

SYMR 7: Biopolymers and Biomaterials

Time: Wednesday 14:00–17:30

Location: H37

Topical Talk

SYMR 7.1 Wed 14:00 H37
Atomic Layer Deposition (ALD) as a Versatile Tool for Nanoscience — ●MATO KNEZ¹, SEUNG-MO LEE¹, ADRIANA SZEGHALMI¹, YONG QIN¹, ECKHARD PIPPEL¹, CHRISTIAN DRESBACH², and GERD HAUSE³ — ¹Max-Planck-Institute of Microstructure Physics, Halle, Germany — ²Fraunhofer Institute IWM, Halle, Germany — ³Martin-Luther-University, Halle-Wittenberg, Germany

Atomic layer deposition (ALD) is a thin film deposition technique which was developed in the 1970s to meet the needs for processing thin film electroluminescent displays (TFEL). Being a non-line-of-sight deposition technique, ALD allows for good coating conformality even with 3D nanostructured substrates or structures with a high aspect ratio together with a good capability for upscaling. An increasing number of researchers make use of the precision of ALD for fabrication or functionalization of nanostructures, optical coatings, catalytically active coatings, encapsulation, corrosion protection or even infiltration of soft materials with metals.

The most recently evolving application of ALD deals with the modification of mechanical properties of soft materials after infiltration of metals by ALD. Although the detailed chemistry behind the approach is not yet understood, biological materials, such as spider silk or collagen, can positively change their mechanical properties after being treated with pulsed vapors of metal precursors. The toughness of such materials increased by up to 10-fold, outperforming most manmade materials.

SYMR 7.2 Wed 14:30 H37
Interplay between nanostructure and mechanical properties in natural and artificial polymer fibers — ●PERIKLIS PADOPOULOS, ROXANA ENE, and FRIEDRICH KREMER — Universität Leipzig, Institut für Experimentelle Physik I

The comparison of mechanical with infrared spectroscopy can be used to explore the multi-level nanostructure of semi-crystalline polymers. In this study we attempt to determine the interconnection of the nanocrystal and amorphous phases in two states of spider dragline silk, native and supercontracted with water, and compare it with artificial systems, such as polyamide 6. Crystal stress can be measured with a high time resolution through the analysis of frequency shifts of absorption bands, while varying mechanical fields are applied. The results show that in both states of silk a serial arrangement between the crystalline and amorphous phase dominates the nanostructure. Polyamide 6 films and electrospun fibers have a similar morphology. In silk, however, water can break the hydrogen bonds of the amorphous chains, and, in combination with hydrophobic effects, it induces the formation of a physical network in the amorphous phase. This network increases in stiffness, until a stress limit is reached. At higher stress, the nanostructure of supercontracted silk is irreversibly transformed to one similar to native silk. This enables one to make a complete description of the mechanical properties of silk in both states, by taking into account the energy required to break these bonds in the previous structural model that assumed a pre-strain distribution of worm-like amorphous chains.

SYMR 7.3 Wed 14:45 H37
Interplay between morphology and mechanical properties of silk investigated by X-ray microdiffraction on single fibers combined with *in situ* tensile tests — FLORIAN KUNZE¹, IGOR KRASNOV¹, ●CHRISTINA KRYWKA¹, MARTIN MÜLLER², MALTE OGURRECK², MANFRED BURGHAMMER³, and CHRISTIAN RIEKEL³ — ¹IEAP der CAU, Kiel, Germany — ²GKSS Forschungszentrum, Geesthacht, Germany — ³ESRF, Grenoble, France

Silk is a natural composite material known to have special mechanical properties. Produced by the silkworm (*Bombyx mori*) it provides high tensile strength and elasticity combined with low weight. It is extremely stretchable with a high degree of toughness and great elongation before breaking. It would be highly desirable to produce artificial fibers with such mechanical properties. Silk fibers have a semicrystalline morphology, which means they are composed of a crystalline and a disordered phase. To determine the characteristics of the mechanical properties and the composition of the silk fibers we are using a combination of *in situ* tensile tests and X-ray microdiffraction.

Utilizing the Microfocus Beamline ID13 at the European Synchrotron Radiation Facility (ESRF) it was possible to execute first Wide Angle X-Ray Scattering (WAXS) measurements combined with *in situ* stretching experiments on single silk fibers. The detected effects are similar to those of measurements on small bundles of silk fibers. Overall we have observed a strong interplay between the morphology of silk and the fibers' mechanical properties.

