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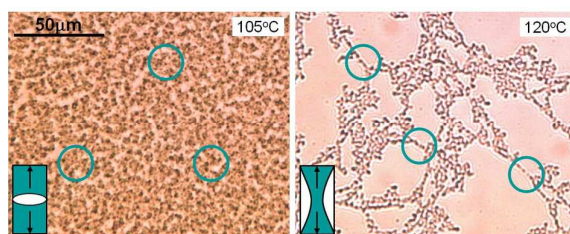


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A brittle-to-ductile transition in the phase morphology is found in dynamically asymmetric PS/PVME blend with increasing quench depth.

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ARTICLE TYPE

Phase Morphology Map in LCST-type Polymer Blends with Dynamical

Asymmetry under Different Quench Depths

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With increasing temperature, a transition from fracture phase separation (FPS) to viscoelastic phase separation (VPS) was found in dynamically asymmetric PS/PVME blends with LCST behavior. Typical morphology formed via VPS disappeared under large quench depths, indicating some other specific might control the morphological evolution during VPS besides the dynamic asymmetry.

Multicomponent polymeric materials undergoing viscoelastic phase separation (VPS) can form a network-like structure when the more elastic phase is the minority.¹⁻³ During VPS process, the slow phase cannot catch up with a deformation rate spontaneously generated by phase separation itself, and thus forms a network structure to store elastic energy created by the driving force of phase separation itself.⁴ The morphology evolution is dominated by the elastic force balance, during which the viscoelastic relaxation plays a decisive role. Materials with network structure can be made light weight and high mechanical strength,⁵⁻⁶ and thus are promising candidates for bone tissues, film filters, foamed plastics and so on. Exploring the precondition for the occurrence of VPS during processing is vital for the structure design of these functional materials. However, the specific experimental conditions for the occurrence of VPS are still unclear. At present, the precondition for the occurrence of VPS in polymer blends is usually correlated to the large dynamic asymmetry between components.⁶ Polystyrene/poly(vinyl methyl ester) (PS/PVME) blend satisfies this condition very well due to the large difference between the glass transition temperature (T_g) of PS (~100°C) and PVME (~-20°C). Recently, Yeganeh *et al.*³ found that a lowest content of the more elastic PS component was required to observe VPS behavior in PS/PVME blends because a very small fraction of PS was difficult to form network structure. In our previous studies,^{1,7} the VPS behavior in PS/PVME blend was investigated in the presence of fumed silica nanoparticles. It was suggested that the preferential affinity of nanoparticles to polymer component would be utilized to manipulate the dynamic asymmetry between two phases, which was embodied in the changes in the rheological relaxation time of two phases, and to induce morphology transition during phase separation.¹

Theoretically, the rheological relaxation time τ of each phase in the PS/PVME blend is proportional to $\exp\{-A[T-T_g(\phi_s)]\}$.² A larger quench depths should lead to the formation of two phases

with larger difference in composition, and therefore should facilitate the occurrence of VPS because of larger dynamic asymmetry. However, for a LCST (lower critical solution temperature) system such as PS/PVME blend, large quench depths also mean higher experimental temperatures, under which the retraction of the irregular interfaces will be accelerated. This is unfavorable for the slower component to shrink slowly into a network. These two opposite effects brought by a large quench depth in LCST system may reveal some new illumination for the prerequisite of VPS. Thus, studying the effect of quench depth on the morphology evolution will provide new insight into the structure manipulation of dynamically asymmetric polymer blends with a LCST behavior.

