

LETTER

Suppression of Phase-Separation Pattern Formation in Blend Films with Block Copolymer Compatibilizer

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The structure of thin films is sensitive to surface-tension variations that can cause the free surface of films to buckle.^{1–4} Many different types of film perturbations cause surface-tension variations and thus film-surface pattern formation. Recent studies^{2,3} have shown that phase separation within very thin polymer blend films leads to a range of surface patterns (bumps, holes, and labyrinthine ridges and valleys) that depend on the polymer composition. These patterns disappear when the films are returned into the one-phase region of the fluid mixture, verifying their phase-separation origin.^{2,3} Although in some situations the surface patterns are beneficial, the surface patterns can sometimes compromise film-barrier properties or create other undesirable changes in polymer-coating properties (optical appearance, friction, tendency to attract impurities from the atmosphere, etc.). This technological problem led us to seek methods of inhibiting surface-pattern formation in thin-blend films.

Previous investigations^{5–8} have indicated that small-molecule surfactants can have a striking impact on surface patterns created by surface-tension variations within thin films. For example, the surface-tension origin of cellular Bénard–Marangoni surface patterns^{5–8} was first recognized in a simple experiment in which a small amount of surfactant (literally sweat) was added to a fluid exhibiting a Bénard–Marangoni pattern, causing the pattern to disappear.^{9,10} This simple measurement showed that the presence of a density gradient within the film was not the predominate source of the surface-pattern formation, as originally supposed by Raleigh and Bénard in their model-

ing.^{5,6,11} We can similarly anticipate a dramatic change in the structure of the phase-separating blend films upon adding block copolymer surfactant additives, and this communication investigates this possibility.

Although we did not measure the interfacial tension γ change arising from adding block copolymer to our blend, it is known that adding only a small quantity of block copolymer surfactant is sufficient to substantially change γ in bulk polymer blends. This point is illustrated by the measurements by Anastasiadis et al.¹² on the same block copolymer system that we investigate [polystyrene (PS)/polybutadiene (PB)/PS-*b*-PB]. Moreover, the molecular masses of each polymer in both measurements are comparable (i.e., the molecular mass of each species in ref. 12 is within a factor of 2–3 of its counterpart in our measurements) so that a similar order of magnitude changes in γ can be expected in our block/blend system. Anastasiadis et al.¹² found that an approximately 1% concentration of block copolymer by relative mass to the blend causes an approximately 50% reduction in γ from the blend value. They also summarize previous research indicating generally larger, but similar order of magnitude shifts in γ for other blend/block copolymer mixtures. These observations support our expectation that substantial changes in γ can be expected for small amounts of added block copolymer. Indeed, Anastasiadis et al.¹² found that the γ change is still appreciable for a relatively low 0.3% relative mass concentration of block copolymer in which they discovered a 23% reduction in γ from the bulk blend.

We used a blend of deuterated polystyrene (dPS) having a weight-average molecular weight (M_w) of 1000 g/mol [polydispersity (M_w/M_n): 1.13], polybutadiene (PB) with $M_w = 5300$ g/mol ($M_w/M_n = 1.07$), and a symmetric diblock copolymer (dPS-*b*-PB) in which each block has $M_w = 5300$ g/mol.^{13–18} The mass fraction of

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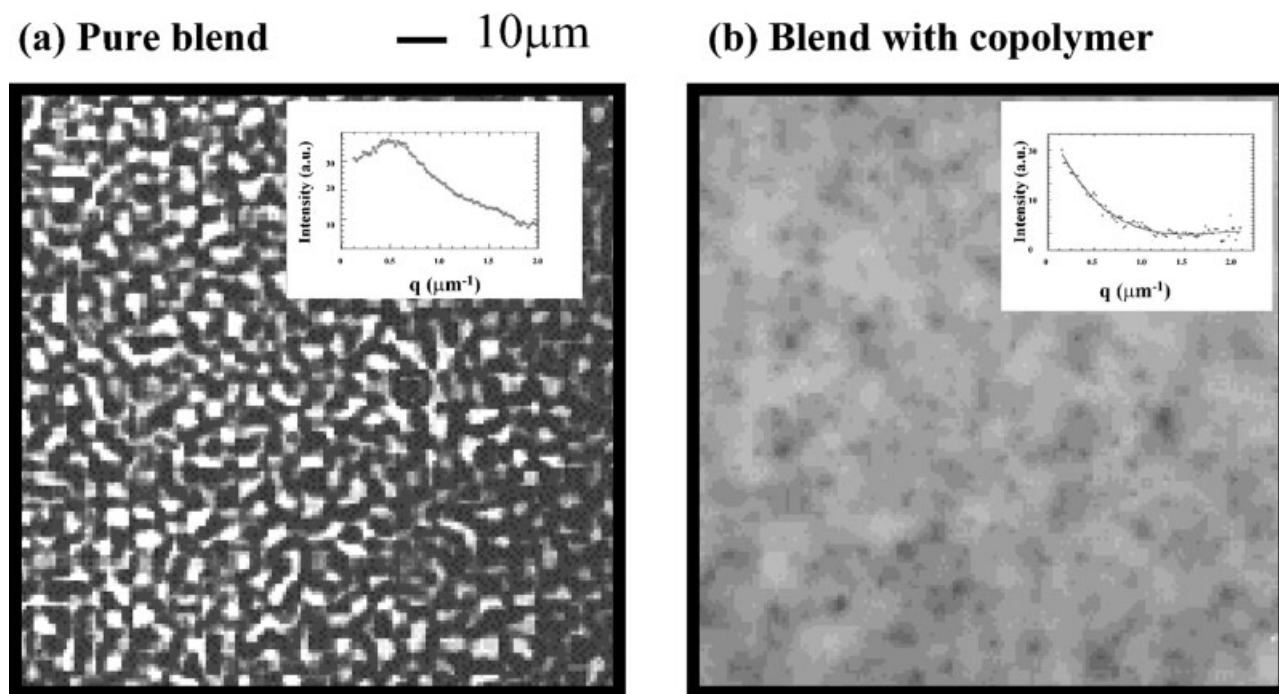


