

## CPP 34: P6: Biomaterials and Biopolymers

Time: Tuesday 14:00–16:00

Location: Poster C

CPP 34.1 Tue 14:00 Poster C

**Nanoscale viscoelastic properties of hydrated collagen-based films probed with static and dynamic AFM** — ●MANUEL UHLIG, EIKE-CHRISTIAN SPITZNER, and ROBERT MAGERLE — Chemische Physik, Fakultät für Naturwissenschaften, TU Chemnitz, 09107 Chemnitz, Germany

The amount and distribution of water in collagen-based films determines their mechanical properties and shape. We investigate the effect of hydration on reconstituted collagen fibrils and gelatin films (i.e., denaturated collagen) by controlling the relative humidity of the surrounding air. Measurements are performed with atomic force microscopy (AFM) including static and dynamic force spectroscopy as well as stress relaxation experiments. By combining these methods, the mechanical response is characterized over a wide range of time scales. We obtain maps of the specimen's viscoelastic properties in the near-surface region. For each material, one single AFM probe (Si, with a force constant of 15 N/m) is used during the entire experiment, thus allowing comparison of different tip-sample interaction mechanisms. Gelatin films show a distinct, humidity induced transition from a stiff to a compliant, viscoelastic state. In contrast, collagen fibrils soften more gradually with increasing relative humidity.

CPP 34.2 Tue 14:00 Poster C

**A pressure-dependent FTIR-spectroscopy study on spider silk's non-equilibrium nanostructure** — ●ARTHUR MARKUS ANTON<sup>1</sup>, CHRISTOF GUTSCHE<sup>2</sup>, WILHELM KOSSACK<sup>1</sup>, and FRIEDRICH KREMER<sup>1</sup> — <sup>1</sup>Institut für Experimentelle Physik I, Universität Leipzig, Germany — <sup>2</sup>Poliklinik für Zahnerhaltung und Parodontologie, Universität Leipzig, Germany

To investigate the molecular structure and the interaction between internal and external constraints in spider silk a pressure dependent analysis by means of a diamond anvil cell (DAC) has been carried out. On the one hand, the spectral shift of a structure-specific IR-absorption band provides evidence of the inherent non-equilibrium nanostructure in spider silk, as composed of alanine-rich nanocrystals embedded in a glycine-rich and *prestressed* amorphous matrix [A. M. Anton et al., *Macromol.* **46** (2013)]. On the other hand, combining polarization-dependent IR-transmission and optical microscopy measurements allows for separating between order and disorder at macroscopic and microscopic scales for a variety of (bio)macromolecular fibers. Thus, on the example of spider silk the molecular order parameter of the alanine building blocks is determined and found to decrease reversibly by 0.01 GPa<sup>-1</sup> when varying the external hydrostatic pressure between 0 and 3 GPa [A. M. Anton et al., *manuscript submitted*].

CPP 34.3 Tue 14:00 Poster C

**Interactions of Radical Oxygen Species with Phosphatidylcholine Monolayers and Liposomes** — ●ANDREAS GRÖNING<sup>1</sup>, HEIKO AHRENS<sup>1</sup>, FRANK LAWRENZ<sup>1</sup>, THOMAS ORTMANN<sup>1</sup>, GERALD BREZESINSKI<sup>2</sup>, FRITZ SCHOLZ<sup>3</sup>, DORIS VOLLMER<sup>4</sup>, and CHRISTIANE A. HELM<sup>1</sup> — <sup>1</sup>Physik, Uni Greifswald, 17487 Greifswald, Germany — <sup>2</sup>MPI KGF, 14476 Potsdam, Germany — <sup>3</sup>Biochemie, Uni Greifswald, 17487 Greifswald, Germany — <sup>4</sup>MPIP, 55128 Mainz, Germany

