Controlling the Assembly of Nanoparticles in Polymer Nanocomposites

ABSTRACT

Controlling the morphology of nanoparticles in a polymer matrix is crucial for tuning the macroscopic properties of the resulting polymer nanocomposites. In thin film, due to the presence of a substrate/ air interface, nanoparticles are entropically pushed to the surface. When the surface is grafted with polymer chains that are chemically similar to the matrix chains, the tethered chains shield the depletion attraction between the surface and nanoparticles and prevent the particles from migrating to the surface. At low grafting density, both polymers and nanoparticles penetrate into the brushes. But as the grafting density increases, the matrix dewets the brush due to strong steric repulsions between the grafted monomers and the matrix chains, causing the nanoparticles to occupy the interfacial region. In systems consisting of polymer matrix, bare ungrafted spherical nanoparticles and polymer-grafted nanoparticles, where the particle cores are identical and grafted chains are similar to matrix polymer, we observed that the introduction of grafted particles to the blend prevents the migration of bare particles to the surface. This unusual behaviour is caused by the formation of binary aspherical clusters due to the presence of grafted particles. Hence, parameters including grafting density and the length of the grafted polymer play a significant role in dictating the spatial arrangement of bare particles in the blend film. In bulk systems, we observe that addition of grafted nanoparticles to a blend of polymer and bare particles can result in the formation of anisotropic structures. By carefully selecting the grafting density and molecular weight of the grafted chains, the clusters go from spherical to cylindrical to branched cylinders. The formation of anisotropic structures are mainly due to the difference in tendencies of the two types of nanoparticles to aggregate that is controlled by the intrinsic balance between the enthalpic and entropic forces governing the self-assembly. Varying of interactions and type of nanoparticles, allows clusters for many ways in which behavior can be tuned and controlled. Our study suggests that it is indeed possible to control the morphology of bare nanoparticles in polymers without directly modifying their surface properties. We believe that this phenomenon might be of high importance, especially in cases such as polymer-based solar cells, where it is not feasible to graft the nanoparticles with polymer chains to achieve a greater level of control over the morphology.

Keywords: Polymer Nanocomposites, Morphology, Depletion attraction, Segregation,

Polymer brush, Polymer grafted Nanoparticle, Self-assembly.