This work aims to exploit the condition for the occurrence VPS behavior in terms of quench depth. In this work, PS with a weight-averaged molecular of $M_w=1.78\times10^5$ g/mol and a polydispersity of 2.21 was provided by Sigma-Aldrich Co. PVME with $M_w=5.45\times10^4$ g/mol and a polydispersity of 2.60 was purchased from Tokyo Chemical Industry. PS/PVME blend films with thickness of ~20 μm were prepared by casting their toluene solution on glass slides. A critical composition of $\phi_s=10$ wt.%, with a cloud point temperature of 85.4°C was chosen.⁷ An optical microscope (Olympus BX51, Japan) equipped with a PixelINK CCD camera and a hot stage (Linkam LTS350, UK) was used to follow the phase morphology evolution between 105°C and 133°C in the unstable region of PS/PVME (10/90) blend. A home-made small-angle light scattering (SALS) equipment with He-Ne laser source ($\lambda=632.8$ nm) was employed to study the phase separation dynamics of blend under different temperatures.

The optical microscopy results in Figure 1 show that, the morphology characteristic and kinetics of phase separation exhibited a strong dependence on temperature. Network-like structure was observed at 105~120°C (Figure 1a-c) but the detailed processes revealed some differences. First, it took much longer time for the blend at 105°C to form the network with a same size as that observed at 120°C. Second, when the transient PS-rich network with small size formed at 105°C, the PVME-rich phase displayed like irregular cracks as shown in Figure 2a. These cracks grew with time uniformly as in the usual fracture process, resulting in the increase of network size. A similar phase separation mechanism called as fracture phase separation (FPS) has been reported by Tanaka *et al.*⁸ when studying the

temperature dependence of phase behavior in PS/diethyl malonate (DEM) solution possessing an upper critical solution temperature (UCST) behavior. FPS formed similar network structure to VPS but was characteristic of mechanical fracture.⁸ A transition from VPS to FPS was found under large quench depths and was ascribed to the brittle nature of PS-rich phase at lower temperatures. The essential difference between VPS and FPS was regarded as the “ductile-to-brittle transition” during the fracture of materials under shear deformation. Figure 2a showed that the transient network formed at 105°C exhibited brittle fracture during phase separation, manifesting a solid-like behavior. This suggested that FPS was the dominant coarsening mechanism at 105°C.

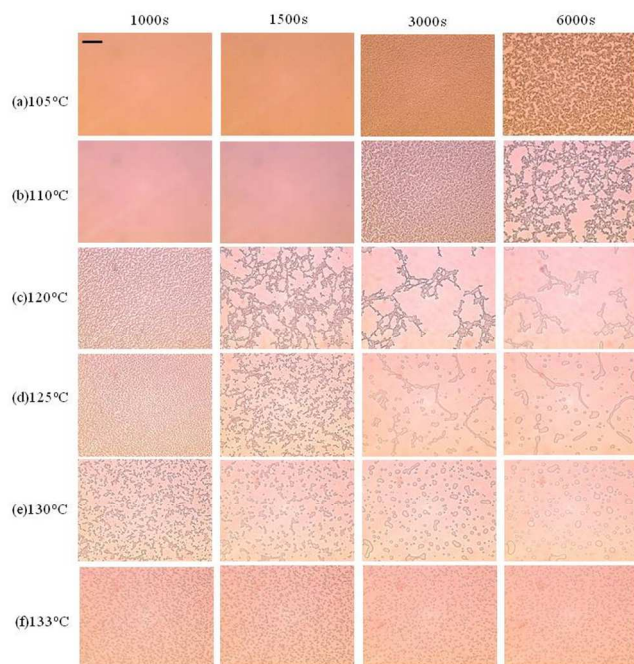


Figure 1 Morphology evolution of PS/PVME (10/90) blends during annealing at different temperatures. The dark region is PS-rich phase while the bright region is PVME-rich phase. The scale bar is 50 μm .

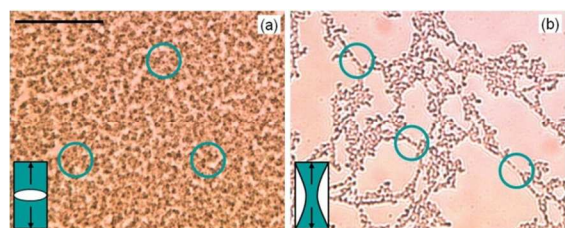


Figure 2 Typical morphology of PS/PVME (10/90) blend after annealing at (a) 105°C for 5183 s and (b) 120°C for 1657 s, respectively. The scale bar denotes 50 μm . The dark region and bright region represent the PS-rich phase and PVME-rich phase, respectively.

