

CPP 9: Nanoparticles and Composite Materials II (joint session CPP, BP)

Time: Monday 15:00–18:45

Location: C 243

CPP 9.1 Mon 15:00 C 243

Do Macroscopic Properties of Nanocomposites Require Glassy Layers? — KLAUS NUSSER and ●GERALD J. SCHNEIDER — Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science & Institute of Complex Systems, 52425 Jülich, Germany

Inorganic/organic hybrid materials receive steadily growing interest due to their capability to show unprecedented properties. Most likely, at the length-scale of single chains, many different phenomena add and form the final material. Due to the small diameters, their specific surface area is very high, and thus may contribute significantly. To predict the material properties, many concepts have been developed to understand the influence of those chains close to surfaces. For example, a very common picture is the assumption of an immobilized or glassy layer when the polymer is very close to solid substrates.

In our contribution, we present macroscopic properties and show that these can be explained perfectly by the concept of a glassy layer. However, for these examples, our microscopic information by neutron scattering experiments evidence that the underlying assumptions are wrong, but our experiments permit a different explanation.

Based on our toolbox of hybrid materials, we used a well-defined system. As a consequence it allows us to formulate a theorem under which conditions new materials can be designed on the computer based on our results. Therefore, we believe that our achievements represent a major progress toward the prediction of macroscopic properties of nanocomposites based on information at the length-scale of a single chain.

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Dynamics of polymers in composites — ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V.

Magnetic resonance is applied to study the dynamics of polymers interacting with inorganic solid surfaces. The dynamics of polymers over a wide range of correlation times is determined using magnetic resonance relaxation experiments for the investigation of systems in contact with solids and inorganic materials. In highly dispersed systems, these are nanoparticles coated with thin films have been investigated. Measurement of T₂ or T₁ρ is ideally suited for the dynamics of chain segments, which is mostly affected by the interaction with the solid surface. Because of sensitivity issues only proton NMR signals have been detected. In order to obtain sufficient chemical resolution for instance to exclude solvent signals in swelling experiments high-resolution solid-state and NMR based on CRAMPS has been applied. These line narrowing techniques permit the selection or suppression of the solvent signal and thus one can focus on the polymer dynamics. It is seen, that there is much stronger motion and dynamics and putting the brushes compared to polymers of the same molecular weight. To investigate that further dedicated techniques for the selective excitations at the interface part based on magnetization transfer from the inorganic particle to the polymer has been applied. Spin-labels on polyelectrolytes permit the selective study of the dynamics of the polymer in the vicinity of the label. Because of the high sensitivity of EPR dynamics of individual layers in a multilayer system can be studied.

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Disentanglement in polymer-star mixtures — ●HENDRIK MEYER — Institut Charles Sadron, CNRS UPR22, 67034 Strasbourg, France

We present a molecular dynamics simulation study of entangled melts mixed with particles of the order of the tube diameter. The choice of compact stars represents a model system of nanocomposites without polymer-particle adsorption. The particles remain well dispersed over the whole concentration range and the stars are sufficiently compact that the pure system is jammed. For this system, we observe a weak compression of the matrix chains with increasing volume fraction of stars. Short (unentangled) matrix chains get slowed down by adding particles to the system. When the matrix chains become significantly longer than the entanglement length, this trend is inverted and the matrix chains become faster because the particles dilute the entanglement network. The center-of mass (CM) dynamics exhibits regimes of anomalous diffusion in accordance with viscoelastic hydrodynamic interactions (VHI) [1]. At low and intermediate star-particles concentration, the particles themselves vary little in mobility, only at high

concentration (above percolation), they become slowed down because of colloidal packing. As a result, the viscosity as a measure of the collective mobility drops when adding few particles to the melt because of disentanglement, and at high particle volume fraction the viscosity increases again because of colloidal caging. [1] J. Farago et al. PRL 107, 178301 (2011); PRE 85, 051807 (2012).