Figure 1. Optical micrographs of (a) dPS/PB pure blend film and (b) blend film with 1% dPS-*b*-PB copolymer additive by relative mass. The pure film is on the left, and the block co-polymer-filled film is on the right. Inserts show radially averaged fast Fourier transforms of images expressed in arbitrary units. Films have a thickness, $L \approx 100$ nm. The measurement results have a relative expanded uncertainty of 1.5%.

diblock copolymer examined by optical microscopy ranged from 0.1 to 8.6%. Additional polymer characterization information for these polymers is described in refs. 13–18. For comparison, thin-blend films of dPS/PB with and without dPS-*b*-PB were cast from toluene solutions on 100-mm-diameter \times 5-mm-thick polished acid-cleaned silicon substrates.¹ All samples in this study had a fixed (75/25) relative dPS/PB mass fraction, which was near the critical composition of the bulk blend.^{13–18} The (≈ 100 nm) films were prepared by spin-coating at an angular speed of 2000 rpm from a polymer solution having 2% (by mass fraction) polymer on etched silicon wafer (100 mm diameter \times 5 mm). Each film was placed under quiescent conditions at ambient temperature (25 °C) and was observed with a Nikon reflection camera.¹⁹ The blend films were also examined by atomic force microscopy (AFM) with an Explorer Topometrix instrument.¹⁹ Neutron reflection measurements were conducted to determine the average composition depth profile in a representative blend-film sample containing 8.6% relative mass of copolymer to total polymer mass.

Figure 1 displays optical micrographs of dPS/PB blend films (100 nm) with and without a small amount ($\approx 1\%$ by mass relative to the blend) of dPS-*b*-PB of copolymer additive. For the pure blend [Fig. 1(a)], we observe a spinodal decomposition pattern that grows in

time as found in previous work.¹ In contrast, the blend film with the block copolymer additive [Fig. 1(b)] appears to be relatively smooth. AFM measurements (not shown because of their blank appearance) indicated that the block co-polymer-filled films are smooth (the root-mean-square height fluctuations are less than 2 nm averaged over 20 μ m), and the films remained smooth on the timescale of our measurements (≈ 14 days). Thus, we observe a dramatic suppression of surface-pattern formation through the addition of a small amount of diblock copolymer to the film.

Although the block co-polymer-filled films are geometrically featureless, optical micrographs of these films [Fig. 1(a)] exhibit curious splotchy patterns that persist on the timescale of our measurements. These patterns are caused by refractive-index fluctuations, and they appear geometrically similar to previous observations²⁰ of concentration fluctuations observed in critical binary fluids (e.g., isobutyric acid and water near its critical temperature). We checked this intuition by taking two-dimensional fast Fourier transforms (FFTs) of the optical image intensity pattern and radially averaging the transform [inset to Fig. 1(b)]. For comparison, we also performed FFTs and averaged the FFT of the pure blend data, and these are included as an inset to Figure 1(a). The pure blend has a peak at a finite wavevector that defines the average pattern

size,¹ whereas the blend with the block copolymer has no maximum. The curve in the inset to the right figure depicts a fit to the Ornstein–Zernicke function, confirming its resemblance to critical scattering.

