

CPP 43: Nanoparticles and Composite Materials I

Time: Thursday 14:00–18:30

Location: ZEU 222

Topical Talk CPP 43.1 Thu 14:00 ZEU 222
NanoModel - Multi-Scale Modelling of Nano-Structured Polymeric Materials — ●HORST WEISS — Polymer Research, BASF SE

The practice of adding micron sized inorganic filler particles to reinforce polymeric materials can be traced back to the early years of the composite industry. With synthetic methods that can produce nanometer sized fillers, resulting in an enormous increase of surface area, polymers reinforced with nanoscale particles should show vastly improved properties. Yet, experimental evidence suggests that a simple extrapolation of the design paradigms of conventional composites cannot be used to predict the behavior of nanocomposites. The origin of these differences between conventional and nanocomposites is still unknown. This, unfortunately, precludes yet any rational design. Though some property improvements have been achieved in nanocomposites, nanoparticle dispersion is difficult to control, with both thermodynamic and kinetic processes playing significant roles. This talk reports on the progress made in a European project called NanoModel. The goal of this project is to develop, implement and validate multi-scale methods to compute the mechanical, thermochemical and flow behavior of nano-filled polymeric materials * based on the chemistry of selected model systems.

CPP 43.2 Thu 14:30 ZEU 222

Modelling of stress and strain amplification effects in filled polymer melts — ●JAN DOMURATH, MARINA SAPHIANNIKOVA, and GERT HEINRICH — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden

When hard filler particles are added to a polymer melt, it is usually assumed that it's zero-shear viscosity and therefore the stress increase according to Einstein's or a similar formula. In some papers one finds an alternative approach in which the local strain field is increased according to these formulas. Although both approaches provide the same increase of the shear stress in the linear limit, it can be shown that the second approach violates the energy conservation law as the macroscopic and microscopic dissipated energies are not equal anymore. In this contribution we propose a new stress and strain amplification approach in which both the stress and strain tensors are modified to describe the behaviour of filled polymer melts in the non-linear shearing regime. The new approach is tested using relatively simple constitutive models for description of nonlinear viscoelastic behaviour in polymer melts. The stress and strain amplification approach enables us to explain the peculiar behaviour of the overshoot peak observed recently in filled LDPE melts [1].

[1] F.R. Costa et al. Adv. Polym. Sci. 210, 101 (2008)

CPP 43.3 Thu 14:45 ZEU 222

Structure Property Relationships of Nanocomposites based on Polypropylene and Layered Double Hydroxide — ●PURV PUROHIT, JESUS SANCHEZ, and ANDREAS SCHÖNHALS — BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

Nanocomposites based on Polypropylene (PP) and modified ZnAl Layered Double Hydroxides (ZnAl-LDH) were prepared and investigated by a combination of differential scanning calorimetry (DSC), Small and Wide angle X-ray scattering (SAXS & WAXS) and Dielectric Relaxation Spectroscopy. Space resolved SAXS investigation show that the samples are homogeneous on a length scale of several cm and have a predominantly exfoliated morphology. DSC and WAXS show that the degree of crystallinity decreases with the increasing content of LDH. The extrapolation of this dependence to zero estimates a limiting concentration of c.a. 40% LDH where the crystallization of PP is completely suppressed. The dielectric response of the nanocomposites shows several relaxation processes. The intensity of the dynamic glass transition increases with the concentration of LDH. This is attributed to the increasing concentration of the exchanged anion dodecylbenzene sulfonate (SDBS), which are adsorbed at the LDH layers. Therefore, analysis of the beta-relaxation provides information about the interfacial region between the LDH layers and the PP matrix. The glass transition temperature in this interfacial region is by 30 K lower than that of PP. This is accompanied by a change of the fragility deduced from the relaxation map.