During times of environmental stress (e.g., UV or heat exposure), levels of reactive oxygen species (ROS) can increase. This may result in significant damage to cell structures. Here we focus on the effect of hydroxyl radicals (produced by Fenton reaction) on model membranes. Combining isotherms, X-ray diffraction, X-ray reflection and IRRAS, we find a partial cleavage of the head group leading to a reduced head group size with negative charge for DPPC monolayers at the air/water interface. Free iron ions are produced by the Fenton reaction, they bind to the head group. Fluorescence microscopy showed immediate nucleation of new domains in the condensed phase, followed by solidification. Similar effects are observed with differential scanning calorimetry and confocal microscopy for DMPC liposomes. The use of EDTA in high excess to catch all free iron ions prevents the solidification of the monolayers and liposomes. The chemical changes of the lipids due to radical attack have no direct effect on the phase transition and solidification. Solidification and destruction of the model membranes after the Fenton reaction are attributed to the iron ions, which bind very strongly to the lipids after the radical attack.

CPP 34.4 Tue 14:00 Poster C

**Synchrotron Radiation- based FIR/THz spectroscopy for studying Membrane-targeting interactions of antimicrobial peptides** — ●ANDREA HORNEMANN<sup>1</sup>, ARNE HOEHL<sup>1</sup>, MICHAEL ANDERSCH<sup>1,2</sup>, PEGGY EMMER<sup>1</sup>, MICHAEL VOLLMER<sup>2</sup>, GERHARD ULM<sup>1</sup>, and BURKHARD BECKHOFF<sup>1</sup> — <sup>1</sup>Physikalisch-Technische Bundesanstalt, Berlin, Germany — <sup>2</sup>University of Applied Sciences in Brandenburg, Brandenburg, Germany

The development of new infrared radiation sources has initiated opportunities for exploring the molecular structure of many (bio-) materials in the far-infrared/terahertz spectral region. The identification of thin organic films derived from peptide layers at polymer/organic interfaces was performed by Synchrotron Radiation (SR-) based FTIR spectroscopy at PTB's Metrology Light Source. For bioanalytical applications, the FIR/THz spectroscopic technique offers a unique tool for a distinct identification of biochemical components by their vibrational spectra. Peptide films were studied in the spectral region from 400 cm<sup>-1</sup> to 5 cm<sup>-1</sup>. This spectral region complements the mid-infrared spectral range where molecules such as proteins deliver characteristic modes, and entails additional molecular information on torsion and bending modes of the carbon backbone and H-bonds of biomolecules. We discuss the signatures of different membrane-targeting antimicrobial peptides that display defined secondary-structure motifs. Our approach entails T-dependent studies between 298 K and 10 K.

CPP 34.5 Tue 14:00 Poster C

**An x-ray diffraction study of vulcanized fiber and paper exposed to hydrostatic pressure** — ●KARIN ESCH<sup>1</sup>, DOMINIK DUMKE<sup>2</sup>, MICHAEL PAULUS<sup>1</sup>, CHRISTIAN STERNEMANN<sup>1</sup>, JULIA NASE<sup>1</sup>, JULIAN SCHULZE<sup>1</sup>, JOHANNES MÖLLER<sup>1</sup>, KOLJA MENDE<sup>1</sup>, IRENA KIESEL<sup>1</sup>, THOMAS BÜNING<sup>1</sup>, SIMON WULLE<sup>1</sup>, SERGIUS JANIK<sup>1</sup>, HOLGER GÖRING<sup>1</sup>, DOROTHEE WIECZOREK<sup>2</sup>, and METIN TOLAN<sup>1</sup> — <sup>1</sup>Fakultät Physik / DELTA, Technische Universität Dortmund, D-44221 Dortmund, Germany — <sup>2</sup>Fakultät Maschinenbau, Technische Universität Dortmund, D-44221 Dortmund, Germany

