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Fall 11-9-2015

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### Recommended Citation

Jacinta Conrad, Ryan Poling, Firoozeh Babaye, and Ramanan Krishnamoorti, "Transport of nanoparticles in polyelectrolyte solutions as a model of polymer nanocomposite processing" in "Composites at Lake Louise (CALL 2015)", Dr. Jim Smay, Oklahoma State University, USA Eds, ECI Symposium Series, (2016). [http://dc.engconfintl.org/composites\\_all/29](http://dc.engconfintl.org/composites_all/29)

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# TRANSPORT OF NANOPARTICLES IN POLYELECTROLYTE SOLUTIONS AS A MODEL OF NANOCOMPOSITE PROCESSING

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Key Words: Nanoparticle, Non-Newtonian fluid, Polyelectrolyte, Transport, Nanocomposite

The transport properties of nanoparticles in complex confined media play a significant role in the processing of advanced polymer nanocomposites. In polymer nanocomposite processing, nanoparticles suspended in polymer resins must be efficiently dispersed to obtain optimal mechanical, electrical, thermal, and/or optical properties and eliminate stress concentrators. Here, we investigate the diffusion and dispersion of nanoparticles in solutions of unentangled polyelectrolytes as a model system in which to understand the coupling between particle and polymer dynamics in flow conditions representative of those encountered during nanocomposite processing.

First, we measure the long-time quiescent diffusivity of fluorescent polystyrene nanoparticles in dilute and semidilute solutions of partially hydrolyzed polyacrylamide. At short time scales, the particles exhibit subdiffusive behavior, as characterized by sublinear scaling of the mean-square displacement with time. On long time scales, the particles exhibit Fickian diffusion from which the diffusivities are extracted. Whereas diffusivities of the large particle agree with predictions using the Stokes-Einstein equation and bulk zero-shear viscosity, the smaller particles diffuse much faster than predicted. To capture the particle- and polymer-size dependence of the long-time diffusivity, we propose a model in which particles diffuse in a matrix with relaxing constraints caused by the diffusion of polymer segments. We derive an effective length scale that collapses the long-time diffusivities onto a single curve and cleanly captures a smooth crossover to bulk behavior when the particles are much larger than the polymer chains. Furthermore, the effective length scale controls the crossover time scale between subdiffusive and Fickian behavior for all particle sizes and polymer concentrations. These results demonstrate that polymer mobility controls the size-dependent deviations from Stokes-Einstein behavior for nanoparticles diffusing in unentangled polymer solutions

Second, we visualize transport of nanoparticles suspended in Newtonian and non-Newtonian solutions through porous media using confocal microscopy. We flow nanoparticles suspended in glycerol-water mixtures or in solutions of unentangled polyelectrolytes through porous media of varying pore size. Both the longitudinal and transverse distributions of normalized velocities scale onto master curves, which are independent of solution viscoelasticity, pore size, and flow properties. Although the polymer elasticity may affect the time over which the dispersion coefficients approach asymptotic limits, the long-time (asymptotic) dispersion coefficients of nanoparticles in both the longitudinal and transverse directions scale onto master curves as a function of the Péclet number characterizing the flows, again independent of viscoelasticity, pore size, and flow properties. These results suggest that flow through rigid porous media, such as matrix fibers in certain polymer nanocomposites, may “break” the non-Newtonian characteristics of a complex polymeric solution.