CPP 9.4 Mon 15:45 C 243

Polymer/metal hybrids: Adhesion behaviour and polymer dynamics before and after corrosion treatment — ●MARIEKE FÜLLBRANDT^{1,2}, ANDREAS SCHÖNHALS², and REGINE VON KLITZING¹ — ¹Technische Universität Berlin, Str. des 17. Juni 124, 10623 Berlin — ²BAM Bundesanstalt fuer Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin

Polymer/metal hybrids are of high interest for example in lightweight constructions used in the automotive industry. They combine a high functional integration with a lower weight compared to pure metal parts. The joining of these dissimilar materials without using additional material is a central challenge. In a first step, the metal/polymer interface is characterized with regard to the adhesion behaviour on a macro- and microscopic length scale using contact angle (CA) measurements and colloidal probe atomic force microscopy. The latter method determines the adhesion force and energy which can be analysed and related to a work of adhesion per area. The effect of a (sub)micrometre scale roughness is considered using the Rabinovich approach. With CA measurements the surface energy of the solids is determined using the Owens-Wendt-Rabel-Kaelble method and further be related to the corresponding work of adhesion per area. In a second step, the influence of a corrosion treatment on the adhesion behaviour is investigated. Complementary, broadband dielectric spectroscopy measurements in a wide frequency (0.01 Hz to 1 MHz) and temperature range (-120 to 180 °C) are performed in order to characterize the polymer dynamics in bulk and at the metal interface before and after treatment.

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Organic inorganic hybrid PU-POSS networks: A multi-length-scale investigation of morphology and a multi-time-scale investigation of dynamics — ●KONSTANTINOS N. RAFTOPOULOS^{1,2}, STEFANOS KOUTSOUMPI³, MALGORZATA JANCIA², KONSTANTINOS KYRIAKOS¹, EDYTA HEBDA², CHRISTINE M. PAPADAKIS¹, KRZYSZTOF PIELICHOWSKI², and POLYCARPOS PISSIS³ — ¹TU München, Physik-Department, Fachgebiet Physik weicher Materie, Garching — ²Cracow University of Technology, Department of Chemistry and Technology of Polymers, Poland — ³National Technical University of Athens, Department of Physics, Greece

Polyhedral oligomeric silsesquioxanes (POSS) bridge the gap between nanoparticles and conventional chemical reagents. A wide variety of organic, ligands bind on a sub-nm siliceous core, and allow it to participate as a nanobuilding block on the very structure of the macromolecular chain. Here, octa-OH functional moieties crosslink a phase separated polyurethane. On the basis of X-ray diffraction in a wide q-range covering both WAXS and SAXS and atomic force microscopy we show that POSS reside in the soft phase, and the hard microdomains become progressively thinner with increasing POSS content. The segmental dynamics of the soft phase slow down as a result of both crosslinking and diminishing microphase separation, as evidenced by differential scanning calorimetry and broadband dielectric spectroscopy. Interestingly, all the effects show a step-like behavior between 4 and 6 wt% of POSS, possibly as a result of a percolation of the POSS crosslinked phase.

CPP 9.6 Mon 16:15 C 243

Nanomechanical Investigation of Rubber-modified Epoxy Resins — ●LISA MARIA UIBERLACKER and SABINE HILD — Institute of Polymer Science, Johannes Kepler University, 4040 Linz, Austria

Epoxy resins have a broad application scope due to the wide range of properties which can be easily modified by mixing various basic components - e.g. to modify the toughness of epoxy resins rubber auxiliaries are added.

This study focused on epoxy mixtures based on a bisphenol A diglycidyl ether cured with diethyltoluenediamine with various amounts of nitrile rubber. Both, morphology and the mechanical properties of

these two phase systems were examined with scanning force microscopy (SFM).