CPP 43.4 Thu 15:00 ZEU 222

Small-angle scattering study of dispersion ability of polystyrene modified carbon nanotubes. — ●ANASTASIA GOLOSOVA^{1,2}, JOSEPH ADELSBERGER¹, ALESSANDRO SEPE¹, MARTIN NIEDERMEIER¹, SERGIO S. FUNARI³, PETER LINDNER⁴, RAINER JORDAN², and CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physikdepartment, Fachgebiet Physik der weichen Materie, Garching — ²TU München, Department Chemie, Lehrstuhl für Makromolekulare Chemie, Garching — ³HASYLAB at DESY, Hamburg — ⁴ILL, Grenoble, France

Carbon nanotubes (CNTs) are attractive for nanocomposite applications due to their unique physical properties. In order to optimize their use as fillers, thorough characterization of their dispersions is of importance. Using small-angle scattering, we have studied the effect of the level of the CNTs' modification with polystyrene grafts on both, the morphology of CNTs and their agglomeration behavior in toluene dispersions. By contrast matching with the solvent in neutron experiments, we highlighted the polymer shell or the CNTs themselves, whereas X-rays gave overall information. The structure of the CNTs and their agglomerates were modeled as fractal aggregates of rods or of core-shell cylinders. The models were found to be consistent with the results of AFM and thermo-gravimetric analysis. Though agglomeration is observed even for the modified CNTs, an increase of the mesh size in the agglomerates with the increase of the modification level indicates that the modification procedure indeed leads to an improved dispersion ability of the CNTs.

CPP 43.5 Thu 15:15 ZEU 222

Experimental study of the structure of aligned CNT/PS composites — ●MARINA KHANEFT¹, BERND STÜHN¹, JÖRG ENGSTLER², JÖRG SCHNEIDER², and TINKA SPEHR¹ — ¹Institut für Festkörperphysik, Technische Universität Darmstadt — ²Eduard Zintl-Institute für Anorganische und Physikalische Chemie, Technische Universität Darmstadt

We present experimental studies of the infiltration of polystyrene (PS) into the free interstices of 3D aligned carbon nanotube arrays. The aligned CNT structures were prepared by a template assisted non catalytic CVD approach. Herein porous alumina (PAOX) is used as template material in which CNTs are deposited. After removal of PAOX CNT arrays are achieved. We infiltrated PS of two different molecular weights ($21 \cdot 10^3$ and $88 \cdot 10^3$ g/mol) into CNT arrays with 40 and 100 nm tube diameter. For the investigation of the composites we used different experimental techniques like microscopy (TEM, AFM) and scattering (SAXS, SANS). We determined structure of nanotubes (diameter, wall thickness, interactions between tubes) in each step of sample preparation. We are able to see the variation of the scattering during the process of growing CNT in PAOX, removing of the alumina matrix and finally the filling of the system with polystyrene. All these changes were described within a model of cylindrical core-shell particles with two dimensional hexagonal order. Investigation of polymer location in composites shows that filling depends on tube size and molecular weight. Moreover, we applied small angle neutron scattering (SANS) for studying the polymer conformation in composites.

CPP 43.6 Thu 15:30 ZEU 222

Free volume of interphases in model nanocomposites studied by positron annihilation lifetime spectroscopy — STEPHAN HARMS¹, ●KLAUS RÄTZKE¹, FRANZ FAUPEL¹, GERALD J. SCHNEIDER², LUTZ WILLNER², and DIETER RICHTER² — ¹Materialwissenschaft-Materialverbunde, Universität Kiel, 24143 Kiel — ²Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich

Free volume studies were performed in nanocomposites by positron annihilation lifetime spectroscopy (PALS) to explore the influence of the interphase nanoscale character of the hydrophobically functionalized filler particles and the nanoscale particle size on positron parameters [1]. A weakly repulsive system, not forming an interphase, was obtained by mixing of low molecular weight poly(ethylene-alt-propylene) (PEP) and hydrophobically modified silica with varying concentration. DSC experiments showed a constant glass transition temperature T_g and a decrease in heat capacity at T_g with increasing filler concentration. In contrast, PALS measurements showed decreasing T_g and a strong drop of the thermal expansion coefficient above T_g . These

seemingly conflicting results are due to nanoscale character of filler particles with sizes in the range of the positronium diffusion length. This requires taking into account out-diffusion of positronium from the particles. In particular, the changes on PALS parameters with increasing filler content cannot be attributed to the formation of an interphase with properties different from the polymer matrix.

