



NONLINEAR RHEOLOGY AND MORPHOLOGY OF LCST BLENDS WITH HIGH VISCOSITY RATIO

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We investigated the correlation between the time evolution of the different phase-separating morphologies and corresponding transient rheological behaviors for the dynamically asymmetric PS/PVME blend in which there is a large difference between glass transitions of the pure components (about 125 oC). The phase diagram was obtained from dynamic temperature sweep experiments. Phase contrast optical microscopy was employed to investigate morphological evolution of PS/PVME blends at various regions of obtained phase diagram at a constant temperature of 105 oC. At this temperature depending on sample composition, the viscoelastic phase separation (VPS) was observed besides the usual phase separation mechanisms (nucleation and growth (NG) and spinodal decomposition (SD)), indicating the interplay between thermodynamics and viscoelasticity in phase-separation behavior of PS/PVME blends. the stress growth behavior of different phase-separating morphologies was investigated by transient start-up of shear flow. For sample in binodal region, with increasing phase separation time, which corresponds to the increase of droplet size, the magnitude of stress overshoot increased. This was attributed to tendency of the larger droplets to be more deformed. This trend was predicted by the Cheffery-Brenner model. The sample located in unstable region, exhibited a strong stress overshoot at early stages of phase separation, and in contrast to sample located in the binodal region, stress overshoot decreased with phase separation time in agreement with Doi-Ohta theory. The sample phase separating under VPS exhibited a strong overshoot at early stages of phase separation which decreased with phase separation time. The pronounced stress overshoot was attributed to the percolated network structure of viscoelastic phase separating sample. This behavior was investigated by dynamic equations derived based on time-dependent Ginzberg-Landau model. It was found that the stress growth behavior can be described by Lacroix's approach in using Palierne's model, if the self-generated stresses induced during the phase separation are taken into account.