In SFM phase images the epoxy phase was clearly distinguished from the rubber phase. The nitrile rubber formed spherical domains in the epoxy matrix. Phase separation occurred also in the rubber matrix. Mechanical properties of both phases were quantified by nanoindentation experiments. In addition, the influence of different amounts of rubber additive on the toughness of the epoxy matrix was examined.

15 min. break

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Matryoshka-Doll-like Shish-Kebab Nanocomposite: Nanohybrid Shish-Kebabs within Nanofiber Shish-Kebabs — ●MATTHIAS M.L. ARRAS¹, RICHARD JANA¹, CHRISTIAN GRASL², and KLAUS D. JANDT¹ — ¹Chair of Materials Science (CMS), Otto Schott Institute of Materials Research, Friedrich Schiller University Jena, Jena, Germany — ²Center for Medical Physics and Biomedical Engineering, Medical University of Vienna, Austria

The shish-kebab morphology in semi-crystalline polymer fibers is a key to the outstanding properties of polymer fibers. Here, we present the creation of a two-level hierarchical fiber structure by combining two recent artificial shish-kebab nanostructures: The nanohybrid shish-kebab (NHSK), i.e., a carbon nanotube (CNT) overgrown by polymer kebabs and the nanofiber shish-kebab (NFSK), i.e., an electrospun nanofiber decorated by larger lamellae crystals. We tested the hypothesis that during electrospinning of a CNT/polymer solution the NHSK can form directly and that the resulting fibers can be used to subsequently create the NFSK. The resulting nanocomposite was analyzed by transmission and scanning electron microscopy and revealed the successful creation of both the NHSK and the NFSK. Thus, for the first time, we demonstrated the creation of the NHSK morphology during electrospinning. The two-level hierarchical nanocomposite is a proof of principle that the shish-kebab morphology can be extended from the nanoscale to the macroscale which may contribute to future high strength nanocomposites.

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Structural changes of diisocyanates covalently attached to the semiconducting carbon nanotube — ●MARIANA KOZLOWSKA¹, JAKUB GOCLON², and PAWEŁ RODZIEWICZ¹ — ¹Institute of Chemistry, University of Białystok, Poland — ²Interdisziplinäres Centrum für Molekulare Materialien(ICMM) und Computer-Chemie-Centrum (CCC), Department Chemie und Pharmazie, Friedrich-Alexander-Universität Erlangen-Nürnberg

Reinforced polymers are of a great interest since the individual properties of the initial materials can be combined, resulting in a new hybrid material with better properties. Carbon nanotubes are popular polymer filler and reinforcing agent. They enhance the mechanical strength and corrosion resistance.

We performed first-principles DFT calculations of the covalent and noncovalent sidewall functionalization of metallic (6,0) and semiconducting (10,0) single-walled carbon nanotubes (SWCNTs) via the attachment of two aromatic diisocyanates: 4,4'-methylene diphenyl diisocyanate (MDI) and toluene-2,4-diisocyanate (TDI).

In this work, we focus on the structural rearrangements of the diisocyanates molecules covalently attached to the SWCNT(10,0) surface at the finite temperature, using the Car-Parrinello molecular dynamics (CP-MD) scheme.

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Formation of anisotropic gold nanoparticles with different morphologies analysed by UV-Vis spectroscopy, SAXS and TEM — ●TILO SCHMUTZLER, TORBEN SCHINDLER, MARTIN SCHMIELE, and TOBIAS UNRUH — Friedrich-Alexander-University Erlangen-Nuernberg, Chair for Crystallography and Structural Physics, Staudtstrasse 3, 91058 Erlangen, Germany

Au nanoparticles (NPs) have been the subject of widespread research in the last two decades. Therefore, numerous studies dealing with the synthesis leading to exact shape and size control were made. Applications are expected in biological imaging, drug delivery and phototherapeutics.[1]

Especially anisotropic Au NPs show interesting optical behaviour

due to their ability to absorb light at different wavelengths for more than one surface plasmon resonance. Via a modified seed-mediated growth synthesis route for gold nanorods[1] we were able to synthesize various morphologies of Au NPs with defined absorption bands (500-800 nm) in the UV-Vis spectrum and narrow distributions of the particle dimensions which could be determined by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

The particle formation of Au nanorods in contrast to other morphologies like star-like nanoaggregates under different conditions (temperature, concentration of precursors, ...) was investigated by UV-Vis spectroscopy, SAXS and TEM to understand indirectly the formation mechanism of such particles.