On the contrary, the morphology evolution at 120°C resembled VPS and proceeded via three stages. At the initial stage (<1000 s), the dynamically fast phase (majority PVME-rich phase) formed “holes” or “droplets” dispersed in the minor PS-rich matrix, which can be regarded as phase inverted structure. In the intermediate stage (1000–1500 s), PVME-rich holes grew continuously while the PS-rich phase transformed into a network

structure. In the final stage (>1500 s), PS-rich network kept shrinking and broke up gradually into disconnected droplets. The formation and breakup of network structure was fast at 120°C properly due to the synergistic effect of the large thermodynamics driven force during phase separation and the fast relaxation of polymer chains under higher temperatures. Moreover, the network formed at 120°C exhibited a hierarchical growth feature. The network of PS-rich phase at 120°C (Figure 2b) stretched continuously under stress, revealing the ductile nature of materials at 120°C. This hierarchical growth of network structure might stem from the rapid hydrodynamic coarsening and the slow relaxation of the bulk stress.⁹ The difference in the capillary pressure between interconnected PS-rich strips of different sizes produced a hydrodynamic flow therein and led to fast hydrodynamic coarsening.² Finally, thin PS-strips became thinner, resembling a fibering process, and eventually broke, left the thick junction parts as isolated droplets. Therefore, hydrodynamics impelled the continuous PS-rich phase to lose its connectivity and led to the formation of droplet-matrix phase structure. The isolated droplets formed would eventually retract into spherical shape to low the total interfacial free energy. Combined with their morphological features, the phase separation of PS/PVME blend at 105°C and 120°C can be regarded as FPS and VPS, respectively. Therefore, the “ductile-to-brittle transition”, as reported by Tanaka⁸ in the UCST PS/DEM system with decreasing temperature, should be expected if the phase separation of PS/PVME blends with LCST behavior proceeds at declined temperatures.

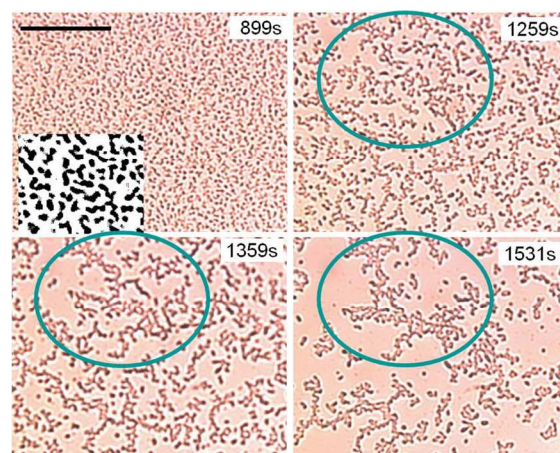


Figure 3 Phase morphology evolution of PS/PVME (10/90) blend at 125°C during 899–1531 s. The scale bar denotes 50 μm . The dark and bright region represents the PS-rich and PVME-rich phase, respectively.

When the temperature was elevated to 125°C, the PS/PVME blend exhibited irregular fractal aggregates at 1500 s (Figure 1d). To study the origin of fractal aggregates, the detailed morphology evolution during 899–1531 s was revealed in Figure 3. It was difficult to distinguish whether the dense structure at 899 s was of co-continuous or droplet-matrix type. But the corresponding binary picture presented clearly showed that lots of irregular PS-rich domains possibly resulted from the destruction of network structure were isolated and dispersed in the PVME-rich matrix. These small isolated PS-rich domains aggregated with each other and grew in size quickly. The morphology observed is similar to that reported in some dewetting processes.^{10–12} Accordingly, long-

