583d Rheology of Homopolymer and Blends of Dense Star Polystyrene Soft Nanospheres

Ajay C. Kulkarni and Rangaramanujam M. Kannan

Highly branched polymeric materials exhibit significantly different rheological behavior compared to linear polymers, suggesting that controlled branch density can have technological benefits. For example, we have synthesized a dense star polystyrene (DS-HBPS) molecule with 50 arms, each arm having a molecular weight of molecular weight of 5,000 g/mol (arms are unentangled). Using rheo-optics and triple-detection GPC, we have established that these materials act as soft spheres, with a size of ~ 8 nm. We are studying the effect of molecular architecture on rheological behavior of miscible Polystyrene/ Poly (vinyl methyl ether) (PS/PVME) blends with the help of dynamic stress-optical measurements. In DS HBPS/PVME blends, at higher loading of DS HBPS the interparticle distance between DS HBPS molecule is much smaller than radius of gyration, Rg of PVME. Therefore we expect to see the conformational changes in PVME chains induced by DS HBPS molecules and compare it with L-PS/PVME blends. However the rheology and flow birefringence data on these blends suggests that the relaxation dynamics of PVME is not significantly altered by DS HBPS whereas for L-PS/PVME blends the relaxation dynamics of PVME is slowed down by higher Tg component (L-PS). In contrast to linear PS/PVME blends, DS HBPS/PVME blends show thermorheological simplicity. Also the shift factors for DS HBPS/PVME blends are similar to that of pure PVME. DSC results on these blends show a single narrow transition suggesting miscibility. Therefore our results suggests that, the segments of PS near the periphery of DS HBPS may be miscible, but the segments near the core would be immiscible, resulting in a molecularly dispersed blend, rather than a segmentaly miscible blend as in the case of linear PS/PVME blends.

To understand the effect of molecular architecture on mechanical and morphological behavior, both miscible and immiscible as well as immiscible blends of linear PS/ PVME and DS-PS/ PVME are studied using a tensile tester. In the miscible state, the mechanical properties such as Young's modulus (E), tensile strength and elongation at break of linear PS/PVME blends are much superior to those of DS-PS /PVME blends even though the total molecular weight of both linear PS and DS-PS are similar, perhaps due to the fact that these dense star PS molecules are unentangled. The effect of phase separation temperature on tensile properties of these blends is investigated after phase separation above their cloud point. The results are analyzed in terms of the phase connectivity, interfacial adhesion.