

Transient Target Patterns in Phase Separating Filled Polymer Blends

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ABSTRACT: Recent simulations suggest that the presence of filler particles in a phase separating blend can induce the development of composition waves having the symmetry of the filler particles. We investigate these predictions through atomic force microscopy (AFM) measurements on ultrathin ($L \approx 100$ nm) polystyrene and poly(vinyl methyl ether) blend films containing a low concentration of model filler particles (silica particles having a nominal diameter ≈ 100 nm). The filled blend films were spun-cast on acid-cleaned silica wafers, and phase separation was induced by a temperature jump into the two-phase region ($T \approx 145$ °C) of the bulk polymer blend. By rinsing off the polymer film with solvent, we show that the silica particles are associated with the substrate so that the filler particles represent a quenched disorder perturbation of the film phase separation. The presence of the filler particles leads to the development of circular composition waves ("target patterns") about the filler particles during the intermediate stage of phase separation. These target patterns disintegrate as the background spinodal phase separation pattern becomes much larger than the filler particles. Our observations are consistent with idealized two-dimensional Cahn–Hilliard–Cook simulations of the phase separation of polymer blends having a small concentration of filler particles.

Introduction

The properties of fluid mixtures are characteristically insensitive to their microscopic structure near the critical point for phase separation and are instead governed by large-scale equilibrium fluctuations in the local composition. Apart from shifts in critical parameters describing the average properties of the fluid (e.g., critical temperature and composition, apparent critical exponents), the influence of microscopic heterogeneities on the properties of near critical mixtures tends to become "washed out" in the large-scale fluid properties. This situation changes when the fluid mixture enters the two-phase region. The fluid is initially far from equilibrium and can become sensitive to small perturbations that can grow to have a significant influence on the large-scale phase separation morphology. Inevitably, the theoretical description of this kind of self-organization process is complicated by various non-universal phenomena associated with the details of the simulation model or the experimental system. It becomes important, for example, whether the fluids are nearly Newtonian or viscoelastic (glassy, entangled, exhibiting hydrogen-bonding interactions or other transient associations, etc.) or whether a density mismatch or some other differential response of the mixture to its environment exists between the fluid components. The beneficial aspect of this sensitivity of phase separation to perturbations is that it offers substantial opportunities to *control* the structure of the phase separating mixture.

Many previous studies have considered the application of external fields (electric and flow fields, temperature gradients, gravity, etc.) to perturb phase separation, but there are fewer investigations of *geometrical perturbations*. Recent investigations of the perturbation of phase separation arising from the presence of a plane wall are perhaps the simplest and best understood example of a geometrical perturbation of phase separation.^{1–8} Measurements^{1–5} and simulations^{6–8} both show the development of "surface-directed" composition waves away from the boundary under the normal condition

where one component has a preferential interaction with the interface. The coarsening dynamics of these composition wave patterns is similar to bulk phase separation.

Apart from the scientific interest in studying the perturbation of phase separation by idealized surfaces, there are practical reasons for studying perturbation by more complex geometrical constraints such as in filled polymer blends. Polymer materials are hardly ever used in their pure form in applications. They are often filled with additives that improve their processability (lubricants and stabilizers) and filler particles that modify modulus and strength (carbon black, silica, glass beads and fibers, chalk, clay, mica), appearance (pigments and surfactants), conductivity (metal flakes, carbon black, carbon nanotubes), and flammability (flame retardants).⁹ Moreover, a large number of applications necessitate the use of polymer blend materials (impact modified blends, barrier polymers for packaging, filled elastomers) so that the situation where the filler particles interact with the phase separation process is widely encountered.⁸ An understanding of polymer–filler interactions and the ramifications for the properties of filled polymer blends is clearly a matter of practical interest that requires further investigation.

