Dynamics of Linear Entangled Polymers Reinforced with Nanoscale Rigid Particles

K. Kabanemi¹, J.-F. Hétu²

¹ National Research Council of Canada, Industrial Materials Institute, Boucherville, Canada, Kalonji.Kabanemi@nrc.ca
² National Research Council of Canada, Industrial Materials Institute, Boucherville, Canada, Jean-Francois.Hetu@nrc.ca

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. Using the theory of the activation process, it is shown that the polymer-particle interactions give rise to an exponential increase of the characteristic time, \( \tau_g \), for the detachment of all trapped monomers in the chain, from nanoparticle surfaces, i.e.,

\[
\tau_g \propto \exp \left( \varepsilon \theta_a \frac{\phi f n_{as}}{d_f} N^{3/2} b^3 \right),
\]

where \( N \) is the number of monomers per polymer chain, \( b \) the length of a monomer, \( d_f \) the diameter of nanoparticles, \( \varepsilon \) a parameter representing the polymer-particle energetic interaction, \( \theta_a \) the fraction of attractive sites on the nanoparticle surface occupied by monomers, \( n_{as} \) the number of attractive sites per unit surface of the nanoparticle, and \( \phi_f \) the nanoparticle volume fraction. Hence, the effective reptation time for the overall motion of the chain turns out to be exponentially large with the nanoparticle addition, leading to a slowing down of the reptation dynamics. 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, $\eta$, for the neat PEO P700 and the PEO/silica nanocomposites. Comparison of numerical predictions and experimental data of Zhang and Archer [5]

References