[1] S. Harms K. Rätzke, F. Faupel, G. J. Schneider, L. Willner, D. Richter in press *Macromolecules* 2010

CPP 43.7 Thu 15:45 ZEU 222

Unique Splitting Behavior of the C-C Symmetric Stretching Mode as a Raman Signature of Conformational Order of Intercalated Alkyl Chains in Modified Clay Composites — ●PATRICE DONFACK¹, ELENA A. SAGITOVA^{1,2}, KIRILL A. PROKHOROV², KIRILL V. VODOPIANOV², GOULNARA YU. NIKOLAEVA², VIKTOR A. GERASIN³, NADEZHDA D. MEREKALOVA³, ARNULF MATERNY¹, EVGENY M. ANTIPOV³, and PAVEL P. PASHININ² — ¹Center of Functional Materials and Nanomolecular Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany — ²A.M. Prokhorov General Physics Institute of RAS, Moscow, Russia — ³A.V. Topchiev Institute of Petrochemical Synthesis of RAS, Moscow, Russia

A specific conformational insight into clay modified by alkylammonium salts is presented. It is associated with the splitting of the symmetric C-C stretching mode at $\approx 1128 \text{ cm}^{-1}$ into two bands at 1128 and 1139 cm^{-1} in the Raman spectra of sodium montmorillonite clay modified by alkylammonium surfactants, such as cetyltrimethyl ammonium bromide. We demonstrate that this splitting appears if two trans-segments of nonequivalent lengths and terminal groups coexist for the chains of the alkylammonium ions embedded into the clay interlayer space. Interestingly, this correlates with the conformational reorganization of alkylammonium molecules confined within clay galleries, as a function of the modifier content. Moreover, we show that the integral intensity ratio, $I_{(CH_2)}/I_{(705)}$, allows a rapid and nondestructive quantification of the content of alkylammonium ions in the modified clays.

15 min. break

CPP 43.8 Thu 16:15 ZEU 222

Fabrication, Characterization of Multifunctional Tetrapod-ZnO/Polymer Composites for Bioinspired Applications — ●XIN JIN, XINWEI ZHU, SEBASTIAN WILLE, ARNIM SCHUCHARDT, YOGENDRA KUMAR MISHRA, and RAINER ADELUNG — Functional Nanomaterials, Institute of Materials Science, CAU Kiel, Germany

Composite materials design is a fascinating research subject because of the challenge to combine the functionalities of each component and simultaneously give improved properties to the entirety. In biomedical researches, polymers composites play a key role as hard tissue restoratives, like prosthetics, dental implants, etc. One of the most important methods to improve the performance of polymers composite, is to alter the type, amount and size of the filler material. In this work, composites of tetrapods-ZnO micro/nano-particles embedded in PDMS matrix are fabricated. Tensile tests, photon-responsive IV characterization and wettability tests are performed. The results show favorable change in mechanical and electrical properties induced by the special shape of filler. The mechanism of reinforcement is discussed. Researches of this composite material in bio-inspired adhesion applications are in progress. Experiments of tetrapod-ZnO as fillers for dental polymer are also performed.

CPP 43.9 Thu 16:30 ZEU 222

Structure formation during evaporation of a droplet of PEG coated gold nanoparticles on a heterogeneous surface of block copolymers- an in situ μ GISAXS combined with ellipsometry study — ●MOTTAKIN M. ABUL KASHEM¹, VOLKER KÖRSTGENS², MONIKA RAWOLLE², ADELIN BUFFET¹, GERD HERZOG¹, MATTHIAS SCHWARTZKOPF¹, GUNTARD BENECKE¹, JAN PERLICH¹, RAINER GEHRKE¹, PETER MÜLLER-BUSCHBAUM², and STEPHAN V. ROTH¹ — ¹DESY, Hamburg, Germany — ²TU München, Physik Department, LS Funkt. Mat., Garching, Germany

We have investigated the nanostructures formed on top of a block copolymer film surface during evaporation of the solvent of a dispersion of gold nanoparticles coated with PEG ligands. The copolymer film contained regular array of PMMA domains in the matrix of PS [1]. Presence of ligands can, in the one hand, enhance the selectivity of adsorption and in the other hand, can slow down the migrational flow

of the nanoparticles. As a result, several phenomena including selective adsorption, evaporation induced multiscale nanostructures formation and mesoscopic crystallization can be observed [2]. All these open questions have been investigated with in situ micro-beam grazing incidence small angle X-ray scattering (in situ μ GISAXS) in combination with in-situ ellipsometry [3, 4] at P03 (MiNaXS) beamline of PETRA III storage ring of HASYLAB at DESY, Hamburg, Germany. [1] Abul Kashem et. al. *Macromolecules*, 42, 6202 (2009). [2] Roth et. al. *Langmuir*, 26, 1496 (2010). [3] Müller-Buschbaum, P. *Anal. Bioanal. Chem.* 376, 3 (2003). [4] Körstgens et. al. *Anal. Bioanal. Chem.* 396, 139 (2010).