[1] C.J. Murphy et al., J. Phys. Chem B. 2005, 109, 13857-13870.

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Local Chemical Characterization of Nanoporous Materials with Atom Probe Tomography — ●CARSTEN NOWAK, PHILIPP SAUERBIER, and BJÖRN PFEIFFER — Georg-August-Universität Göttingen, Institute for Materials Physics, Göttingen, Germany

Because of their high surface-to-volume-ratio and their chemical activity, nanoparticles and nanoporous materials receive a lot of interest in the areas of catalysis and electrochemistry. To obtain a detailed insight into reaction mechanisms, knowledge of the local chemical composition and structure, particularly at the surface of the material, is desirable.

Here we present experimental results on the local chemical characterization of nanoporous gold with atom probe tomography. The nanoporous gold with pore and ligament size of 50 nm, chosen as model system, is converted into a compact material by electron beam induced deposition of metalorganic precursors. Subsequently, the material is characterized with atom probe tomography which essentially is a combination of single molecule time of flight spectroscopy and atomic scale microscopy, thus allowing to characterize the local chemical composition of the filled material and particularly its former surface with sub-nanometer spatial resolution.

Although the preparation involves a chemical reaction of the surface with the precursor and thus alters the active surface of the nanoporous material, this approach offers the potential to detect chemical species at the surface of irregularly shaped nanoparticles with sub-monolayer sensitivity.

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Semiconductor Nanocrystal Blinking monitored via Fast Spectrally and Intensity Resolved Single Molecule Spectroscopy — ●CLEMENS GÖHLER, CORNELIUS KRASSETT, and CHRISTIAN VON BORCZYKOWSKI — Fakultät für Naturwissenschaften, TU Chemnitz, D-09126 Chemnitz

Colloidal CdSe Semiconductor Nanocrystals (NCs) are promising candidates for improving different applications, e.g. in photovoltaics or sensing, due to their size-dependent optical and spectroscopic properties. With techniques from Single Molecule Spectroscopy, we avoid ensemble-averaging and investigate these characteristics on individual NCs. On that level, luminescence intermittency (so called blinking) is observable, for which the underlying mechanisms are yet not fully understood.

To contribute, we applied Change-Point-Analysis to time-correlated single-photon counts from single NC photoluminescence (PL) emission, which allows resolving discrete PL intensity levels [1]. In addition, we splitted the PL-signal with a dichroic beamsplitter towards two detectors. By combining these techniques, we were able to examine spectral diffusion within the single NC PL on a μ s-timescale and to correlate that to the fluctuating emission intensity. The results are in agreement with blinking models based on a multiple recombination-center approach.

[1] Schmidt, R., Krasselt, C., Göhler, C., & von Borczykowski, C. (2014). *ACS nano*, 8(4), 3506-3521.

CPP 9.12 Mon 18:00 C 243

Interrelation of fluorescence and morphology of molecular aggregate structures — ●MOHAMMADREZA BAHRAMI¹, TAMAM BOHAMUD¹, CLEMENS SCHINDLER¹, LUKAS RATHJE¹, HANNES HARTMANN¹, J.A.A.W. ELEMANS², INGO BARKE¹, and SYLVIA SPELLER¹ — ¹University of Rostock, Institute of Physics, 18051 Rostock, Germany — ²Radboud University Nijmegen, Institute for Molecules and Materials, 6525 AJ Nijmegen, The Netherlands