Vulcanized fiber, consisting of cellulose, is a material of various applications. It is used as an insulator in electrical industry, and can be found in washers/gaskets and welding shields. As vulcanized fiber and paper are made from renewable resources, these materials gained increasing interest in recent years. A way to produce vulcanized fiber is parchmmentising. Raw paper is soaked with a ZnCl<sub>2</sub> solution, pressed, rested for a certain time, and washed out in steps of descending concentrations. Paper consists mostly of cellulose I<sub>α</sub> and I<sub>β</sub>. During the process of parchmmentising cellulose I transforms to cellulose II and changes the material's structure on a molecular level. Consequently, macroscopic properties change, e.g. the material becomes harder and stiffer. The underlying structural changes can be analysed by x-ray diffraction. We studied changes in the diffraction pattern of paper and vulcanized fiber at high hydrostatic pressure up to 4 kbar. An anisotropic reversible compression was found. The experiments were performed at beamline BL9 of the synchrotron lightsource DELTA, Dortmund.

CPP 34.6 Tue 14:00 Poster C

**AFM studies of adsorbed xylan on cellulosic materials** — ●CATERINA CZIBULA<sup>1,2</sup>, CHRISTIAN GANSER<sup>1,2</sup>, ALBRECHT MILETZKY<sup>2,4</sup>, STEFAN SPIRK<sup>3</sup>, ROBERT SCHENNACH<sup>2,5</sup>, and CHRISTIAN TEICHERT<sup>1,2</sup> — <sup>1</sup>Institute of Physics, Montanuniversität Leoben, Austria — <sup>2</sup>Christian Doppler Laboratory for Surface Chemical and Physical Fundamentals of Paper Strength, Graz University of Technology, Austria — <sup>3</sup>Institute for Chemistry and Technology of Materials, Graz University of Technology, Austria — <sup>4</sup>Institute for Paper- and Fibre Technology, Graz University of Technology, Austria — <sup>5</sup>Institute of Solid State Physics, Graz University of Technology, Austria

Xylan is the predominant hemicellulose in plants and wood. It is a byproduct in papermaking and the production of regenerated cellulose fibers. To find an additional use of xylan, its ability to positively influence mechanical properties of paper is investigated at the example of a variety of cellulosic substrates. The adsorption of xylan to amorphous cellulose thin films, viscose fibers, and paper fibers is studied. Atomic force microscopy (AFM) is employed to characterize the to-

pography of the samples and to analyze their surfaces. The size of the randomly distributed xylan aggregates varies between 20 nm - 30 nm. The shape, either globular or elongated, is dependent on the electrolyte concentration.

CPP 34.7 Tue 14:00 Poster C

**The adsorption of a cellulose binding module on cellulose surfaces** — ●SERGIO MAURI<sup>1</sup>, JIM PFAENDTNER<sup>2</sup>, MISCHA BONN<sup>1</sup>, and TOBIAS WEIDNER<sup>1</sup> — <sup>1</sup>Max Planck institute for polymer research, Mainz, Germany — <sup>2</sup>Dept. of chemical engineering, University of Washington, Seattle, US

The conversion of biomass, like other biological processes, is rate-controlled by interfacial phenomena. In the case of enzymatic biomass conversion, cellulose enzymes present specific carbohydrates binding modules (CBM) to provide an increase in concentration of enzyme sites near the cellulose interface. Here we propose to study the interaction of a CBM with cellulose surfaces by a combination of methods, to quantify the adsorption of CBM on cellulose surfaces and to elucidate the CBM/cellulose interfacial structure. We follow the concentration dependent adsorption kinetics of CBM on cellulose surfaces by means of QCM-D and we determine the Langmuir adsorption isotherm. On the same substrate we perform XPS to compare wet and dry adsorbed mass. We finally determine the orientation of the adsorbed protein on such cellulose surfaces by using sum frequency spectroscopy (SFG). SFG is a nonlinear optical technique which provides surface-specific vibrational spectra of sub-monolayers of interfacial molecules. SFG, in conjunction with simulation results, is well-suited for determining the orientation of CBM on cellulose surfaces.

