

CPP 41: Biopolymers, Biomaterials and Bioinspired Functional Materials II (joint session CPP/BP)

Time: Wednesday 16:30–18:00

Location: MER 02

CPP 41.1 Wed 16:30 MER 02

Low-Temperature and Water-Based Biotemplating of Nanostructured Foam-Like Titania Films using β -Lactoglobulin

— ●JULIAN E. HEGER¹, WEI CHEN¹, SHANSHAN YIN¹, NIAN LI¹, VOLKER KÖRSTGENS¹, CALVIN J. BRETT^{2,3}, WIEBKE OHM², STEPHAN V. ROTH^{2,3}, and PETER MÜLLER-BUSCHBAUM^{1,4} — ¹TUM School of Natural Sciences, Chair for Functional Materials, Garching, Germany — ²DESY, Hamburg, Germany — ³Royal Institute of Technology KTH, Stockholm, Sweden — ⁴MLZ, TUM, Garching, Germany

Energy-related applications such as solar cells, batteries, and the photocatalytic production of hydrogen are broadly built up on titania nanostructures. A tailored titania morphology is necessary to match the required charge diffusion lengths and the crystallinity beneficial for efficient performance. In the context of large-scale fabrication, the aspect of sustainability becomes essential. Biopolymer templating based on β -Lactoglobulin (β -lg) and spray deposition promotes low-temperature and water-based synthesis of nanostructured, crystalline, foam-like titania films. During spray deposition, the β -lg biopolymer matrix sterically directs the titania morphology. Afterwards, the biotemplate is removed by UV-light exposure. To understand the kinetics of film formation during the spray deposition on the nano and crystalline length scale, we simultaneously perform in situ grazing-incidence small-angle and wide-angle X-ray scattering (GISAXS/GIWAXS). Together with scanning electron microscopy (SEM), the results explain the role of β -lg as a biotemplate.

CPP 41.2 Wed 16:45 MER 02

Structural changes in cellulose nanofibril-colloid hybrid films during humidity cycling

— ●STEPHAN V. ROTH^{1,2}, CALVIN J. BRETT^{1,2}, ALEXANDROS ALEXAKIS², LUCAS P. KREUZER³, MARTIN MANSSON², SARAH ROGERS⁴, EVA MALMSTRÖM², PETER MÜLLER-BUSCHBAUM^{3,5}, and L. DANIEL SÖDERBERG² — ¹Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²KTH Royal Institute of Technology, Stockholm, Sweden — ³TUM School of Natural Sciences, Chair for Functional Materials, Garching — ⁴ISIS-STFC, Rutherford Appleton Laboratory, Chilton, Oxon OX11 0QX, UK — ⁵MLZ, TUM, Garching, Germany

Biocompatible cellulose nanofibrils (CNFs) are an ideal material for sustainable biomaterial templates. Combined with latex colloids, the resulting hybrid colloid-CNF functional materials are excellent candidates for bio-inspired structural colors. Due to the hydrophilic nature of CNFs, we investigate the stability against humidity cycling in terms of reversible/irreversible structural rearrangements. We applied depth sensitive grazing incidence small-angle neutron scattering to evaluate the humidity-induced rearrangements in hybrid latex colloid:CNF templates in situ during cyclic humidification. After the first humidity cycle, a change in morphology on the scale of several 10 nm was observed, which is attributed to latex particles which diffused in the network and enlarged the pores of the network. The measured kinetics resolve the time- and depth-dependence of the differently sized colloids' penetration into the porous CNF network.

CPP 41.3 Wed 17:00 MER 02

Fluorescence correlation spectroscopy for studying the aggregation of nanoplastics in model biofilm substances

— ●TOBIAS GUCKEISEN, ROZALIA ORGHICI, and SILKE RATHGEBER — Universität Koblenz, Deutschland

Nanoplastics in the environment are a growing problem. Pollutants can adhere to their surfaces and therefore be easily transported into the natural systems. Biofilms are found everywhere in the environment; they are formed by microbial communities that produce a matrix of extracellular polymeric substances. The interaction between nanoplastics and biofilms can lead to aggregation and sedimentation of nanoparticles and determines the transport and fate of nanoplastics. A better understanding of the transport and fate of nanoplastics is important to improve our ability to predict risks associated with these ubiquitous contaminants. In this project, we use fluorescence correlation spectroscopy (FCS) to study the aggregation and interactions of nanoplastics with model biofilm substances. Protein-polysaccharide mixing ratio and pH-dependent aggregation studies show that it is crucial to consider correlative effects between multiple biofilm components to better understand the impact biofilms have on nanoplastic aggrega-

tion. Biofilm model systems with only one component, as commonly considered, may lead to an incorrect assessment of the tendency to aggregation.