Blend films having copolymer concentrations above and below 1% by mass fraction were examined at the same film thickness (≈ 100 nm). Surprisingly, surface-pattern formation was suppressed with as little as 0.1% mass fraction copolymer additive, a copolymer concentration notably far below the estimated bulk critical micelle concentration.^{13–18} Experimentally indistinguishable results were observed for an 8.6% mass fraction copolymer concentration. These block co-polymer-filled blends are contrasted with our previous bulk measurements that exhibited only a small shift of the phase boundary at these copolymer concentrations [the critical temperature (T_c) is lowered by ca. 2.5 °C for 8.6% mass fraction copolymer additive] and that the kinetics of phase separation were essentially the same as the pure blend when compared at an equivalent quench depth.^{13–18} We also performed neutron reflection measurements on these films and found that the block copolymer was distributed nearly uniformly normal to the plane of the film to a good approximation. After these measurements were performed,¹⁸ Akpalu et al.²¹ considered the effect of a block copolymer additive on the phase separation of a polyolefin film having a thickness comparable to the measurements of this communication. These measurements also demonstrated a suppression of surface-pattern formation and a uniformity of the block copolymer distribution within the film.

In an even more striking observation, suppression of surface-pattern formation was observed in thin films of a highly immiscible polymer blend of PS and poly(methyl methacrylate) (PMMA) with about 15% PS-PMMA block copolymer added, by relative weight to the blend. M_w for each type of molecule was on the order 10^5 so the polymers should be entangled.²² Despite the rather different conditions from our measurements (weak segregation blend, relatively low block copolymer concentrations in some cases, and unentangled polymers), a similar suppression of surface-pattern formation was observed in these films for a thickness range of less than 50 nm.²² Zhu et al.²² noted that the scale in which the stabilization occurs is on the order of the estimated diameter of the micelles that form for the same mixture in the bulk, and they provide simulation evidence indicating a sharp increase in the critical micelle concentration to higher concentrations for films thinner than this characteristic scale. On the basis of these observations, they attribute their film stabilization to an enhanced decrease of γ for the blend because of the resulting larger buildup of block copolymer at the blend interface in these highly confined emulsions arising from inhibited micelle formation.²² Theoretically, the interfacial tension can become zero or negative if enough block copolymer accumulates at

the interface of the blend.^{23,24} Zhu et al.²² additionally suggested that this finite size effect leads to the formation of stable microemulsions in these thin films.

There has been much interest²⁵ in the formation of polymeric block copolymer microemulsions of polymer blends and block copolymers in the bulk. However, the microemulsions described in ref. 25 correspond to an equilibrium state where the critical temperature for phase separation in the blend and the block copolymer order–disorder transition both drop to zero because of mutual dilution effects. In practice, this concentration range in bulk blends with high molecular weights is typically of the order of 10% block copolymer by mass relative to the blend. This type of microemulsion explanation for the film stabilization would require that the concentration range in which the microemulsion phase occurs become much larger in these quasi-two-dimensional films. If this is true, it offers an interesting possible explanation for the film-stabilization phenomenon. It also seems plausible to us that the “microemulsion morphology” could actually be a long lived phase-separation morphology in which a substantial slowing of the kinetics occurs because of the buildup of the block copolymer at the interface of the blend in the course of phase separation. Of course, this corresponds to a kinetic rather than an equilibrium explanation of the bicontinuous morphology observed within the films (phase separation occurs within the film, while the surface remains smooth).

We propose that the observed effect of the block copolymer additive is similar to the disappearance of the Benard–Maragani pattern in a fluid by introducing a small amount of surfactant onto the surface. Here the block copolymer surfactant decreases the surface-tension variations within the film so that the inplane surface spinodal pattern is suppressed, the effect perhaps being enhanced by the finite size effects suggested by Zhu et al.²² In this view, we are simply losing our source of contrast for the phase-separation processes occurring within the film. This interpretation is consistent with previous arguments^{1–3} that surface-tension variations within the films are the origin of the observed surface-pattern formation in phase-separated polymer films and obviously points to a potentially strong influence of impurities on this type of measurement. The mechanism for the formation of the optical intensity fluctuations resembling critical fluctuations in fluid mixtures near their critical point is unclear, however. Neutron reflection measurements indicated that the block copolymers do not segregate strongly to the boundaries, but the splotchy optical patterns strongly suggest the presence of diffuse block copolymer in-plane composition fluctuations in the films. Future work should concentrate on the temperature dependence of these block copolymer compositional fluctuations, γ measurements in thin films, and kinetic measurements of scattering properties and film morphology conducted over very long timescales (i.e.,

months). These measurements should help resolve the mechanism(s) of film stabilization. Regardless of the exact explanation (e.g., formation of a polymeric microemulsion²⁵ because of finite size effects or a kinetically arrested phase-separation morphology), it is clear that trace amounts of the block copolymer can inhibit surface-pattern formation in blend films. This observation could have important implications on developing coatings without the defects that compromise the function of polymer coatings. Its full scientific explanation remains a challenge for future work.

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