Recent measurements have also shown that the surface-directed composition waves can be *suppressed* in blend films that are thin relative to the "spinodal wavelength" governing the initial scale of phase separation.¹⁰ In these "ultrathin" films ($L < 200$ nm) we observe that surface tension variations associated with phase separation within the plane of the film cause the height of the film to undulate.^{10–12} These height fluctuations provide a source of contrast for imaging by AFM and optical microscopy (OM). Kinetic studies show that the in-plane phase separation in ultrathin blend films follows a pattern similar to light scattering and OM studies of phase separation from bulk fluid mixtures.^{10,11,13} The phase separation origin of these patterns is further confirmed by returning the films into the one-phase region through a temperature jump,

whereupon the phase-separated structures “dissolve” to form a homogeneous film.¹¹ Some unique aspects of the ultrathin film phase separation are the tendency of the late-stage phase separation to “pin” at a film thickness-dependent scale¹⁰ and the observation that the kinetics of phase separation approaches the behavior of model calculations for idealized two-dimensional phase separation.¹⁰ Ultrathin films provide a convenient geometry for exploring the influence of perturbations on phase separation, since the morphology can be imaged in real space using AFM in its early stages and OM at later stages.

In our initial measurements aimed at manipulating the morphology of phase separating blend films using a boundary perturbation, we introduced a chemical modulation on the substrate through alkanethiol self-assembled monolayers patterned at the micrometer length scale.¹⁴ These symmetry breaking perturbations were sufficient to direct the coexisting phase of the blend film to local regions of the substrate having a favorable interaction.^{14–16} More recent work has shown a film thickness-dependent coupling between phase separation and height fluctuations¹⁷ and a tendency for phase separation structures of very thin films to break up by capillary waves. This suggests there are lower limits on the size of structures that can be made by pattern-directed phase separation.¹⁸

In the present paper, we take this boundary perturbation strategy further by introducing filler particles into the blend that break the local translational invariance symmetry of the blend phase separation and thereby induce the development of composition waves into the medium having the symmetry of the perturbing object. In these ultrathin film measurements we add small particles that can be considered as “circular” inclusions within a near two-dimensional film. We observe transient circular composition waves that are similar to patterns found in Cahn–Hilliard–Cook (CHC) model simulations of phase separation in two dimensions with circular inclusions.¹⁹ The filler particles are shown to be strongly adsorbed onto the substrate surface, and the circular inclusions are likewise fixed in the simulations so the filler in each case represents a quenched disorder perturbation of the phase separation process.

We do not consider the case of the filled blends in which the filler particles are free to migrate to the component with the most favorable interaction. Our observations on this type of system indicated that the phase separation is qualitatively similar to the blend without the filler.²⁰ In general, the mobility of the filler within the film is greater for smaller particles so that the degree of particle “localization” on the time scale of the phase separation process is a function of particle size as well as the particle–surface interaction. We anticipate that the depth of quench can also have an important impact on the segregation of free particles to the interface of the coexisting phases. The driving force for the segregation should be larger for deep quenches, leading to significant changes in the coarsening kinetics and even pinning. However, little effect on the kinetics of phase separation (apart from changes in viscosity and the critical temperature) are expected for relatively shallow quenches. The present paper focuses on the case where the filler particles are *localized* to determine the influence of this quenched disorder on the phase separation morphology. We also consider

relatively shallow quenches since the phase separation and the drying of the spun-cast films can occur on comparable time scales in highly immiscible blends, leading to film patterns reflecting other processes than phase separation (e.g., Marangoni patterns associated with composition and temperature gradients, flow under spin-casting conditions, etc.). Measurements are also restricted to relatively dilute filler concentrations to avoid strong interference effects between the concentration waves induced by the filler particles.

