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Thickness Dependence of Liquid−Liquid Phase Separation in Thin Films of a Polyolefin Blend

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Spinodal decomposition of binary polymer blends has been well studied in bulk. The growth of the characteristic length between phase-separated domains in the late stage can be predicted by the dynamic scaling hypothesis, $\xi(t) \approx t^{\alpha}$.[1] The growth exponent α depends on the mechanism of domain coarsening. The discrete growth controlled by domain attraction or diffusion is a slow mechanism; that is, $\alpha = 1/3$.[2−5] Coarsening through a hydrodynamic flow mechanism of a percolated cocontinuous structure is proven to accelerate phase separation in fluids, resulting in $\alpha = 1$ in the viscous hydrodynamic regime, which is often the case for bicontinuous morphology evolution.[2] Although phase separation in 2D binary fluids has been investigated both theoretically and experimentally for its fundamental and technological relevance,[6−8] the mechanism of phase separation in real thin film systems is still far from resolved. In such a system, the problem is usually more complicated because of the existence of preferential wetting, percolation, and confinement.[9,10] In the thin film of deuterated poly(methyl methacrylate) and poly(styrene-*r*-acrylonitrile) blends, Composto et al.[11] reported a bicontinuous domains growth with decreasing exponent, 0.62 to 0.28, as the thickness decreased from 900 to 90 nm. This slowing down with reduced dimensionality suggests a suppression of lateral hydrodynamic flow mechanism. Sung and Han[12] reported that as the thickness of the polystyrene and polybutadiene blend film decreases from 100 to 20 nm, there is a crossover from 3D to 2D spinodal decomposition kinetics in the viscous hydrodynamic regime, with α changed from 1 to a value near 0.46.

In this note, the liquid−liquid phase separation (LLPS) in poly(ethylene-co-hexene) (PEH)/poly(ethylene-co-butene) (PEB) blend thin films with thickness (h) ranging from 190 nm to 10 μm was investigated by atomic force microscopy (AFM). The growth of in-plane correlation length (ξ) is monitored as a function of time, which can be described as t^{α}. The reduced dimensionless domain size defined as ξ/h was used to discuss the film-thickness dependence of LLPS. The variation of α is also compared with the previous result on the nucleation rate of the fluctuation-assisted crystallization in this system.

The polyolefins used in this work are statistical copolymers of ethylene/hexane (PEH) (M_w = 110 kg/mol, 2 mol % hexene comonomer, $M_w/M_n \approx 2$) and ethylene/butene (PEB) (M_w = 70 kg/mol, 15 mol % butene comonomer, $M_w/M_n \approx 2$) supplied by ExxonMobil. PEH is the only crystallizable component of the PEH/PEB blend system above 60 °C. The blend of PEH and PEB with PEH mass fraction of 40% was prepared with the same procedure as that in the previous report.[13] Silicon substrates were cleaned with piranha solution (H_2SO_4/H_2O_2 3:1) at 80 °C for 1 h and then copiously rinsed in deionized water and dried with pure N_2 gas flow. (*Caution: Piranha solution is hot and corrosive, and extreme care should be taken when handling this solution.*) The polymers were dissolved in *o*-xylene at 120 °C and then blade-coated onto preheated substrates. A custom-built flow coater[14] was used to control the speed and height of the blade, which produce well-controlled film thickness in a range of 190 nm to 1 μm. The blend films with thickness range of 1 to 20 μm were prepared by hot pressing at 160 ± 2 °C between two pieces of silicon wafer (10×10 mm^2) with one piece removed after cooling. The film thickness is measured by the AFM scrape test (for $h \leq 1$ μm) or from the scanning electron microscopy image of the cross section of films (for $h > 1$ μm). All of the blend films were melted at 160 °C for 60 min to eliminate the thermal history before being quenched to 135 °C for LLPS. All of the heating processes were under an N_2 atmosphere to avoid thermal degradation. The morphology was investigated using a Dimension 3000 AFM (Digital Instruments) operated in tapping mode. To reveal the morphology of the midlayer, amorphous PEB was selectively removed by etching in acid $KMnO_4$ solution.[14] For the films thicker than 5 μm, phase contrast optical microscopy (OM) was also used to investigate the phase morphology evolution in situ. To ensure consistency, images of the morphology (up to 100^2 μm^2) were taken from a number of regions and then converted into reciprocal space using a 2D fast Fourier transform (FFT). Radial averaging of the FFT spectrum yielded a peak at k_{max}, which was used to determine the in-plane correlation length between domains.

