CHARACTERISTICS OF INTERFACES IN ABA TRIBLOCK COPOLYMER/HOMOPOLYMER SYSTEMS FROM SIMULATIONS AND THEORY

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Introduction

Triblock copolymers that are comprised of glassy end-blocks and rubbery mid-blocks have been studied widely due to their applicability in a diverse range of applications. Recent development in the blends and mixtures of such copolymers with homopolymers has revealed unparalleled potential to realize self-assembled nanostructured
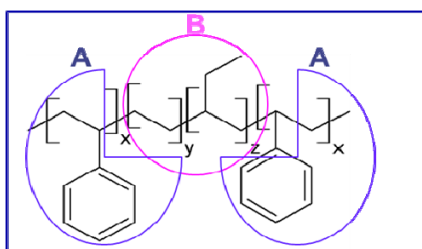

Figure 1. Chemical structure of the SEBS triblock copolymer of symmetric ABA architecture.

soft materials.[1]. Although the thermodynamics of the phase segregation in such systems is well documented, the dynamics and non-equilibrium characteristics of self-assembly in these materials are not yet fully understood. Therefore, we employ a combination of mesoscale simulations and self-consistent field theory (SCFT) calculations to explore the interfacial characteristics of homopolymer/triblock copolymer systems. This study is of particular relevance to the behavior of block copolymers having glassy end-blocks and rubbery mid-blocks such as poly(styrene-co-isoprene-co-styrene) and poly(styrene-co-ethylene butylene-co styrene) (SEBS, Figure 1) and their blends with polyolefin homopolymers.

Results and Discussion

Self-consistent field theory calculations. The triblock copolymer structure included in this study is a symmetric triblock copolymer (ABA) similar to the SEBS molecular architecture given in Figure 1. The SCFT code implemented in this work follows the work of Rasmussen and coworkers[2] on triblock copolymer/solvent systems and is extended to accommodate homopolymer/copolymer systems. The system under consideration is comprised of a homopolymer component (H) that is compatible with the mid-block component. The thermodynamics incompatibility between the end-blocks and mid-blocks (χN_{AB}) and between the end-blocks and the homopolymer (χN_{AH}) are varied in this study. We investigated the density profiles, morphology and interfacial characteristics at various compositions of the triblock copolymer ($f_{A/B}$). A wide range of thermodynamics incompatibilies (χN_{AH}) were also explored between the homopolymers and the end block component of the copolymer.

A symmetric triblock (ABA) system was studied initially at 50% each block composition by weight. These calculations were run in a two dimensional grid with a 64x64 lattice. The thermodynamic incompatibility between the A and B blocks (χN_{AB}) was varied from 30 (weak segregation to 100 (strong segregation). From these calculations, the extent of phase segregation was observed to increase and a stable lamellar morphology was predicted. Figure 2 compares the density profiles of the two blocks as the incompatibility increases.

Dissipative particle dynamics simulations. Dissipative particle dynamics simulations were also employed to study the dynamics of self-assembly and predict the interfacial interaction of the two polymeric constituents. The effect of temperature and shear on the interfacial interactions will be discussed in detail.
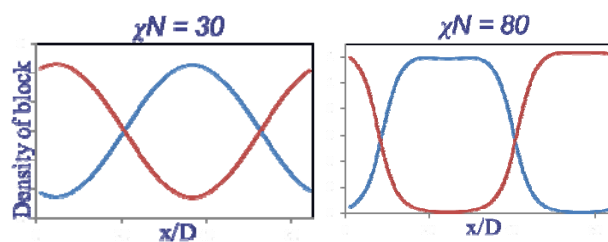

Figure 2. Density profiles of A(red) and B (blue) blocks for a 50/50 ABA triblock system at (χN_{AB}) = 30 (left) and (χN_{AB}) = 80 (right) along the repeat length.

The dissipative particle dynamics simulations were done with the LAMMPS code at the High Performance Computing Center at NC State University. A total of 80,000 beads were used in all simulations. For parameterizing the DPD system, one bead corresponds to one monomer of each polymer for the molecular structure. Our simulations implemented a bead-spring model for polymer chains with angle parameters. A time step of 0.05τ was utilized for these simulations. The bond repulsion parameters and angle parameters were evaluated in accordance to the work of Li and coworkers.[3]

Figure 3 provides the initial and equilibrated snapshots of the dissipative particle dynamics simulation. The simulation results in a very sharp interfacial region between the two blocks as expected from our parameterization of the system. The dissipative particle dynamics simulation results for a 50% copolymer composition by weight resulted in a lamellar morphology as predicted by the SCFT calculations. The dynamics of the simulation indicate that the morphology evolves in to a stable lamellar morphology at 45 μs of the simulation duration at room temperature conditions.
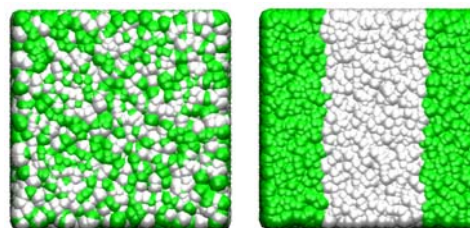

Figure 3. Snapshots at initial (left) and at 60 μs (right) of the DPD simulation for ABA triblock system with 50% composition.

Conclusions

The SCFT calculations predict the density profiles and equilibrium morphologies of the triblock copolymer system under different thermodynamic incompatibilities between the blocks. The dissipative particle dynamics simulations provide the dynamics of the self-assembly as well as the interfacial characteristics of the two phases. The results for the pure triblock copolymer system are consistent with the literature. Studies on triblock copolymer/homopolymer systems will reveal the self-assembly and interfacial behavior of the two components with varying compatibilities and temperature conditions. These results are of significant relevance to multicomponent systems such as SEBS/polyolefin blends.

References
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