strip like domains formed in the blend at 3000 s (Figure 1d), and finally retracted into spheres after longer times to reach the lowest interfacial free energy. The presence of fractal aggregates instead of network-like structure at 125 °C may be attributed to the fast viscoelastic relaxation of slow PS-rich phase under higher temperatures, and relevant details require further study. The morphology evolution of blend at 130°C (Figure 1e) was similar to that observed at 125°C. Irregular fractal aggregates formed even at 1000 s. These aggregates did not assemble into structure with larger size but retracted into spheres. At a higher temperature of 133°C, the blend exhibited droplet structure with relatively uniform size and regular shape directly at 1000 s, and no network structure or aggregates was observed. In our opinion, the fast dynamics of components at higher temperatures (125~133°C) led to a rather rapid disintegration of network structure formed via the growth of holes before a discernable network structure via hydrodynamic coarsening could develop. As a result, droplet structure instead of network structure was observed under microscope in the early stage of phase separation. The morphology results presented above suggested a strong dependence of phase morphology in the PS/PVME blend on the annealing temperature. Four kinds of phase morphology can be classified roughly, namely fracture network in 105-115°C, viscoelastic network at ~120°C, irregular fractal aggregates in 125~130°C, and droplet-matrix structure >133°C.

The transition from FPS to VPS, occurred as temperature increased from 105°C to 120°C, can be also recognized from the volume (area) shrinking kinetics of the PS-rich phase besides characteristics of pattern evolution (Figure 1a-c). Figure 4a shows the relative volume shrinking $[V(t) - V(\infty)]/[V(0) - V(\infty)]$ against the phase-separation time t , where $V(0)$, $V(\infty)$ and $V(t)$ represent the initial, the final and the volume (area) fraction of PS-rich phase at time t , respectively.² The volume fraction was estimated by binarization of optical micrographs. For both VPS and FPS, the volume shrinking dynamics satisfies the equation $[V(t) - V(\infty)]/[V(0) - V(\infty)] = \exp(-t/\tau_c)$,⁹ in which τ_c denotes the characteristic time of volume shrinking. Figure 4b showed that, the τ_c decreased rapidly from 2180 s to 480 s as the temperature increased from 105°C to 120°C, indicating a change in the rheological response of the PS-rich phase from a slow solid-like one (FPS) to a fast viscoelastic one (VPS).⁸ The presence of a crossover in τ_c revealed a strong dependence of PS relaxation on the bulk stress as the temperature diverged gradually from the T_g of PS (~100°C), which is consistent with previous report.⁹

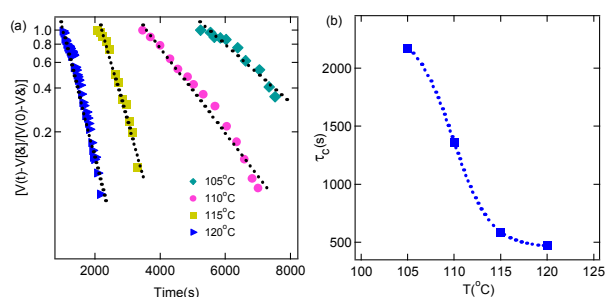


Figure 4 (a) Volume shrinking kinetics of the PS-rich phase under different temperatures and (b) characteristic time of volume shrinking τ_c as a function of temperature. The dash lines are to guide the eye only.

Figure 5 shows the temporal evolution of scattering intensity (I)-scattering vector (q) correlation at different temperatures obtained by the SALS technique. For each temperature, the intensity increased gradually as phase separation proceeded, and then a clear peak was observed after some times. The scattering peak shifted towards lower q values, suggesting the increase of characteristic size of phase structure. The temporal evolution of peak position in Figure 5 was revealed in Figure 6a to study the phase separation kinetics of initial stage. For all temperatures, the q_m kept almost invariant at the beginning of phase separation, which is an indication of spinodal phase separation. After that, the q_m decreased with time according with a power law $q_m(t) \sim t^{-\alpha}$ as shown in Figure 6a, suggesting that scaling relations were satisfied.¹³⁻¹⁵ The α values obtained by fitting the data at different temperatures after the initial stage of phase separation were plotted in Figure 6b. The α value increased gradually from 1.4 at 105°C to 1.8 at 120°C. The large α value below 120°C was close to that reported by Tanaka ($\alpha=1.5$),² which was an indication of fast coarsening mode dominated by mechanical fracture in FPS or elastic force balance in VPS.