SYMR 7.4 Wed 15:00 H37
SANS on Silkworm Silk under Tensile Stress — ●MALTE BLANKENBURG, MARTIN MÜLLER, and MELISSA SHARP — GKSS Research Centre Geesthacht, Germany

Natural silks exhibit extraordinary mechanical properties, combining high tensile strength with a high elongation at failure. Due to their remarkable mechanical properties and potential medical applications the ability to synthesize silk is still a matter of debate. Silkworm silk fibroin is a semicrystalline nanocomposite, with ordered regions (β -sheet protein nanocrystals) embedded in a softer, amorphous matrix of disordered material [1]. Therefore the contrast between matrix and crystallites could be improved for neutron experiments by deuterating the silk. SANS experiments performed *in situ* during tensile stretching experiments at the SANS-2 instrument at the GKSS showed a peak in the meridional direction of the scattering pattern of deuterated silkworm silk. Since this peak moves to lower q-values by stretching the fibres, an enlargement of the scattering structure could be observed. It was shown before in X-ray experiments [2], that the crystals in the matrix are stretched proportionally to the applied external tensile stress but by a factor of 4 to 18 less than the macroscopic strain. As the percentage elongation is nearly the same for fibre and scattering structure, the scattering objects are not the crystals but rather the ensemble of crystals and disordered material in a periodic arrangement, reflecting the mean distance between crystals in fibre direction.

[1] Y. Shen *et al.*; *Macromolecules* **31** (1998), 8857

[2] I. Krasnov *et al.*; *Phys. Rev. Lett.* **100** (2008), 048104

SYMR 7.5 Wed 15:15 H37
Rheological properties of wheat dough and corresponding model systems — ●BIRGITTA SCHIEDT and THOMAS VILGIS — Max-Planck Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz,

Wheat dough is a complex material exhibiting non-linear rheological properties, whose underlying molecular origin is still not fully understood. To dumb it down, the macropolymer gluten (protein) present in wheat flour, forms upon hydration and energy input (kneading) an elastic network, into which starch granules are embedded as filler particles. In order to gain more information about the dough formation process as well as the influence of network (protein) - filler (starch) interactions on the overall behaviour of the dough, rheological measurements and microscopy studies are conducted.

The systems investigated include natural wheat dough made from flour and water at different water contents as well as artificial model dough. The latter consists of gluten and various amounts of starch or other filler particles such as glass beads or silica with different chemical surface modifications. The resulting different types of interactions between the starch and filler particles provide deeper insight about the physics of the temporary network.

15 min. break

SYMR 7.6 Wed 15:45 H37
Influence of humidity on casein films - an *in situ* investigation with a combination of μ GISAXS and imaging ellipsometry — ●VOLKER KÖRSTGENS¹, ROBERT MEIER¹, JOHANNES WIEDERSICH¹, JAN PERLICH², STEPHAN VOLKHER ROTH², and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München Physikdepartment LS E13, James-Franck-Str. 1, D-85747 Garching — ²HASYLAB at DESY, Notkestr. 85, D-22607 Hamburg

Glues based on casein are known since ancient Egypt. Nowadays casein-based adhesives are being used in versatile labeling applications. Already pure casein shows adhesive properties depending on humidity as shown with tack experiments in this work. The structural changes of thin casein films are investigated *in situ* with a combination of μ GISAXS (grazing incidence small angle x-ray scattering with

a μm -sized beam) and imaging ellipsometry. With this new instrument [1] built up at HASYLAB, DESY, Hamburg, a comprehensive sample characterization is possible including local film thickness and optical properties combined with structural information with a spatial resolution depending on the size of the x-ray beam. Swelling and drying cycles with casein thin films are performed in situ and the relation between structure and adhesive properties is discussed.

[1] V. Körtgens et al., *Anal. Bioanal. Chem.*, DOI 10.1007/s00216-009-3008-1

This project is financially supported by BMBF grant 05KS7WO1.

SYMR 7.7 Wed 16:00 H37

Biofunctionalization of Diamond Microelectrodes — ●ANDREAS ADAM REITINGER¹, NAIMA AURELIA HUTTER², SIMON QUARTUS LUD¹, GERHARD RICHTER², RAINER JORDAN², MARTIN STUTZMANN¹, and JOSE ANTONIO GARRIDO¹ — ¹Walter Schottky Institut, TU München, Germany — ²WACKER-Chair of Macromolecular Chemistry, TU München, Germany

In this work we present two main routes for the biofunctionalization of nanocrystalline diamond films, aiming at the application of diamond microelectrodes as amperometric biosensors. We report on direct covalent grafting of biomolecules on nanocrystalline diamond films via diazonium monophenyls and biphenyls as well as other linker molecules, forming self-assembled monolayers on the diamond surface. Monolayers with different functional head groups have been characterized. Patterning of the available functional groups using electron beam-induced chemical lithography allows the selective preparation of well-localized docking sites for the immobilization of biomolecules. Furthermore, polymer brushes are expected to enable novel paths for designing more advanced biosensing schemes, incorporating multifunctional groups and a higher loading capacity for biomolecules. Here, we will focus on the preparation of polymer grafts by self-initiated photografting and photopolymerization. Further chemical modification of the grafted polymer brushes results in the introduction of additional functional molecules, paving the way for the incorporation of more complex molecular structures such as proteins. In a comparative study we investigate the advantages and disadvantages of both approaches.