CPP 43.10 Thu 16:45 ZEU 222

Gold Nanoparticles Decorated with Oligo(ethylene glycol) Thiols: Protein Resistance from Single Particle to Superlattice — ●FAJUN ZHANG¹, MAXIMILIAN W. A. SKODA², ROBERT M. J. JACOBS³, CLAIRE PIZZEY⁴, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, Tübingen, Germany — ²ISIS, Rutherford Appleton Laboratory, Chilton, UK — ³Department of Chemistry, Chemistry Research Laboratory, University of Oxford, UK — ⁴Diamond Light Source, UK

Self-assembled monolayers (SAM) with oligo(ethylene glycol) (OEG) termination are of great importance in biomedical applications due to their protein resistance property. We have successfully prepared OEG-thiol decorated gold colloids and studied various interactions, stability and aggregation kinetics of colloid in the mixture with proteins by SAXS and UV-vis spectroscopy [1]. The results show that the protein resistance of the OEG SAM is maintained at curved interfaces. It is also shown that the colloids lose their stability and form aggregates upon adding protein above a critical concentration due to the depletion-attractive interaction [1]. The stability of the mixtures of the functionalized AuNP and proteins in solution strongly depends on the nature of added salts, which follow the Hofmeister series [1]. Further, a superlattice of SAM coated AuNP on a substrate is obtained, which provides a new model interface with protein resistance property. SAXS measurements indicate an FCC structure of the superlattice.

[1] F. Zhang, et al. *J. Phys. Chem. A* 2007, 111, 12229. *Eur. Biophys. J.* 2008, 37, 551. *J. Phys. Chem. C* 2009, 113, 4839.

CPP 43.11 Thu 17:00 ZEU 222

Structure and dynamics of poly ethylene glycol grafted gold nanoparticles studied by neutron scattering — ●MARCO MACCARINI — Institut Laue Langevin, Grenoble, France

Polymer-capped gold nanoparticles (AuNP) have many peculiar aspects like quantum size effects and single electron transitions. Their properties are highly dependent on their size and shape and upon spatial relationship of one particle to another. Coating nanoparticles with polymers tethered to their surface by means of specific ligands stabilizes them, and allows functionalization for specific applications in nanotechnologies, biology and biomedical studies. We studied the structure and the dynamics of a key class of polymer-capped AuNP, those coated with poly ethyleneglycol (PEG). A novel synthesis was developed by ligand exchange procedure, which ensure the production of NP with little excess of functionalizing ligand and high stability. The structure PEG AuNP were studied by combining small angle neutron scattering as a function of temperature, and of the length of the interfacial polymer chains. PEG Au NP functionalized with short (PEG400) and long (PEG2000) polymer reflected substantial differences in the structure of the polymer at the interface. The dynamics of PEG AuNP in the nanosecond timescale was also studied by neutron spin echo (NSE) spectroscopy. NSE experiments showed two dynamical processes, one related to the translational diffusion of the nanoparticles, and a faster due to internal motion of the polymer chains. For comparison, NSE experiments were performed on PEG2000 polymer in solutions. Analogies and differences between free and anchored polymer will be discussed.

CPP 43.12 Thu 17:15 ZEU 222

Surface Layering of suspended Au-Nanoparticles — ●VOLKER SCHÖN¹, PATRICK HUBER¹, PHILIP BORN², and TOBIAS KRAUSS² — ¹Saarland University, 66123 Saarbrücken, Germany — ²Leibniz-Institut für Neue Materialien gGmbH, 66123 Saarbrücken, Germany

We present x-ray reflectivity measurements performed on our home made spectrometer showing that thiolated Au-nanoparticles suspended in toluene constitute layers at the toluene-air interface.

The experiments were performed in a closed cell with virtually no evaporation taking place, the height of the liquid being stable over

several days.

The number and density of these layers strongly depends on the concentration of said suspensions and is also influenced by temperature.