Metallo-porphyrins are widespread in nature and act as a key component in photosynthesis as well as in oxygen transport in blood cells. They have attracted much attention in view of applications like

molecular wires, fluorescence switches, and light-energy conversion [1]. We study the spatially resolved photoluminescence from Copper-based porphyrin [2] aggregates as one of the deexcitation pathways of excitons. Among the different observed morphological motifs of the aggregates we here focus on branched strands with typical diameters of 50 - 100 nm. Fluorescence microscopy images show varying intensity along strands and junctions. In combination with atomic force microscopy we correlate fluorescence and structural properties to elaborate possible reasons of such morphology-dependent fluorescence. We further present fluorescence data on a composite system of silver nanostructures in the vicinity of molecule aggregates, and address the role of these metal systems as local sources of electromagnetic fields.

[1] Wenqi Zheng, et al., *Dyes and Pigments* 77 (2008) 153e157 [2] M.J.J. Coenen, et al., *Phys. Chem. Chem. Phys.* 15, 12451 (2013)

CPP 9.13 Mon 18:15 C 243

Electric detection of ortho and para water in fullerene cages — ●BENNO MEIER, SALVATORE MAMONE, JAVIER ALONSO-VALDESUEIRO, MARIA CONCISTRÈ, ANDREA KRACHMALNICOFF, RICHARD J. WHITBY, and MALCOLM H. LEVITT — School of Chemistry, University of Southampton, SO17 1BJ Southampton, United Kingdom

Water, like molecular hydrogen, exhibits spin isomerism, a phenomenon in which the entanglement of spatial and spin states leads to ortho and para spin isomers with different symmetry. The physical properties and the interconversion of the two isomers of molecular hydrogen are central to fields as diverse as astrophysics and nuclear magnetic resonance, but much remains unknown about the different isomers of water, owing to the difficulty of separating the two isomers. Here, we use fullerene cages to provide freely rotating water molecules at cryogenic temperatures in the form of the supramolecular endofullerene H₂O@C₆₀. Unlike molecular hydrogen, water has an electric dipole moment and we show that the dielectric constant,

a bulk property, that is linked to the spin states via their molecular polarizabilities, changes upon ortho-para conversion that is induced by a sudden temperature change. Our findings are in excellent agreement with previous NMR studies and suggest the possibility to detect and eventually manipulate H₂O@C₆₀ molecules selectively depending on the nuclear spin state of the comprised water molecule.

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Effective mechanical properties of graphene obtained by computational mechanical tests — ●MARKUS A. HARTMANN¹, MELANIE TODT², and FRANZ G. RAMMERSTORFER² — ¹Institute of Physics, Montanuniversität Leoben, 8700 Leoben, Austria — ²ILSB, Vienna Institute of Technology, 1040 Vienna, Austria

Carbon nanostructures combine a high stiffness with low weight and an exceptional toughness making carbon a promising candidate for applications in structural mechanics. Understanding the mechanical properties of these structures on every length scale is of utmost importance to be able to exploit the full potential of these materials. In the presented work the effective mechanical parameters of graphene are assessed that are the necessary input parameters for large scale finite element calculations. Of special interest is the "effective thickness" in combination with the "effective Young's modulus" of monolayer graphene. Potentials obtained by ab initio calculations [1] were used in subsequent Monte Carlo simulations to assess the effective mechanical properties of graphene [2]. The membrane stiffness and the bending stiffness (and consequently the effective thickness) of graphene were evaluated. The results showed that the elastic modulus as well as the Poisson ratio corresponds well to values known from literature. For structures too small the continuum approximation breaks down and the effective thickness decreases, while it attains a constant value of approximately 0.132 nm for structures large than 5 nm.

[1] Holec et al., *Phys. Rev. B* 81, 235403 (2010)

[2] Hartmann et al., *Europhys. Lett.* 103, 68004 (2013)