SYMR 7.8 Wed 16:15 H37

Real-time in-situ study of oligo(ethylene glycol) reordering dynamics and immersion effects using PMIRRAS — ●STEFAN ZORN, ALEXANDER GERLACH, and FRANK SCHREIBER — Institut für Angewandte Physik, Universität Tübingen, Germany

Owing to their high importance in biological and medical applications, e.g. as tethering group for specific binding or, importantly, for passivation of surfaces against unspecific protein absorption, oligo(ethylene glycols) have been the subject of extensive studies. SFG and IR studies revealed strong interactions of water and SAM and strong conformational changes [1]. However, the exact mechanism of protein repulsion is still not fully understood. Here we present a real-time in-situ study of the reordering of the SAM structure during its growth in solution. Using a home build liquid cell with a very thin solution layer (ca. 1 μm) we were able to monitor changes in conformation in real time in aqueous environment. With increasing surface coverage there is a change from an amorphous structure with mixed all-trans and helical conformation to a high ordered structure with predominantly helical conformation. A comparison with spectra measured in air shows differences in conformation due to the interaction with water which are more pronounced for lower surface coverage. We also monitored the stability of the SAM over long periods of time and the change in conformation with increasing temperature in solution. Our results shed new light onto the role of water on the structure and protein resistance of OEG SAMs and help to explain the conflicting results in various recent studies.

[1] M.W.A. Skoda et al., *Langmuir* 23 (2007) 970.

SYMR 7.9 Wed 16:30 H37

Protein-resistant polymer coatings based on surface-

adsorbed poly(aminoethyl methacrylate)/poly(ethylene glycol) copolymers — ●LEONID IONOV¹, ALLA SYNYTSKA¹, ELISABETH KAUL¹, STEFAN DIEZ², and MANFRED STAMM¹ — ¹Leibniz-Institut fuer Polymerforschung Dresden e.V., Dresden, Germany — ²Max-Planck-Institute of Molecular Cell Biology and Genetics, Dresden, Germany

We report on the protein-resistant properties of glass substrates coated with novel copolymers of 2-aminoethyl methacrylate hydrochloride and poly(ethylene glycol) methyl ether methacrylate (AEM-PEG). In comparison to currently available protein-blocking polymer systems, such as poly-L-lysine - poly(ethylene glycol), silane-based poly(ethylene glycol) and poly(ethylene glycol) brushes prepared by surface-initiated polymerization, the proposed AEM-PEG offers the combined advantages of low cost, simplicity of use and applicability in aqueous solutions. We demonstrate the capability of AEM-PEG to block the surface binding of globular proteins (tubulin), their assemblies (microtubules) and functional motor proteins (kinesin-1). Moreover, we demonstrate the applicability of AEM-PEG for surface patterning of proteins in microfluidic devices.

SYMR 7.10 Wed 16:45 H37

Protein folding monitored at six different magnetic field strengths — ●MICHAEL KOVERMANN and JOCHEN BALBACH — Institut für Physik/Fachgruppe Biophysik, Martin-Luther-Universität Halle-Wittenberg, Betty-Heimann-Straße 7, D-06120 Halle/Saale, Germany

The folding mechanism of an elongated polypeptide chain into its native three dimensional structure is still of high common interest. Using NMR spectroscopy we are able to follow the permanently occurring folding and unfolding of the cold shock protein B from *Bacillus subtilis*, *BsCspB*, in equilibrium and kinetically on a ms timescale.

So-called NMR relaxation dispersion experiments are able to monitor these dynamic events on a ms - to - μs timescale at atomic resolution. We performed these kind of experiments at six different magnetic field strengths to get reliable results. As the folding (and the unfolding) rate of a protein should be independent of the external magnetic field strength we fitted this kinetic parameter in a global procedure to the NMR relaxation data. In addition to these folding rates we get out structural and thermodynamic information by these dynamic NMR experiments.

Topical Talk

SYMR 7.11 Wed 17:00 H37

Recognition dynamics and kinetics for ubiquitin — ●CHRISTIAN GRIESINGER — MPI for Biophysical Chemistry, Goettingen, Germany

We measured residual dipolar couplings in a large number of alignment media for ubiquitin and derived an ensemble with the EROS method that reflects motion up to the microsecond time scale. The ensemble fits very well the NMR parameters used for the refinement and cross validates other unused NMR parameters such as J-couplings and other dipolar couplings. The ensemble has an rmsd of approximately 1Å and shows large fluctuations in loops as well as in secondary structure elements. The ensemble reflects mainly motion on the previously inaccessible time scale between ns and microseconds. Its implications for molecular recognition will be discussed. We have further measured the time scale of the recognition dynamics and find a previously unobservable sub- β -peak in dielectric relaxation spectroscopy in solution that can be explained by a modulation of the ion conductance by the conformational ensemble. From the temperature dependence of this effect, one can expect to slow down the dynamics in supercooled solution to approximately 50 μs . Indeed, relaxation dispersion measurements in supercooled solution reveal that the time scale of major conformational interconversions is 50 to 100 μs and that the above mentioned ensembles predict correctly the relaxation dispersion data. Furthermore, correlated motion in the ensemble has been quantified experimentally with cross correlated relaxation. We find that the above mentioned rdc derived ensembles agree much better with the cross correlated relaxation data than ensembles that reflect only individual motion.