

Synopsis

Multiphase materials with precise structures are essential in designing materials for applications in various diverse areas like sensors, photovoltaics, porous membranes, etc. The transient morphology developed during demixing of polymer blend is a new class of materials. Hence, it is important to understand the underlying dynamics behind the intriguing transient morphologies in phase separating polymer blends. The thesis entitled “**Mapping the transient morphologies and demixing behavior of Polystyrene/ Poly(vinyl methyl ether) blend in the presence of multiwall carbon nanotubes**” systematically studies the effect of multiwall carbon nanotubes (MWNTs); where the characteristic dimension is of the order of radius of gyration of the components, on the chain dynamics, demixing temperature and evolution of morphology. PS/PVME is a classical Lower Critical Solution Temperature (LCST) polymer blend. Due to the large difference in the glass transition temperature between the components ($\Delta T_g \sim 100$ °C), it shows a phenomenal demixing called viscoelastic phase separation (VPS).

The thesis comprises of seven chapters. **Chapter 1** is an introductory note outlining the fundamentals of polymer blend demixing and also briefs about various theoretical models currently available, which explains the effect of fillers (nano and micro) on the demixing of polymer blend. The chapter also gives an overview of the reported studies with fillers of various shapes and surface modifications on the demixing. In **Chapter 2**, the materials used to carry out experiments, experimental set-up and procedures are explained.

Chapter 3 of the thesis focuses on understanding the effect of MWNTs on the chain dynamics of the polymer blend in their miscible region, i.e., in temperature regimes close to the glass transition temperature (T_g) and $T_g < T < T_g + 60K$. The effect of MWNTs on the length of cooperatively rearranging region (CRR) (ξ_{CRR}) around the T_g was assessed using modulated differential scanning calorimetry (MDSC) measurements. The T_g , the broadness of T_g and the corresponding heat capacity has been used to analyse the effect on ξ_{CRR} by the incorporation of MWNTs in the blend. The concentration fluctuation close to T_g was also assessed using the

same concept. It was observed that the ξ_{CRR} was moreover composition independent. There is no significant change in glass transition temperature in these blends with the addition of MWNTs; though a significant change has been observed in the effective glass transition temperature of the blend. The observed variation of effective glass transition of PVME (low T_g component) on blending with PS (high T_g component) and by the addition of MWNTs accounts for the dynamic heterogeneity introduced by MWNTs in the system.

Further, the studies were extended to a temperature regime of $T_g < T < T_g + 60\text{K}$, where chain connectivity dominates the thermodynamic concentration fluctuation. This was carried out using dielectric relaxation spectroscopy (DRS). A bimodal relaxation was obtained in DRS in presence of MWNTs, plausibly due to different environments experienced by the faster component (PVME) surrounded by the stiffer slower component PS and the MWNT network. These heterogeneities are induced due to the particle and polymer interaction compared to the polymer-polymer interaction in case of blends.

Chapter 4 gives a comprehensive analysis of demixing temperature and thermal concentration fluctuation in these blends. This was carried out using low amplitude isochronal temperature sweep by rheology. The demixing behavior in PS/PVME blends was greatly altered in presence of very low concentration of MWNTs. The specific interaction of the nanoparticles (NPs) with PVME has altered the chain dynamics in the interfacial region as compared to bulk, which later affects the demixing temperature in these blends. The addition of MWNTs has increased the rheological demixing and also the spinodal temperature in both PS rich and PVME rich blends. The localization of MWNTs in one of the phases has changed the dynamic asymmetry by inducing heterogeneity even at low concentrations. These observations are in corroboration with the various theoretical models proposed in the similar field.

Chapter 5 illustrates the effect of MWNTs on the unique phase separation mechanisms observed in PS/PVME blends like aggregating nucleation and growth (ANG), coalescence induced viscoelastic phase separation (C-VPS), transient gel induced viscoelastic phase separation (T-VPS), etc. The evolution of morphology has been assessed using *insitu* temperature ramps in Polarized Optical Microscopy (POM); where the blend films were heated

at a constant rate from the initial homogeneous regime to the phase separated regime. The micrographs of the annealed films using AFM (atomic force microscopy), Peak force quantitative nanomechanical mapping (PFQNM) and Scanning electron Microscopy (SEM) confirms the observation.

The use of chain-end grafted nanoparticles to improve the spatial distribution of nanoparticles in a polymeric host has been described in the **Chapter 6** of the thesis. The improved dispersion is due to the enhanced interfacial interaction with the host. Different molecular weight of PS (13 kDa, 31 kDa and 46 kDa) was synthesized using RAFT (reversible addition-fragmentation chain transfer) polymerization and was grafted onto MWNTs *insitu* using thiol-ene reaction. Besides changing the material properties of the host, these grafted nanoparticles also strongly alter the dynamics of the polymer chain at both local and cooperative length scales (relaxations) by manipulating the enthalpic and entropic interactions. The slower dynamics induced by these chain-end grafted nanoparticles has improved the connectedness of the slow domains. It becomes difficult to map the distribution of these chain-end grafted nanoparticles in the blend by conventional techniques and therefore unique technique like PFQNM. The results from DRS support the observation from PFQNM.

Chapter 7 summarizes the improratnt results and future directions of the work. In the narrowest sense, the addition of MWNTs creates a spatial and temporal heterogeneous environment, which can be attributed as a key reason for the development of these intriguing morphological changes and also the demixing behavior. The MWNTs change the dynamic asymmetry in the blends by introducing heterogeneity even at low concentrations. The morphology evolution proceeds by a fracture transition; the ductile fracture for near critical composition and brittle transition at off-critical composition. All these observations were correlated with the chain connectivity effects by evaluating the effective glass transition of the PVME phase and the bimodal relaxation, as observed from MDSC and DRS. Taken together, the free energy balance has to be take into account, considering the enthalpic interactions between the grafted PS and the free PVME or PS in the case of chain-end grafted nanoparticles. The deformational entropic losses on blending, translational entropic loss of PVME and the conformational entropic loss of

the grafted PS and the interface of the particle and the free chains contribute to the miscibility of the blend. Understanding the dynamics at a length scale closer to Kuhn length helps to design different structures by thermally induced phase separation (TIPS) for various applications, like creating porous structures and also aligning the rod shaped nanoparticles to achieve low percolation threshold.