CPP 59: Composites and Functional Polymer Hybrids

Time: Thursday 15:00–17:30 Location: H8

Invited Talk CPP 59.1 Thu 15:00 H8

Polymer-Grafted Nanoparticle Membranes with Exceptional Gas Separation Performance — •Sanat Kumar — Columbia University, Department of Chemical Eng., New York, NY 10025, USA

Polymeric membranes represent an efficient solution for separating gas mixtures, e.g., for natural gas purification. Several recent reviews emphasize that improved mechanical and gas separation (i.e., increased permeability and selectivity) performance is required from next-generation constructs; achieving these goals require that predictive structure-property relationships be developed for these materials. In this vein, here we leverage our evolving understanding of polymer brush physics to systematically design membranes which show exceptional improvements over the current state-of-the-art. We show that, while pure polymer-grafted nanoparticle (GNPs) membranes yield increased gas permeability through graft density and chain length variations, mixing GNPs with ungrafted polymers improves selectivity so that we routinely outperform the best currently available polymers. Surprisingly, we find that transport in pure GNPs is spatially inhomogeneous with large gases moved primarily through interstices, while smaller solutes diffuse more homogeneously in the polymer layer. Free chains segregate into these interstices, preferentially hindering large solute motion, thus dramatically improving selectivity. The ability to exploit spatial inhomogeneities in GNPs with ungrafted chains is a new, apparently general, paradigm to design membranes with unprecedented performance even using common polymer architectures.

CPP 59.2 Thu 15:30 H8

Insights into the porous structure of metal-imidazolate frameworks having high gas uptake — •Ahmed. G. Attallah[1], Suvendu. S. Mondal[2], Hans-Jürgen Holdt[2], and Reinhard Krause-Rehberg[3] — [1]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Radiation Physics, Bautzner Landstr. 400, 01328 Dresden, Germany — [2]Institut für Chemie, Anorganische Chemie Universität Potsdam, Karl-Liebknecht-Str. 24-25, 14476 Potsdam, Germany — [3]Institut für Physik, Martin-Luther-Universität, Von-Danckelmann-Platz 3, 06120 Halle, Germany

Several methodologies, like pore surface-amines functionalization, defect engineering, and others have been evolved to improve gas uptake by Metal-Organic-Frameworks(MOFs). It was reported that microwave(MW)-assisted synthesis of MOFs exhibited an enhancement of N2 and CO2 uptake capacity, compared to the analogous Conventional Electric(CE)-heating based materials. However, no detailed investigations on the origin of the high guest uptake capacity of MW-assisted materials have been carried out. In this work, three MW-assisted isostructural Imidazolate-Framework-Potsdam(IFP) which showed an enhancement of CO2 and H2 uptake capacities are investigated. These three samples have flexible methoxy and ethoxy linker arms. Thus, the aim here is to understand the reasons for the high gas uptake of materials synthesized by the MW-assisted conditions compared with the same materials synthesized by CE-heating methods. This study is performed by Positron Annihilation Lifetime Spectroscopy (PALS) in addition to other characterization methods.

CPP 59.3 Thu 15:45 H8

Touching and detachment: Nickel-particle movement in an elastomer matrix under exertion to magnetic field — •Henrik Schmidt[1] and Günter K. Auernhammer[2] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]Leibniz Institute for Polymer Research, Dresden, Germany

Magnetorheological elastomers are hybrid materials comprising a non-magnetic polymer matrix with interspersed magnetic filler particles. As they are complementary to MR fluids and MR foams they gained a lot of interest for applications. To be useful the volume ratio of particles has to be in the order where the particle distance is roughly around one particle diameter. To get a basic idea of the mutual interaction under a rotating magnetic field we reduced the system to two superparamagnetic nickel particles enclosed by a PDMS-matrix. For the correct parameters of particle diameter, distance and elastic modulus of the surrounding matrix the system exhibit a new state described in the following: After applying the magnetic field particles snap into contact. During rotation the particles separate at certain points to take their original position. Thus the particle distance shows a hysteresis in relation to the angle between magnetic field and particle axes. Calculating the dipole interaction shows an agreement with the experiments even though in contact a treatment of the particles as point-like dipoles should be not valid. Presented state of the MREs needs to be compared to theoretical models.

CPP 59.4 Thu 16:00 H8

Simulation of magnetodielectric effect in magnetorheological elastomers — •Danil Isaev[1], Anna Semisalova[1,2], Yulia Alekhina[1], Liudmila Loginova[1,3], and Nikolai Perov[1,3] — [1]Lomonosov MSU, Faculty of Physics, Moscow, Russia — [2]Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany — [3]Baltic Federal University, Kaliningrad, Russia

We present the computer model of the magnetodielecric effect (MDE) in magnetorheological elastomers. The effect is based on the assumption about the displacement of magnetic particles inside the elastic matrix under the external magnetic field and the formation of chain-like structures. Such displacement of metallic particles inside the elastic matrix of the sample between the planes of capacitor leads to the change of capacity, which can be considered as a change of effective dielectric permittivity of elastomer caused by magnetic field (MDE). In the model of the MDE the systems consist of around 100000 particles which are considered as isotropic and anisotropic samples varying with concentration of magnetic filler, size and space distribution of particles, elastic properties of the matrix. The influence of orientation of magnetic field and the capacitor plane was studied, the anisotropy of the effect was observed. The developed model resulted in a good qualitative agreement with experimental data obtained for Fe-based elastomers. It can be used to study these novel functional materials, analyze the features of magnetodielectric effect and predict the optimal composition of magnetorheological elastomers for further profound experimental study.