According to the phase diagram of PEH/PEB[15] and previous studies on this system,[13,14,16] it has been proven that PEH/PEB 40:60 blend is within the unstable (or spinodal) phase separation region at 135 °C, and in thin films of the blend, wetting layers enriched by PEH were found on the interfaces of the thin films during the LLPS.[14] Figure 1 shows representative AFM images of the phase morphology evolution. In an earlier stage, the bicontinuous tubelike structure was formed in blend films, which is a characteristic of the spinodal decomposition. The white (high) and dark (low) regions correspond to PEH domains and the etched PEB phase, respectively. As the phase separation goes on, the bicontinuous structure gradually breaks up and transforms to a “sea-island” structure. The deviation of the etching condition (such as over-etch) and the image processing would affect the area ratio of the black and white domains in the AFM image; however, it will not change the correlation length between domains in the images. Therefore, the time evolution of the in-plane correlation between domains in films with a series of thickness was plotted in Figure 2. The slope of the $\xi(t)$ curves versus time on a log−log plot represent the domain growth exponent, α. It was shown that the average of α on the whole t scale decreases from 0.68 to 0.20 as h decreases from 10 μm to 190 nm. A more detailed analysis of the evolution of the slope at a certain thickness, for example, h = 800 nm, was also indicated in Figure 2. In the first 5 h of LLPS, the $\xi(t)$ is well fitted by a scale law of $\alpha = 0.35$, whereas in the later LLPS time, α varies to a smaller value, that is, $\alpha = 0.16$.

For a better comparison of samples with different film thickness, the correlation length was normalized by h to a dimensionless thickness value, which resulted in a clearer film-thickness

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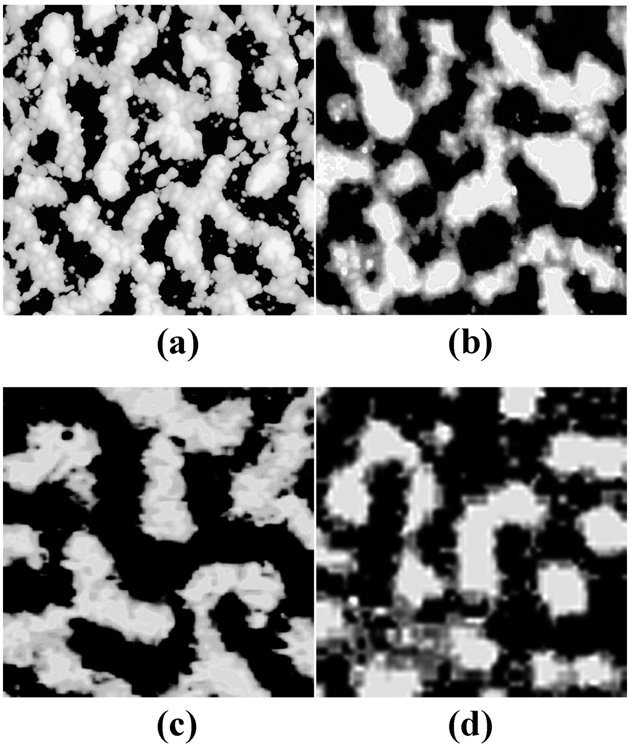

Figure 1. Morphology evolution of PEH/PEB 40:60 blend films with thickness of 800 nm annealed at 135 °C for (a) 2, (b) 8, (c) 24, and (d) 48 h investigated by tapping mode AFM. (image size: 5 × 5 μm^2)

