Suspensions of polymer grafted nanoparticles with added polymers - Structure and Effective pair interactions

Nanoparticles with small inorganic core grafted with polymers, the polymer grafted nanoparticles (PGNPs), have attracted much attention due to the ease of tuning the dispersion behavior by varying the relative molecular weights of the grafting and matrix polymers. It is well established that adding small additives to polymer matrices, enhance their thermal, optical and mechanical properties. For instance, by tuning the morphology of the grafted chains and by varying the graft molecular weight with respect to matrix, we have shown both melting and reentrant dynamic behaviors in melt [1,2]. Inspite of many striking observations, the reasons behind the enhancement in the properties of these systems are still elusive, primarily due to the absence of model potentials that could describe their behavior. This is probably because of the perception that the effective potential between these particles should be similar to the structural analogues, the star polymers. In our recent study [3], we have performed small angle x-ray scattering experiments for measuring the structure factor of the suspensions of PGNPs and of the blends of PGNPs and added polymers in a good solvent. Two different molecular weights of the linear polymers are used for tuning the interface morphology between the PGNPs and polymers. Using the combination of coarse grained molecular dynamics simulation and integral equation theory, we have modeled the structure factor of the suspensions using two different models: (a) Model-X originally developed for describing the star polymers and (b) Model-Y a mean field model based on the interaction of only two PGNPs dispersed in a sea of linear polymers. Based on the simulations, we have observed that both the models partially work for PGNP suspensions and low density of added polymers, but break down for samples with large density of added polymers, irrespective of the molecular weight. We have ascribed the breakdown of these models to the assumptions in both the models. Our results indicate to the need for a better theoretical framework for understanding the behavior of PGNPs and to describe their properties as well.

Figure-1: Partial Success of the Model Potentials: (a) Structure factor of the PGNP suspension is shown in comparison with the data obtained through the simulations using Model-X. The structure factors of the blends (mixtures of PGNPs with linear polymers having higher molecular weight in comparison with the graft polymer) are shown in comparison with the data obtained from both Model-X (b) and Model-Y(c). H1-H3 indicates blends with increasing concentration of added polymers with respect to the PGNPs. Symbols represent the experimental data and continuous lines represent the data generated using simulation. It can be observed that the models are capturing the most essential features of the experimental data, though both the models fail in capturing the evolution of the second peak.
Figure-2: Break down of the Model Potentials: The structure factors of the blends (mixtures of PGNPs with linear polymers having lower molecular weight in comparison with the graft polymer) are shown in comparison with the data obtained from both Model-X (b) and Model-Y(c). Symbols represent the experimental data and continuous lines represent the data generated using simulation. It can be observed that both the models fail to capture even the first peak of the experimental structure factor.

References