

RHEOLOGY OF A LOWER CRITICAL SOLUTION TEMPERATURE BINARY POLYMER BLENDS WITH VISCOSITY CONTRAST IN THE PHASE-SEPARATED, AND TRANSITIONAL REGIMES

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We investigated the correlation between the time evolution of the different phase-separating morphologies and corresponding linear and 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 °C). 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 °C. 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 linear viscoelastic behavior for different phase separating mechanisms (NG, SD, and VPS) was measured to investigate the kinetics of phase separation. It was found that the linear viscoelastic behavior can be described by Palierne's emulsion model, if the self-generated stresses induced during the phase separation in the matrix phase are taken into account. Furthermore, 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.

To the best of our knowledge, there is no study on the rheological behavior of phase-separating blends under VPS mechanism and its comparison with SD and NG ones in the literature.