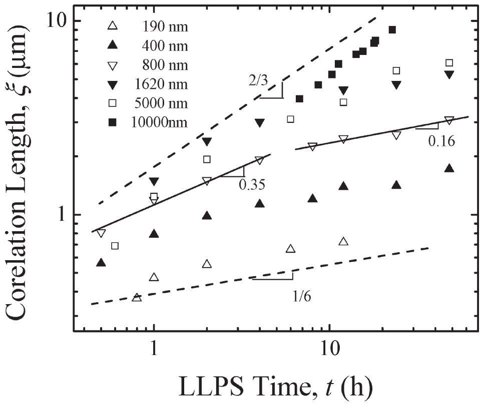

Figure 2. Correlation length (ξ) versus LLPS time (t) for PEH/PEB 40:60 blend films. The overall growth exponent decreases from 0.68 to 0.20 as h decreases from 10 000 to 190 nm. Broken lines are to guide the eye. Solid lines indicate the linear fitting of the evolution in earlier and later stages in 800 nm film, respectively.

dependence (Figure 3). When ξ/h is less than 1, the domain size of LLPS grows faster, and the exponent α is up to 0.68. When ξ/h is between 1 and 2.5, the exponent α keeps a constant value of about 1/3 despite of h. As ξ/h exceeds the crossover value of about 2.5, the exponent α became even smaller. Namely, there are two crossover points of the exponent α in the late-stage spinodal LLPS of thin films.

The first crossover, from about 0.68 to near 1/3, takes place when the domain size approaches the film thickness, that is, $\xi/h \approx 1$. One possible explanation of this crossover of α is that hydrodynamic flow through the bicontinuous tubelike structure is suppressed by the confinement. In previous work, the phase structure of this PEH/PEB blend film was studied.[14] During the spinodal LLPS, a preferential wetting of PEH was found on the surfaces of the blend thin film with the bicontinuous tubelike phases in the midlayer. At earlier LLPS time, the correlation length of the spontaneous spinodal decomposition is much smaller than the film thickness, which is close to the situation in bulk. Percolation of the separated phases accelerates the coarsening of the phase structure in fluids, resulting in an α close to 1 in the viscous hydrodynamic regime. As the phase domains grow in the film, the correlation length approaches the film thickness. The symmetry of phase separation can be broken, resulting in asymmetrical phase growth parallel and perpendicular to the surface.[17−19] The 3D percolation structure is suppressed to 2D by spatial confinement and then breaks up gradually, which can be observed in Figure 1. The effect of hydrodynamic flow vanishes as a result. The domain growth turned out to be controlled by the mechanism of domain diffusion, collision, and coalescence mechanism, which is a slow process with $\alpha = 1/3$. Several other studies [11,20] also support the idea that confinement can suppress the hydrodynamic flow mechanism. Composto et al.[11] reported a similar slowing down in the kinetics of phase separation in thin polymer blend films of deuterated poly(methyl methacrylate) (dPMMA)/poly(styrene-ran-acrylonitrile) (SAN) displaying bicontinuous domain morphologies. The growth of correlation length (ξ) was obtained for thickness values (h) from 1000 to 190 nm. By normalizing ξ by h, the time exponent α was found to deviate from the typical value in the viscous hydrodynamic mechanism (i.e., $\alpha = 1$) when ξ/h exceeds a cross point. However, compared with the cross point of the exponent α in our work on PEH/PEB (i.e., $\xi/h \approx 1$), the cross point is about $\xi/h = 3$ in their system. A possible reason may be that the wetting layer growth and the wetting-induced depletion will change the actual spacing and the boundary conditions of the two interfaces. Therefore, the shift of the cross point is predicted to be caused by different conditions of interfacial wetting, including the component, the temperature, the attraction of substrates, and so on. A further slowing down of the domain growth at $\xi/h \approx 2.5$ is somewhat more surprising. One promising interpretation may be the varying of the surface tension of the discrete domains. As the domain further grows, the domain size becomes much larger than the film thickness. Then, the phase domain is pressed into a pancake-like shape with an elliptical cross section because of the interfacial wetting. At the rim of the phase domains, the local curvature radius in the vertical plane decreases as the domain grows. Because of this, the Laplace overpressure[21] at the rim increases, which therefore suppresses the growth of domains as a result.