Experimental Section

The model binary blend was a critical composition mixture of polystyrene (PS; $M_w = 102\,000$ g/mol, $M_w/M_n = 1.02$, $T_g = 100$ °C) and poly(vinyl methyl ether) (PVME; $M_w = 119\,000$ g/mol, $M_w/M_n = 2.51$, $T_g = -44$ °C).²¹ Bulk phase separation studies of this blend indicate a lower critical solution temperature, $T_c \approx 130$ °C, and a critical PS composition (volume fraction) of $\approx 80\%$.²² The silica beads were made by the Stöber process²³ and had an average size of about 100 nm, as measured by direct imaging of the particles using scanning electron microscopy (SEM) on a JEOL instrument.²⁴ The polymer blend and the silica beads were dissolved in toluene, and these solutions were spun-cast on hydrophobic, HF-etched silicon wafers. The silicon substrates (obtained from semiconductor processing)²⁴ were previously cleaned in a solution with volume fractions of 70% concentrated sulfuric acid and 30% hydrogen peroxide at 80 °C for 1 h, followed by rinsing in deionized water and drying under nitrogen gas. They were then covered by a 2 vol % diluted HF solution for 2 min and then thoroughly rinsed in deionized water. An approximately 100 nm polymer film was prepared by spin-casting from a polymer solution with a mass fraction of 2% of the critical composition blend that also contained a mass fraction of 1% fillers. Phase separation was achieved by annealing the film in the two-phase region at 145 °C under vacuum for different periods of time. Film topography was measured on a Topometrix²⁴ atomic force microscopy (AFM) where the vertical resolution was ± 1 nm.

Results

Simulations of the phase separation of polymer blends with fillers indicate that the filler particles can induce the development of concentration waves having the symmetry of the filler particles. A spherical particle, for example, will induce spherical composition waves in a bulk blend. Likewise, circular inclusions in idealized quasi two-dimensional films produce circular (“target”) waves in the film. In the design of the experiment, it is important that the polymer composition is near critical so that ordinary spinodal decomposition occurs in the film in the absence of filler particles. For the thin film blend system this requires a weakly immiscible blend film with weak surface interactions and having a restricted range of film thickness.^{10,11,13} Typically, the film thickness is limited to $h \leq 200$ nm in this type of measurement, and this restricts our filler particle radius, $r < 100$ nm, to avoid large perturbations of the film surface by the filler particles. The particles must not be too small since the persistence of the composition wave pattern decreases with the size of the particles. A particle diameter near 100 nm was judged as an appropriate size for meeting these conflicting constraints. In addition, the surface interactions of blend components need to be such that one polymer component enriches both boundaries (“symmetric blends”), leaving the residual blend mixture to segregate within the layered film.^{10,11,13} We utilize a model blend film in

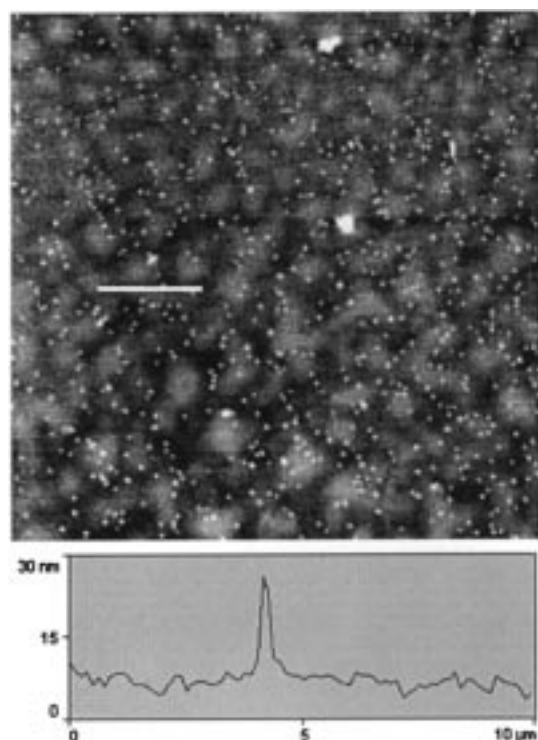


Figure 1. AFM topography of as-cast silica-filled polymer blend film. The film shows a faint image of incipient phase separation at early times and filler specks (not apparent in the spun-cast film without filler particles). Line profiles of the filler "speck" features show their height relative to the surrounding film surface to be ≈ 20 nm, while their apparent widths are larger. This is likely due to some clumping of particles into small aggregates (see Figure 6a) and AFM lateral resolution broadening effects.

a specified thickness range for which in-plane phase separation has been observed in previous studies.^{10,13} Finally, the chemistry of the filler is chosen such that the polymer component that does not segregate to the film boundaries enriches the surface of the filler particle. This ensures that the filler particles are not competing with the boundaries for the enriching polymer.

