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Dynamics of Polymers in Polymer Nanocomposites

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Filling soft polymer matrices with nanoparticles with high specific surface area leads to hybrid materials that may be optimised for a brought range of applications. Although polymer nanocomposites have been extensively studied for several decades a clear microscopic picture relating to the structure and dynamics of the polymer matrix under filling conditions has not yet emerged. Both geometrical confinement effects as well as the interaction of the polymer with the nanoparticles play an essential role.

This talk will present systematic neutron spin echo investigations on the dynamics of polymers in nanocomposites that elucidate the influence of nanoparticles on the intermediate and large scale dynamics of the polymer matrix. Starting with repulsive nanoparticles, where the geometrical effects dominate, hydrophobically modified silica nanoparticles were introduced in a short chain non-entangled polyethylenpropylen (PEP) matrix and into the entangled counterpart. Under these circumstances the segmental (Rouse) relaxation rate is not altered even at high filling rates. The unexpected and dominating effect of nanoparticles in a short chain matrix is a significant reduction of the short time translational diffusion coefficients at filler concentrations where geometrical confinement effects should not play an important role. Intra-chain interaction that transports the reduced chain mobility close to the surface into the bulk and gives rise to anomalous diffusion at high filler concentration was identified as a reason for this phenomenon. Long

entangled PEP chains experience reptation dynamics that expresses itself by the confining virtual tube. The apparent tube diameter decreases significantly with increasing particle content. An evaluation of the geometrical confinement leads to the conclusion that a gradual cross over from polymer-induced confinement at low filler concentrations to particle-induced confinement at high filler concentrations is observed. In this context the chains disentangle, arriving at a situation that corresponds to de Gennes polymer motion under fixed obstacles. These microscopic findings relate well to rheological observations.

The notion of disentanglement under strong confinement has been quantitatively shown on a model system where long chain polymers were confined in narrow alumina nanopores. Under these circumstances a widening of the tube is observed if the pore diameter becomes smaller than the chain end-to-end distance.

The case of nanoparticles interacting with the polymer matrix by attractive interactions has also studied. Polyethylene-oxide (PEO) was filled with neat SiO2 nanoparticles up to 15 vol%. Investigating a short chain matrix, the realisation arose that a fraction of chains is adsorbed at the nanoparticle surface, suppressing completely its translational diffusion. Nevertheless these adsorbed chains undergo an unchanged segmental dynamics seemingly forming a micelle like corona of chains connected with their OH-end groups. Changing to methylene terminated chains, the picture changes drastically - now showing a tightly adsorbed layer that however is not glassy as often assumed but rather undergoes picosecond local dynamics.

These results are corroborated and extended by studying the dynamics of Polydimethylsiloxane (PDMS) confined in nanoporous Alumina. There a partly anchored chain fraction is found that undergoes restricted Rouse motions with segmental mobilities as in the bulk phase. The size of this layer exceeds significantly the length scale of the directly adsorbed polymer, presenting a first direct microscopic evidence for the hypothetical interphase.