart Interfaces, TU-Darmstadt, Germany — ²Max Planck Institute for Polymer Research, Mainz, Germany

We describe in detail a nonimaging technique [1] that allows the measurement of the mass, the radius, and the contact angle of evaporating sessile microdrops of pure liquids and binary mixtures. The microdrops were deposited onto hydrophobized silicon microcantilevers whose bending and resonance frequency were monitored during drop evaporation. We verify the laws of evaporation kinetics for microdrops with diameters from 80 down to 10 μm.

The evaporation of mixtures of water/ethanol drops confirmed previous results with millimeter sized drops. N,N-dimethylformamide drops undergo a transformation from an initial spherical shape to a thin film. Flattening of the drop causes a slowdown of the evaporation kinetics at the end. Two concurring factors are at its origin: the rising disjoining pressure stabilizes the thin liquid film and the increasing radius of curvature of the drop reduces the vapor pressure [2].

[1] Bonaccurso E., Butt, H.-J., *J. Phys. Chem. B* 109, 253 (2005).
[2] Liu C.J. & Bonaccurso E., *Rev. Sci. Instrum.* 81, 013702 (2010).

CPP 7.11 Mon 16:45 ZEU 114

Laser-assisted atom probe tomography of polyelectrolyte multilayers — ●ANDREAS STOFFERS and GUIDO SCHMITZ — Institut für Materialphysik, Westf. Wilhelms-Universität, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany

Atom probe tomography (APT) is a well established tool for analyzing metals at an atomic scale. In order to explore the possibilities of analyzing polymer materials by Pulsed-laser atom probe tomography (PLAP), we have chosen the model case of polyelectrolyte multilayers (PEM). PEMs are adsorbed step by step as a multilayer of poly-anions and poly-cations at the apex of sharp gold tips. This self-assembly is driven by electrostatic forces, where every adsorbed layer induces a charge inversion of the surface. Macroscopic charge neutrality requires an exact 1:1 stoichiometry of polycation and polyanion charges or the presence of counterions within the layer. The presence of counterions in PEMs is controversially discussed and laser-assisted atom probe tomography seems to be an ideal tool to answer this question. By means of laser-assistance it is indeed possible to chemically analyze multilayers of poly(acrylic acid), poly(diallyl dimethyl-ammonium chloride), poly(styrene sulfonate) and poly(allylamine hydrochloride). In all cases the mass spectra are complex, characterized by peaks of multiple fractions of different molecular mass. Different polymer-types might be distinguished based on the intensity ratio between characteristic mass peaks. The proven amount of counterions is obviously negligible. In addition, a 3D reconstruction of a self assembled monolayer (1H,1H,2H,2H-Perfluorodecanethiol) will be presented.

CPP 7.12 Mon 17:00 ZEU 114

Phosphocholine Monolayer Solidification due to Oxygen Radicals — ●ANDREAS GRÖNING^{1,2}, HEIKO AHRENS¹, THOMAS ORTMANN¹, FRANK LAWRENZ¹, GERALD BREZESINSKI³, FRITZ SCHOLZ², and CHRISTIANE A. HELM¹ — ¹Inst. für Physik, Uni Greifswald, Felix-Hausdorff-Str. 6, D-17487 Greifswald — ²Inst. für Biochemie, Uni Greifswald, Felix-Hausdorff-Str. 4, D-17487 Greifswald — ³MPI KGF, D-14476 Potsdam

The reaction of 1,2-dipalmitoylphosphatidylcholine (DPPC) with hydroxyl-radicals has been investigated using monolayer techniques: isotherms, infrared absorption reflection spectroscopy (IRRAS), grazing incidence X-ray diffraction (GIXD), X-ray reflection and fluorescence microscopy. The DPPC monolayer undergoes a transition from a liquid-expanded to a liquid-condensed state characterized by a plateau region. The DPPC monolayer is attacked in the coexistence region and in the liquid-condensed state with different Fenton concentrations.

With increasing Fenton concentration, the plateau region is shifted to a lower surface pressure; eventually it disappears. With higher Fenton concentration, the molecular area in the liquid-condensed phase is decreased. IRRAS experiments indicate a decomposition of the choline group. After Fenton attack, GIXD shows a decrease of the tilt angle, an increase of translational (by 50%) and orientational order which demonstrates monolayer solidification. The highly compressed monolayer exhibits nearly hexagonal order. Additionally, fluorescence microscopy shows that some DPPC domains fuse and new domains nucleate. At zero pressure, solid domains remain.

CPP 7.13 Mon 17:15 ZEU 114

Effect of oppositely charged hydrophobic additives (alkanoates) on the stability of C₁₄TAB foam films — •NATASCHA SCHELERO¹, REINHARD MILLER², and REGINE VON KLITZING¹ —

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Liquid foams are frequently applied in daily life and industrial processes (e.g. cleaning agents, personal care products and fire-fighting). In most of the applications mixtures of several components are used. Model systems for such applications are thin liquid films. Within this work the impact of the hydrophobicity of oppositely charged additives on the stability of C₁₄TAB foam films are investigated. Furthermore, the surface properties of the mixed systems are described to gain a general understanding about the surface characteristics. Since C₁₄TAB and alkanates are oppositely charged, the question arises whether charge reversal at the film surfaces occurs and how it depends on the chain length of the alkanate.