Figure 1 shows AFM topography measurements of a filled PS/PVME film shortly after the spin-casting process. The bulk blend is in the two-phase region for the composition and temperature of this film. The initial film structure is relatively smooth (some incipient phase separation is apparent in Figure 1). The bright regions are identified with individual and/or small clusters of silica particles, and these features are not observed in the identical prepared PS/PVME films without filler. Line profiles of this AFM image indicate that these features are about 20 nm in height relative to the average surface of the film. AFM measurements after solvent rinsing, discussed below, indicate that a large fraction of the filler particles adhere to the solid substrate so that they are relatively immobilized. We also observe in Figure 1 a near random distribution of filler particles, and this is also confirmed by the absence of correlation peaks in a two-dimensional fast-Fourier transform (2-d FFT) of the height distribution in the plane of the image.

In Figure 2 we examine the phase separation of the filled polymer film at an intermediate stage of film phase separation where we expect composition waves to be evident. The blend film was annealed for 30 min at 145 °C. Film surface topography gives only an

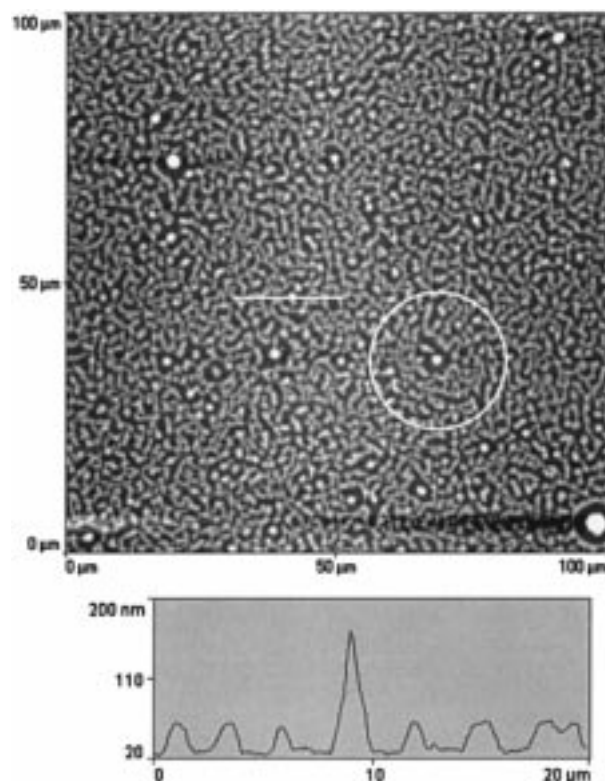


Figure 2. Phase separation pattern of PS/PVME blend film with dilute concentration of filler particles. Film shown was spun-cast from a toluene solution and annealed at 145 °C for 30 min. Contrast was enhanced by washing the film in methanol to selectively dissolve away the PVME-rich regions. Observe a number of bright spots ("targets") surrounded by circular rather than isotropic phase-separated morphology. The spike in the line profile measures a typical filler target center. The outlined circle denotes the area used in deriving the radial average height data shown in Figure 4b.

indirect indication of the morphology within the film, and we can gain direct information about the internal film structure by selectively dissolving the PVME-rich phase with methanol, nearly to the level of the silicon substrate. (Figure 3 provides a comparison of washed and unwashed film.) This selective dissolution procedure leads to AFM images enhanced in contrast relative to the unwashed film. We observe the presence of bright circular regions where the film height is greater than the average and about which the phase separation morphology is perturbed. These bright features are interpreted to be silica beads coated with the polymer of the PS-rich phase (see below). The magnitude of this perturbation can be seen in the line profile image below this figure where the heights of the surface features are an order of magnitude greater than Figure 1 since the baseline is now closer to the silicon substrate.

