Liquid State Theory of the Structure and Phase Behavior of Polymer-Tethered Nanoparticles in Dense Suspensions, Melts and Nanocomposites

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Polymer grafted nanoparticles serve as a new class of nanofillers in polymer nanocomposites. We will present a Polymer Reference Interaction Site Model (PRISM) theory study of polymer-grafted nanoparticles with finite number of polymer grafts. The complex interplay of entropy (translational,conformational and packing) and enthalpy (particle-particle attraction) leads to different structural arrangements with distinctive scattering signatures. Melts of polymer-tethered nanoparticles show strong concentration fluctuations indicative of aggregate formation and/or a tendency for microphase separation as the total packing fraction and/or nanoparticle attraction strength increase. When polymer-tethered nanoparticles are added to a homopolymer matrix there is competition between nanoparticle attractions, steric repulsion between grafted polymers, and polymer matrix induced depletion-like attraction. For nanoparticles with only one grafted polymer, volume of the grafted polymer being equal to the volume of the nanoparticle, the apparent microphase spinodal curve exhibits both dilution-like and depletion-like features, and a non-monotonic dependence on matrix chain length. As the particle size and length of the grafted polymer increases, such that the total space filling volume of the tether continues to equal the nanoparticle volume, the shape of the microphase spinodal curve remains unchanged, but the effect of matrix polymer chain length on the spinodal temperature diminishes. We will present results showing the effect of varying particle sizes, number of grafted polymers, matrix polymer length and composition of the composite on the phase behavior of the polymer nanocomposite.