

We studied dispersion state and dynamics of polymer grafted nanoparticle in photopolymer matrix nanoparticle-polymer blend- and their thermal and rheological properties. While thinking about a nanoparticle-polymer blend, the first question comes in is the dispersion state of nanoparticle in polymer. Especially in case of a blend film, dispersion of nanoparticle is very crucial in deciding its properties. It is still a challenging problem to get the dispersed blend even after 30 years of its invention. So, we started our work with the investigation of nanoparticle dispersion in polymer melt film and its evolution with time at high temperature. Eventually we studied the dynamics of nanoparticle in polymer melts at high temperature and the rheological and thermal properties of these blends.

In **chapter 1**, I have provided the introductory discussion about polymer's conformation, dynamics etc. Polymer grafted nanoparticle dispersion and its dynamical behaviour in polymer matrix has been discussed in this chapter briefly. The experimental techniques used for this work have been explained in **chapter 2**. It is well known that preparation process of a blend film has a significant contribution to the final dispersion state of nanoparticle. A good practice to prepare such blend films is to anneal the film after it spincoated on a hard substrate. The purpose is to remove the trapped solvent as well as removing the unstable/meta-stable state achieved by sudden freezing of the polymers during spincoating. It was observed that the dispersion state of nanoparticle is improved after annealing. We study this evolution of dispersion at annealing temperature using in-situ X-ray scattering measurement and presented in **chapter 3**. We found super-diffusive in-plane and very slow out of plane motion of polystyrene grafted gold nanoparticle (PGNP) in polystyrene (PS) matrix at high temperature ( $T > T_g$ ). The PGNP dispersion becomes homogeneous throughout the film which is otherwise a segregated film. After cooling down to room temperature, even though a partial reversal of the segregation occurs, the final dispersion state is better than that before annealing. We have shown a method of capturing the well dispersed state (the high temperature dispersion state) of PGNP at room temperature.

In **chapter 4** we presented the study of PGNP dynamics in the polymer melt film at high temperature where the particles are expected to be almost homogeneously dispersed as we found in the previous observations. Anomalous relaxation dynamics is observed leading to an unusual temperature dependence of effective viscosity of the

film and the anomaly increases under confinement. The observed anomalous behaviour could be explained in terms of the hydrodynamic slip experienced by the PGNP while the system has a dewetting PGNP-polymer interface. We estimated approximate slip length at the PGNP-polymer interface as a function of temperature and thickness. The slip length diverges at low temperature. Thickness dependent study reveals an increase of slip length under confinement resulting in a stronger anomaly for thinner films. Slip length at a polymer melt-polymer grafted wall interface (flat interface) as well as polymer melt-polymer grafted spherical particle interface (spherical interface) has been calculated by varying temperature and miscibility parameter,  $f$  ( $f$ =ratio of grafted and matrix chain molecular weight) using molecular dynamics simulations. A good agreement established between the simulation and the observed experimental results. In associated with the interface slip, the PGNP-polymer interface layer seems to have an effective interface viscosity which is different from bulk polymer viscosity.

A strong wave vector dependent hydrodynamic interaction between PGNPs was indicated by the observed temperature and wave vector dependent short time diffusion coefficient. This phenomenon could be explained in terms of the full slip boundary condition at the PGNP-polymer interface.

It is not surprising that the properties, e.g. thermal, rheological properties would get affected by the dispersion of PGNP as well as their dynamics. In **chapter 5** we explored rheological properties of nanoparticle-polymer blend film such as viscosity using force-distance spectroscopy for different miscibility parameters,  $f$  and temperature. A reduction in the viscosity of the blend film was observed with respect to its pristine polymer film for a smaller  $f$  value. The deviation of blend film viscosity from pristine polymer film viscosity reduces with increase in  $f$ . The extent of the viscosity reduction for smaller  $f$  increases towards lower temperature. Further, we have studied demixing temperature of a two component polymer blend system (Polystyrene (PS)/Poly (vinyl methyl ether) (PVME) blend) getting influenced by the presence of PGNP dispersed in it.

When the grafted chain length is much higher than the matrix PS chain, the demixing temperature gets increased, while the grafted chain length is much smaller than matrix PS leads almost no change. The PGNPs are observed to be present in the PVME phase while the grafted PS chains are too short compared to the matrix

PS chains and in opposite case while grafted chain is larger compared to matrix PS chains, the PGNPs are located at the PS matrix. Rheological property of the PGNP suspensions in presence of linear PS chains has been studied using diffusing wave spectroscopy and presented in **chapter 6**. A change in frequency dependence of viscous modulus was observed in a case where the linear PS chain is much longer than the grafted PS chains with increasing concentrations of PS linear chains indicating a shear thickening behaviour at higher linear PS concentrations. Presence of shorter linear chains do not show any such change in frequency dependence. To investigate about the observed shear thickening, dynamic light scattering measurement were performed on these samples. A large shrinkage of nanoparticle corona in presence of large linear chains was observed which could lead to the observed shear thickening behaviour. The shorter linear chains inter-penetrate into the grafted chains resulting in a swelling of nanoparticle grafts. Comparatively lower resultant viscosity observed for shorter chains possibly due to the faster mobility of shorter chains penetrating into the grafts. Finally in **chapter 7**, I summarize my thesis work and express my future work plan.