

Bulk and Interfacial Behavior in Polymer-Nanoparticle Melts

Amalie Frischknecht
Sandia National Laboratories
PO Box 5800 MS 1411
Albuquerque, NM 87185

Recent experimental work has revealed interesting behavior both in the bulk and near interfaces for polystyrene nanoparticles blended with polystyrene. We model these materials as mixtures of hard spheres and freely jointed hard chains. In the bulk, it was found experimentally that addition of nanoparticles causes an increase in the chain dimensions. To study this effect we apply a self-consistent version of the polymer reference interaction site model (PRISM) theory. We calculate the dimensions of the chains through a single-chain Monte Carlo simulation done in an effective solvation potential. We find an increase in the average radius of gyration of the chains in the blend (over that from chains in a neat melt at the same density) once the chains start to become confined by the nanoparticles. When the blend is near a hard substrate, the nanoparticles segregate to the substrate. Using a fluids density functional theory, we find that there is a first order phase transition in which the nanoparticles expel the polymer from the substrate to form a monolayer at a certain nanoparticle concentration. The nanoparticle transition density depends on the length of the polymer, the nanoparticle diameter, and the overall bulk density of the system. The phase transition is due to both packing entropy effects related to size asymmetry between the components, and to the polymer configurational entropy, justifying the so-called “entropic push” observed in experiments.

This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the U. S. Department of Energy under Contract No. DE-AC04-94AL85000.