

Nonlinear Rheology of Phase Separating LCST Blends: Polystyrene/Poly (Vinyl Methyl Ether)

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We investigated nonlinear rheology of different time dependant phase-separating morphologies for PS/PVME blends which a large difference between glass-transitions of PS and PVME (about 125oC) make this blend dynamically asymmetric. For this purpose phase diagram of PS/PVME blend, which exhibit lower critical solution temperature (LCST) was determined form the dynamic temperature sweep experiments. Phase contrast optical microscopy was employed to investigate morphological evolution of PS/PVME blends at various region of obtained phase diagram at constant temperature of 105 oC. At this temperature, depending on composition, in addition to the usual phase separation mechanisms (SD, NG) viscoelastic phase separation was observed, indicating interplay of thermodynamics and viscoelasticity in controlling phase separation behavior of PS/PVME blends. For sample at the PVME-rich binodal region of phase diagram, stress overshoot, observed in the shear start up experiments, was increasing function of phase separation time, which was attributed to the greater deformability of larger droplets. In contrast, for sample at unstable region, stress overshoot was decreasing function of phase separation time; and at early stages of spinodal decomposition a strong overshoot was observed which was attributed to the stretching and/or orienting of cocontinuous domains with a large interfacial area. The experimental results of stress growth experiments were compared with the predictions of Lacroix model. It was observed that, even without considering interfacial contribution, Lacroix model predicted much higher than experimental results. This discrepancy was attributed to the combination effects of interfacial slip and self-generated stresses induced in matrix phase. Furthermore, the validity of Doi-Ohta scaling relationships for different morphologies was studied.