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In situ GISAXS investigation of Gold-sputter deposition onto colloidal polymer templates prepared by airbrush coating —

•ADELINE BUFFET¹, GERD HERZOG¹, MATTHIAS SCHWARTZKOPF¹, JAN PERLICH¹, MOTTAKIN ABUL KASHEM¹, VOLKER KOERSTGENS², PETER MUELLER-BUSCHBAUM², and STEPHAN V. ROTH¹ — ¹DESY, Notkestr. 85, 22607 Hamburg, Germany — ²TU Muenchen, Physik Department, LS Funkt. Mat., James-Franck-Str. 1, 85748 Garching, Germany

New applications for metal-polymer nanocomposites have emerged in the field of organic optics and electronics [1], or in the field of hybrid sensors [2]. Therefore, much effort has been put to better understand the growth process and structural transition of nanocomposites [3]. We investigated in situ the growth of a sputter-deposited ultra-thin gold film on top of a pre-structured colloidal polymer template using grazing incidence small-angle X-ray scattering (GISAXS). The underlying colloidal polymer template was deposited by using the novel technique of airbrush-spray coating, allowing for the installation of stripe-type trapezoidal pattern consisting of 3D hexagonally closed-packed colloids [4]. We present our findings on the formation of gold nanoclusters on top of the individual polymer colloids and give an outlook how to open a promising route to generate plasmon waveguides and photonic crystals, e.g. anti-reflective coatings. [1] Biswas, B. et al. *Vacuum Technology & Coating* 1, 54 (2006). [2] Wolkenhauer, M. et al. *Appl. Phys Lett.* 79, 054101 (2006). [3] Metwalli, E. et al. *Langmuir* 24, 4265 (2008). [4] Buffet, A. et al. *Adv. Eng. Mat. Journal*, Accepted (2010)

CPP 43.14 Thu 17:45 ZEU 222

Highly uniform SERS substrates formed by wrinkle-confined drying of gold colloids —

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Metallic nanoparticles, exhibit electric and optical properties which are size and shape dependent. Therefore, they are ideal candidates for

many applications. Big effort has been put in developing new methods to control their shape and size. These achievements allow us to fine tune the materials properties in order to use them for a desired application. However, the lack of capability to form organized structures is still a very important challenge in order to use these materials in many applications. In this work we report a novel method to structure, in a macroscale range, arrays of organized gold colloids into 1 and 2D linear parallel arrays which are highly uniform substrates for Surface Enhanced Raman Scattering (SERS). These structures were fabricated through self-assembly of gold nanoparticles upon solution-drying in a periodic confining structure. The technique leads to uniform, parallel linear nanoparticle arrays with the precise arrangement defined through the dimensions of the particles and the grooves. Moreover, the good reproducibility of these structures among big areas, make them perfect candidates as ultrasensitive substrates for SERS due to the formation of controlled Hot Spots arrays. Which provide high and uniform SERS enhancement over extended areas.

Topical Talk

CPP 43.15 Thu 18:00 ZEU 222

Are nanomaterials safe? Physico-chemical characterization for regulation and for life-cycle assessment of nanocomposites —

•WENDEL WOHLLEBEN — BASF SE, Polymer Physics Research, 67056 Ludwigshafen

Nanocomposites are the dominating class of nanomaterials to come into consumer contact. For the first time, our comprehensive study addresses a systematic series of thermoplastic and cementitious nanocomposite materials with SiO₂, CNT, crystal seeds as embedded nanofillers. We confirm earlier reports that 'chalking', i.e. release of pigments from weathered paints, does occur also for nanocomposites. In contrast, mechanical forces by normal consumer use or do-it-yourself sanding do not disrupt nanofillers from their matrix. Combining SEM, AUC, XPS, SIMS, diffraction we find no free nanofillers up to the detection threshold of 100 ppm. Sanding powder particles still contain the nanofillers. And yet, is there a hazard from these aerosols? We perform in vivo studies in rats and quantify physiological effects of degradation products. A summarizing risk assessment confirms that nanocomposites are indeed safe in consumer settings.

However, occupational safety against inadvertent inhalation of dust must be established by suitable methods for containment of specific nanomaterials. Physico-chemical characterization is key to identify such nanomaterials and to understand their biophysical interactions in a physiological environment.