Theory and Simulation Studies of Structure and Thermodynamics in Polymer Nanocomposites and Polymer Blends

Arjita Kulshreshtha
Advisor: Prof. Arthi Jayaraman
Committee Members: Prof. LaShanda Korley, Prof. Norman Wagner, & Prof. Laure Kayser

In polymeric materials comprised of two or more components (e.g., blends of polymers or composites of polymer(s) and nanoparticles), the macroscopic properties are dictated by the spatial arrangement (i.e., morphology) of the constituent polymer(s) and/or nanoparticles. The molecular design of the constituents and their composition in the mixture dictates the morphologies at various length scales. Therefore, to develop polymeric materials with desired properties needed for applications including chemical separation, electronics, food packaging, automotive and aircraft engineering, there is significant motivation to create fundamental knowledge linking molecular design parameters to morphology and function.

The overarching goal of my doctoral dissertation is to establish how molecular design relates to morphologies of interest specifically within polymer blends (i.e., mixtures of polymers) and polymer nanocomposites (i.e., mixtures of polymers and nanoparticles) and elucidate the thermodynamic driving forces dictating such molecular design-morphology relationships. These driving forces are of entropic and energetic origin and depend on many design parameters including polymer(s') chemistry, molecular weights, architectures, surface functionalization of particles, and composition of each component within the nanocomposite/blend. To sample this large design parameter space, we use molecular simulations and theory to identify optimal molecular design parameters towards desired blend/nanocomposite morphologies. Specifically, we focus on polymer nanocomposites and blends that contain polymer chemistries with dominant directional interactions like hydrogen bonding, π-π stacking, and metal-ligand coordination bonding etc. A challenge with molecular simulation studies of directionally interacting polymers is the lack of models that capture both the short length and time scales associated with localized directional interactions as well as the long length and time scales associated with polymer chains. For example, atomistic models represent atoms participating in directional bonds explicitly, but this detailed representation makes it computationally intensive to simulate the long length and time scales relevant to polymer self-assembly. On the other hand, computationally less intensive coarse-grained (CG) models represent an atom/group of atoms as CG beads with isotropic and symmetric interactions missing effects specifically brought about by directional interactions. To address the limitation with existing atomistic and CG models in capturing directional interactions in polymers, first, I discuss our efforts on the development of a new phenomenological CG model that mimics directional interactions like hydrogen bonds in generic

polymers and show how we parameterize the CG model to specific polymer chemistries [e.g., poly(4-vinylphenol) and poly(2-vinylpyridine)].

Next, I present studies using the developed generic CG model in molecular dynamics (MD) simulations focused on how morphology within polymer nanocomposites is impacted by directional versus isotropic interactions between constituent polymers i.e., the polymers grafted on particle surface (termed as graft polymers) and matrix polymer. Using liquid-state theory along with CG MD simulations, I also show the impact of increasing strength of attractive (isotropic and directional) interactions between graft and matrix polymers on the graft and matrix interpenetration and the spatial arrangement i.e., dispersion/aggregation of the nanoparticles in the polymer matrix. In conjunction with experiments from our collaborators' laboratories, we show how interactions between graft and matrix polymers can be utilized to achieve dispersed morphologies in polymer nanocomposites.

Next, I present theory and simulation studies of morphology and phase behavior in binary polymer blends where the constituting polymers interact via both isotropic polymer interactions and associative interactions (i.e., either hydrogen bonds or other directional interactions). The competition between (directional) associative interactions and (isotropic) segregation of polymer chemistries and the placement and composition of associating groups along polymer chains together dictate the resulting blend morphology. These studies establish design rules for incorporating associating functional groups to promote blend miscibility.

Overall, in this dissertation I demonstrate how liquid-state theory and molecular simulations with coarse-grained models can be used synergistically to understand the thermodynamic driving forces governing morphology in polymer blends and polymer nanocomposites with favorable directional interactions. This research work provides guidelines and future directions for using attractive directional interactions to tune morphology in macromolecular systems.