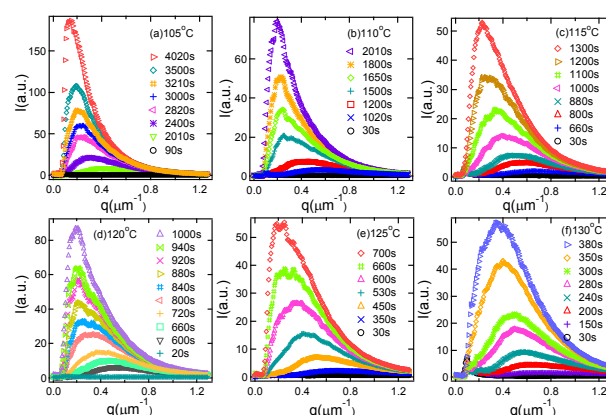


Figure 5 Light scattering profiles of PS/PVME (10/90) blend at different temperatures.

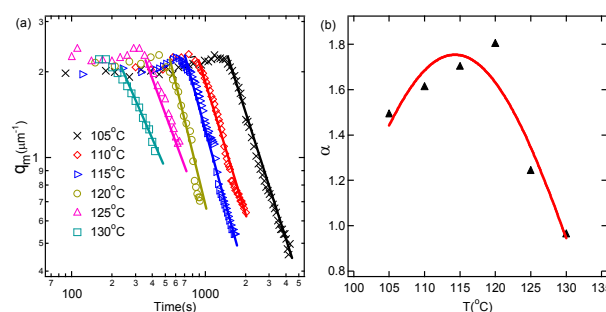


Figure 6 (a) Peak intensity position (q_m) vs. time and (b) exponent α vs. temperature in PS/PVME (10/90) blend.

However, the α value declined rapidly to 1.25 and 0.95 at 125°C and 130°C, respectively. This result was not consistent with the common sense that a faster phase separation kinetic usually present under higher temperatures. This rapid reduction in α can also be regarded as an implication for the disappearance of viscoelastic behavior in PS/PVME blends under higher annealing temperatures. In LCST blend system, large quench depths should

lead to the formation of two phases with large dynamic asymmetry. Therefore, the disappearance of VPS under higher temperatures revealed that there may be other factors controlling the occurrence of VPS behavior besides the dynamic asymmetry of two phases. Usually, high temperatures increase the chain mobility of polymer and reduce its viscosity, and accordingly a slower phase can also behave fluid-like. Thus, it might be difficult for the slower phase to shrink into a network structure. The disappearance of VPS at high temperature highlights the key role of the absolute dynamics of components in phase separation, namely the existence of a critical shortest relaxation time for the slower component to form a viscoelastic network.

Conclusions

The increase in temperature led to a transition from fracture phase separation (FPS) to viscoelastic phase separation (VPS) in dynamically asymmetric PS/PVME blends with LCST behavior. The relaxation process of the slower phase was accelerated under high temperatures (deeper quenching), making the slow phase retract directly into isolated droplets without the formation of a transient network structure. The requisition for the occurrence of viscoelastic phase separation (VPS) in LCST-type systems such as the PS/PVME blend was found to differ significantly to that in UCST system. It was related not only to a large dynamic asymmetry, but also to the absolute dynamics of each phase. Further investigations in terms of the interplay of dynamics asymmetry, compositional asymmetry and quench depth are necessary to have a better understanding on the unique phenomena observed.

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Notes and References

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