CPP 34.8 Tue 14:00 Poster C

**Determination of Amylolytic Activity of Malts by Rheological Measurements** — ●JANYL ISKAKOVA, JAMILA SMANALIEVA, and ASYLBEK KULMYRZAEV — Kyrgyz-Turkish Manas University, Bishkek, Kyrgyzstan

Malting is the most important stage in the processing of the Kyrgyz traditional beverage Bozo. In current study, the amylase activities of maize, millet, wheat, and barley malts were investigated by rheological methods using cooked millet porridge as a substrate for enzymes.

The aim of this work has been to demonstrate the applicability of rheological measurements as alternative, rapid, safe for health and simple method for measuring amylolytic activity of grain malts. The standard colorimetric method for the determination of amylase activity was compared with rheological method. Millet porridge exhibited pseudoplastic behavior and the Ostwald-De-Waele was used as suitable fitting model. The highest amylolytic activity was found in barley malt and the lowest in maize malt. The rheological method is demonstrated to be advantageous, particularly with regard to speed, simplicity, no requirement for chemicals and possibility of the online monitoring of the structural changes.

CPP 34.9 Tue 14:00 Poster C

**A polyethylene glycol /  $\gamma$ -globulin mixture as a versatile depletion interaction system for the study of crowding effects** — ●STEFANO DA VELA<sup>1</sup>, FAJUN ZHANG<sup>1</sup>, CHRISTIAN EXNER<sup>1</sup>, SALIBA BARSAUME<sup>1</sup>, MICHAEL SZTUCKI<sup>2</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — <sup>2</sup>ESRF, Grenoble, France

Bovine  $\gamma$ -globulin is a polyvalent antibody preparation consisting mainly of Immunoglobulin G (IgG), an anisotropic, Y-shaped protein. Solutions of  $\gamma$ -globulin, with polyethylene glycol (PEG) of variable molecular weights added as depletion agent, can be used as a model to study the effect of attractive particle-particle interactions with tunable range and strength. The phase behaviour is comparable to that of monoclonal antibody systems, with the appearance of a gas-liquid coexistence region accessible above the freezing temperature of water, within a range of PEG concentrations. However, the availability of large amounts of protein in the case of  $\gamma$ -globulin allows for an extensive exploration of its phase diagram: regions at high protein volume fraction and the possibility to realize arrested phase transitions are of particular interest. Moreover, by choosing appropriate PEG molecular weights and concentrations, the phase behaviour can be described in conditions beyond those of applicability of the Asakura-Oosawa model of depletion interactions. Typical phase diagrams as a function of PEG concentration and temperature are presented, while dynamic light scattering and small-angle x-ray scattering are employed to characterize the interaction.

CPP 34.10 Tue 14:00 Poster C

**Diffusion in protein solutions upon approaching a liquid-liquid phase transition and its critical point** — ●MICHAL BRAUN, MARCELL WOLF, FAJUN ZHANG, and FRANK SCHREIBER — Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen

We study aqueous solutions of globular proteins and multivalent salts ([1], [2], [3]). In the bovine serum albumin (BSA) system with  $\text{YCl}_3$  liquid-liquid phase separation (LLPS) occurs in a certain region of the phase diagram. We performed temperature dependent dynamic light scattering measurements to monitor the diffusion behavior upon approaching the liquid-liquid phase transition. We found two contributions to the collective diffusion. The faster diffusion is ascribed to small clusters whereas the slower contribution is due to collective diffusion of larger clusters. Both the slow and fast collective diffusion coefficients first increase as expected according to the Stokes-Einstein equation. Upon approaching the phase transition they decrease linearly due to the formation of clusters. A new theoretical model is needed to explain these experimental observations. The Rayleigh ratio as well as the diffusion coefficients may be used to estimate the spinodal and binodal temperatures of the system. The classification of the critical behavior turns out to not be as straightforward as in the case of other binary systems. This is due to the formation of clusters before the onset of phase transition. [1] Zhang et al., *PRL*, **101**, 148101, 2008, [2] Zhang et al., *Soft Matter*, **8**, 1313, 2012, [3] Roosen-Runge et al., *PNAS*, **108**, 11815, 2011