CPP 41.4 Wed 17:15 MER 02

Ensemble inequivalence and negative extensibility in a wormlike chain with fluctuating bending stiffness

— ●PANAYOTIS BENETATOS — Department of Physics, Kyungpook National University, Republic of Korea

Many semiflexible polymers exhibit fluctuations in the local bending stiffness along their contour. This may be due to intrinsic conformational changes (e.g., denaturation bubble formation in double stranded DNA or helix-coil transition in polypeptides) or to the reversible adsorption and desorption of molecules from the polymer's environment. In this presentation, we analyse the tensile elasticity of a strongly stretched wormlike chain which consists of N concatenated segments, where each segment can be in one of two states, A and B, which differ in bending stiffness. We call this model the reversible wormlike chain (rWLC) model. In the Gibbs (fixed-force, isotensional) ensemble, we obtain analytic expressions for the force-extension relation and the mean fraction of B segments. We show that, under certain conditions, there is a tension-induced crossover from a mostly A to a mostly B rWLC. In the Helmholtz (fixed-extension, isometric) ensemble, we obtain analytic expressions up to a summation. We show that, for finite N , there is marked ensemble inequivalence. Remarkably, in the Helmholtz ensemble, the rWLC can exhibit negative extensibility and multiple peaks.

CPP 41.5 Wed 17:30 MER 02

Aging and compressed exponential stress relaxation in mechanoresponsive hydrogels

— ●GEONHO SONG^{1,2}, WOUTER ELLENBROEK³, and KERSTIN BLANK^{1,2} — ¹Johannes Kepler University Linz, Linz, Austria — ²Max Planck Institute of Colloids and Interfaces, Potsdam, Germany — ³Eindhoven University of Technology, Eindhoven, The Netherlands

Biological materials, such as the extracellular matrix (ECM), are viscoelastic and exhibit stress relaxation. Stress relaxation in the ECM is linked to cellular behavior and needs to be considered as a design parameter when developing bioinspired materials for cell culture and tissue engineering. Here, we introduce a collagen-inspired hydrogel with tunable crosslink kinetics. We utilize collagen-mimetic peptides with controlled association and dissociation rates to crosslink star-shaped polyethylene glycol. We show that ultraslow crosslink dissociation rates cause a distinctive relaxation behavior that is reminiscent of soft glassy materials, showing out-of-equilibrium properties. In particular, subjecting the networks to a sequence of pre-stress and aging causes uncommon compressed exponential relaxation. This unique phenomenon has previously only been reported for a small number of soft glassy systems where compressed exponential relaxation was related to ultraslow dynamics that prohibited the release of internal stresses. In such systems, slow crosslink dissociation delays network relaxation until an external trigger is applied. In future work, we aim to investigate the interplay between locally generated stresses, such as cellular traction forces, and network relaxation properties.

CPP 41.6 Wed 17:45 MER 02

Nonaffinity controls critical slowing down and rheology near the onset of rigidity

— ●ABHINAV SHARMA¹, JORDAN SHIVERS², and FRED MACKINTOSH² — ¹Leibniz institute for polymer research, Dresden — ²Rice University, Houston, Texas

Fluid-immersed networks and dense suspensions often reside near a boundary between soft (or fluid-like) and rigid (or solid-like) mechanical regimes. This boundary can be crossed either by varying the concentration or by deformation. Near the onset or loss of rigidity, dissipation-limiting nonaffine rearrangements dominate the macroscopic viscoelastic response, giving rise to diverging relaxation times and power-law rheology. Here, we derive a simple relationship between nonaffinity and excess viscosity in fluid-immersed amorphous materials. We then demonstrate this relationship and its rheological consequences in simulations of stress relaxation in strained filament networks and dense suspensions.