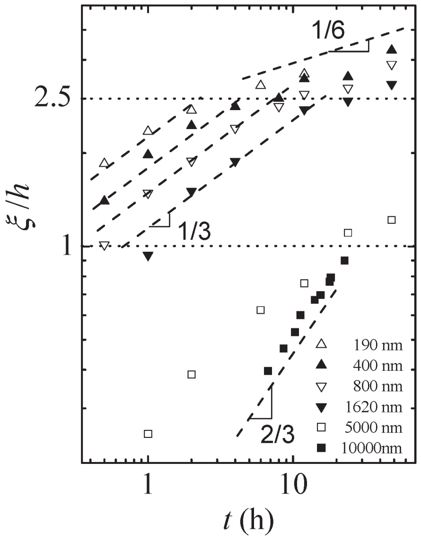

Figure 3. Evolution of ξ/h in PEH/PEB 40:60 blend films. Dotted lines indicate the value of ξ/h equal to 1 and 2.5. Broken lines with slope of 2/3, 1/3, and 1/6 are to guide the eye.

The variation of domain growth exponent α described above is also compared with the previous result about nucleation rate (R)

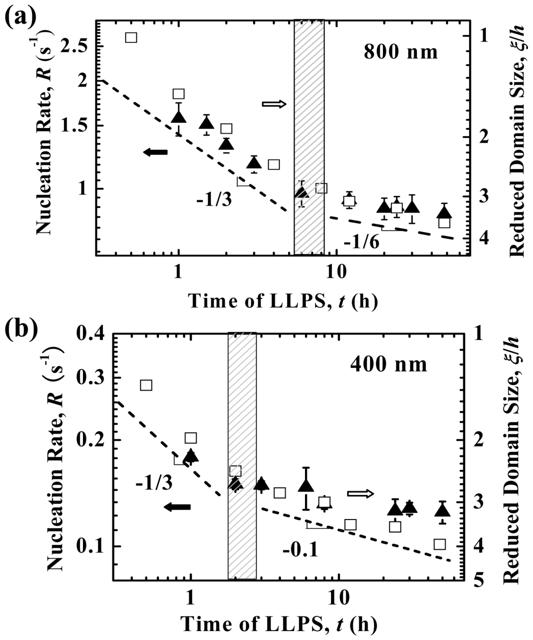

Figure 4. Comparison of the reduced domain size (ξ/h, □) and the nucleation rate (R, ▲) of subsequent PEH crystallization at 120 °C as a function of LLPS time. (a) $h = 800$ nm; (b) $h = 400$ nm.

of subsequent PEH crystallization. In previous studies, simultaneous spinodal decomposition and crystallization in the PEH/PEB blend system were studied systematically in bulk[13,16] and in thin films.[14] The experimental results showed the overwhelming evidence of the concentration fluctuation-assisted nucleation, and the dominant results that most of the nucleation occurs at the interface and that the nucleation rate after spinodal LLPS is proportional to the interfacial area in the polyolefin blend system. Therefore, when the domain size grows as t^{α}, the interfacial area decreases as $t^{-\alpha}$ in the 2D case, which results in the nucleation rate of subsequent crystallization decreasing as $t^{-\alpha}$ or more than $t^{-\alpha}$ if the sharpening of the interphase was further accounted.[13] As shown in Figure 4, the variation of growth exponent α described above is also coincidental with the results about the nucleation rate of subsequent PEH crystallization. The two functions, $\xi(t)$ and $R(t)$, have almost the same trend of evolution. Crossovers can be found on both of the functions at almost the same region at about $t = 6$ and 2 h for films with thickness of 800 and 400 nm, respectively. This result shows the proportional relation between crystal nucleation rate and the coarsening dynamics, which is consistent with the theory of fluctuation-assisted crystallization in polyolefin blend films and contributes convincing evidence of this theory also working in thin films of polyolefin blends.

In this study, spinodal LLPS in PEH/PEB blend thin films with thickness ranging from 190 nm to 10 μm was investigated by atomic force microscopy and optical microscopy. The reduced domain size defined as ξ/h was used to discuss the film-thickness dependence of LLPS. When $\xi/h < 1$, the domain size of LLPS grows faster with the growth exponent (α) up to 0.68 ($h = 10\,\mu$m). When $1 < \xi/h < 2.5$, α keeps the constant value of about 1/3 despite h. As ξ/h exceeds the crossover value of about 2.5, α become even smaller and is reduced to 0.20. Suppression of the spatial confinement on the hydrodynamic flow through the bicontinuous tubelike structure and the varying of Laplace overpressure can interpret this two-step crossover phenomenon. The variation of α also coincides with the previous result on the nucleation rate of the fluctuation-assisted crystallization in this system.

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