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Dynamics of Linear Entangled Polymers Reinforced with Nanoscale Rigid Particles

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Recent molecular dynamics simulations [1-3] suggested that the polymer-surface interactions can be the dominant factor in the rheology of polymer systems filled with nanoparticles. These interactions include the short-range forces between the surfaces and the polymer segments. These forces can be responsible for the suppression of the mobility of the polymer segments at the surfaces and even result in the formation of an immobilized glassy layer at the surfaces. Dionne et al. [3] studied the structure and dynamics of an amorphous polyethylene (PE) melt containing homogeneously distributed spherical nanoparticles. The PE chains were simulated using both molecular dynamics and Monte Carlo methods. The chain dynamics were monitored by computing the Rouse relaxation modes and the mean-square displacement (MSD). The most notable observation they pointed out, was the slowing down in the Rouse dynamics seen on all subsections of the chain no matter how small the subsections were, meaning that on average every monomer feels the confinement of the neighboring particles, slowing the relaxation of every chain subsection. They also showed that the slowing down due to polymer-particle energetic interaction was similar for all relaxation modes, independent of their wavelength.

Taking advantage of these insights, a reptation-based model, that incorporates transient polymer-particle surface interactions, is proposed to describe the dynamics and rheological behaviors of linear entangled polymers filled with isotropic rigid nanoscale particles. Dispersed nanoparticles are sufficiently small such that even at low volume fractions, the average particle wall-to-wall distance is on the order of the chain size. The model predicts a scaling law in the form, $\tau_{d,eff} \sim \tau_d(\phi_{ad}N+1)^2$, where $\tau_{d,eff}$ is the effective reptation time of a chain in the presence of attractive nanoparticles, τ_d is its reptation time in the neat polymer, ϕ_{ad} is the fraction of attached monomers per chain, and N is the number of monomers per chain. Hence, the overall relaxation is extremely retarded by attractive nanoparticles in the limit of strongly adsorbed chains. Also, it is found that the effective reptation time, $\tau_{d,eff}$, can be controlled through five main parameters, i.e., the molecular weight of the polymer chain, N, the size of the nanoparticles, d_f, the density of attractive site on the nanoparticle surface, n_{as}, the monomer-nanoparticle energetic interaction, ε, and the nanoparticle volume fraction, ϕ_f. The nonequilibrium dynamics of detachment/re-attachment of monomers from/to nanoparticle surfaces under flow conditions is incorporated in the model to elucidate the effects of monomer-surface interactions on the nonlinear viscoelastic behavior. The resulting model correctly captures the linear dynamical properties and shear rheological behaviors of nanocomposite systems studied (Figures 1-2). A picture that is based on transient polymer-particle surface interactions, i.e., the detachment/re-attachment dynamics of monomers from/to nanoparticle surfaces is proposed to interpret the observed huge alteration in rheological properties.

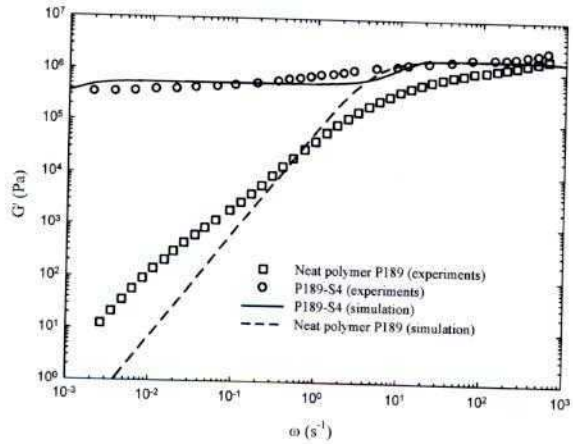

Figure 1: Frequency dependence of storage modulus, $G'(\omega)$, for the neat PEO P189 and the PEO/silica nanocomposites P189-S4 ($\phi_f = 4\%$). Comparison of numerical predictions and experimental data of Zhang and Archer [4]

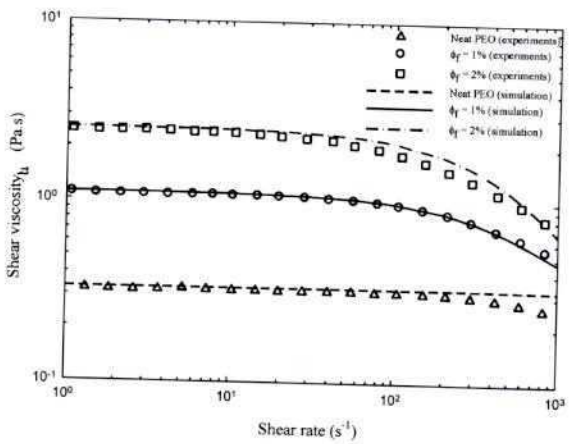

Figure 2: Shear rate dependence of the steady shear viscosity, η, for the neat PEO P700 and the PEO/silica nanocomposites. Comparison of numerical predictions and experimental data of Zhang and Archer [5]

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