CPP 59.5 Thu 16:15 H8

Surface Lattice Resonances in the Visible Optical Range by Soft Lithography Templates and Directed Self-Assembly — •Vaibhav Gupta[1] and Töbias König[1,2] — [1]Leibniz-Institut für Polymerforschung Dresden e. V., hohe straße 6, D-01069 Dresden, Germany — [2]Cluster of Excellence Centre for Advancing Electronics Dresden, Technische Universität Dresden, Mommsenstraße 4, D-01062 Dresden, Germany

We demonstrate a novel approach towards cost-efficient and low-loss plasmonic nanostructures, whose pronounced optical anisotropy can be detected by naked eye. Soft interference lithography and template-assisted colloidal self-assembly are used to fabricate a flexible macroscopic periodic square lattice of gold nanoparticles. Surface scanning methods reveal a full coverage of the array. The high structural quality results in a narrow bandwidth surface lattice resonance with a line width of 25. We show the hybrid nature of the optical response using angle dependent UV-vis spectroscopy and numerical simulations. We propose a platform to curb the rigid nature of optical systems and offers versatile plasmon mode engineering. This real time band edge tunable metasurface can find potential application in long range coherent energy transfer. However the rational design framework established here allows for generalization in account for other wavelength regime and particle type.

15 min. break

CPP 59.6 Thu 16:45 H8

Disentangling the mechanical properties of polymer grafted nanoparticles — •Jiarul Midya and Arash Nikoubashman — Institute for Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany

Polymer grafted nanoparticles are promising materials with a wide range of applications in drug delivery, gas transport, photonic and electric materials. The mechanical properties of such materials can be controlled through the volume fraction and distribution of the nanoparticles, which can be achieved by changing the degree of polymerization of the grafted chains and their grafting density. Previous studies have tried to explain the elastic properties of nanocomposite materials

through the effective medium theory, which relates the elastic modulus directly to the volume fractions of the hard nanoparticles and of the soft polymer matrix. However, recent experiments have shown significant variations of the elastic modulus for nanocomposites with the same volume fractions but different grafting densities and chain lengths. This behavior can not be explained by the existing effective medium theory. To investigate the origin of this effect we have performed molecular dynamics (MD) simulations. We demonstrate that the chain conformations play a crucial role for the elastic modulus of the nanocomposite, a contribution which has not been taken into account in the effective medium theory.

CPP 59.7 Thu 17:00 H8

Rigid Amorphous Phase in Polymer Nanocomposites as Revealed by Dielectric Spectroscopy and Fast Scanning Calorimetry — •Paulina Szymoniak and Andreas Schönhals — Bundesanstalt für Materialforschung und prüfung (BAM), Berlin, Germany

For inorganic/polymer nanocomposites a so-called Rigid Amorphous Phase (RAF) is formed in the interfacial region by adsorption of polymer segments onto the nanoparticles. The segmental dynamics of RAF is expected to be altered, as compared to the pure matrix, which might percolate to the entire system, affecting the overall nanocomposite properties. A combination of two relaxation spectroscopy techniques (Broadband Dielectric Spectroscopy (BDS) and Temperature Modulated DSC (TMDSC)) as well as Fast Scanning Calorimetry (FSC) were employed to investigate the structure and molecular mobility of nanocomposites based on Epoxy and Layered Doubled Hydroxides with different nanoparticle content. First, BDS investigations proved the existence of a process, which is present only for nanocomposites, assigned to the dynamics of polymer segments within RAF. Second, the amount of RAF was quantified by analyzing the change of specific heat capacity step of nanocomposites, comparing to the pure material. Thirdly, the glass transition of nanocomposites was studied with FSC, applying high heating rates (0.5-10 kK/s). Considering that all techniques probe essentially the same molecular process, an activation plot was constructed, delivering a complete picture of the molecular mobility and structure of the polymer nanocomposites including RAF.

CPP 59.8 Thu 17:15 H8

Implicit-medium model for viscoelastic properties of fractal-like aggregates polymer nanocomposites — •François Detcheverry[1], Yang Wang[1], Gaëtan Maurel[2], Marc Couty[2], and Samy Merabia[1] — [1]Univ Lyon, CNRS, Institut Lumière Matière, Villeurbanne, France — [2]MFP MICHELIN 23, Place des Carmes-Déchaux Clermont-Ferrand, France

Dispersing solid fillers into a polymer matrix is a common strategy to enhance its properties. Polymer nanocomposites (PNCs) so obtained with fractal-like aggregates have exceptional rheological behavior long exploited in the tire industry. However, due to disparity of time and length scales, our understanding of the relation between nanocomposites structure and rheology remains incomplete. Here, we propose a mesoscopic model to simulate fractal-like aggregate PNCs. While aggregates are represented explicitly, we use for the polymer matrix an implicit description based on generalized Langevin and Stokes equations, that capture the average effect of a viscoelastic medium. Such a two-level description allows us to simulate large PNCs systems containing dozens of aggregates. Investigating the linear viscoelastic properties of PNCs, we find that compared to nanoparticles, aggregates may induce levels of reinforcement considerably larger and we characterize the influence of aggregate size, rigidity and volume fraction. We also examine the Payne effect and relate it to the alignment of aggregates under the imposed deformation. Our results may help in building connections between the macroscopic mechanical response of the PNCs and the mesoscopic morphology of the fillers.