In Figure 3 we show a higher magnification (5 $\times$) image of a subregion of Figure 2 that provides a clearer indication of the local perturbation of the film structure by the filler. It is apparent from both Figures 2 and 3 that the "background" spinodal pattern resembles previous measurements on intermediate-stage blend film phase separation without filler^{10,11} but that there are local regions about the filler particles where the phase separation pattern is altered. Control measurements (not shown) of the blend phase separation under the same conditions yield films having a bicontinuous spinodal pattern and the circular patterns apparent in Figures 2 and 3 are absent. These AFM images show

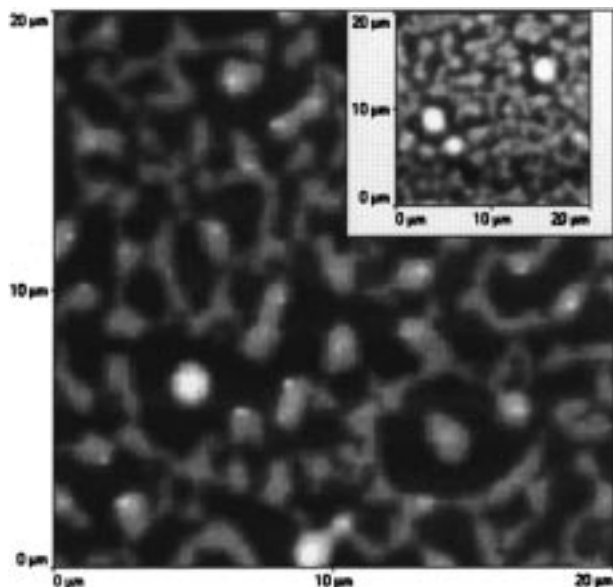


Figure 3. Zoom-in image of Figure 2 showing the development of the PS-rich “target” patterns. Note the presence of rings of enhanced PS concentration about specific target locations. Film patterns of unwashed films are similar as shown in the inset. Since the height variations are weaker in the unwashed film, washed films are used for their greater contrast.

that the translational symmetry of the film phase separation pattern is locally broken by the presence of the filler particles, leading to the formation of PS-rich rings (“target patterns”) in the washed films. A secondary ring of enriched PS composition about the filler²⁵ is also apparent in Figure 3. Since the methanol rinsing provides only an indirect measure of the interior structure of the phase-separated films, we show a section of the unwashed film in the inset to Figure 3. The pattern in this inset is similar, except that the height variations are smaller and thus there is less height contrast.

A more quantitative description of this filler-induced composition wave in Figure 3 is obtained through a Fourier analysis of the AFM height data. The inset to Figure 4 shows a 2-d FFT transform of the methanol-rinsed film at an intermediate-late stage of phase separation corresponding to images shown in Figure 2. The main figure shows a circular average of the power spectrum $P(q)$ of these data that has a maximum at q^* characterizing the average scale of lateral phase separation. The solid line is a fit of the data to a Lorentzian function, and this fitting gives the peak position q^* . The wavelength λ_{sp} of the phase separation pattern is defined²⁶ as $\lambda_{sp} \approx 1/q^*$. The length scale λ_{sp} of the intermediate-late stage of phase separation pattern shown (Figures 2 and 3) is estimated by this Fourier analysis of the surface height data as $\lambda_{sp} \approx 2.4 \mu\text{m}$. The presence of the filler particles should have some influence on λ_{sp} , but we expect the magnitude of q^* in Figure 4a to be predominantly a measure of the scale of the “background” pattern.¹⁹

We next consider a radial average $\Psi(r)$ of the AFM film height data about a representative filler particle. The averaging region shown in Figure 2 corresponds to a relatively isolated target pattern in order to minimize interference between the composition waves. $\Psi(r)$ is defined as the average radial height $h(r)$ about the center of the bright region shown in Figure 2 minus the average film height h_{av} of the entire film, and this

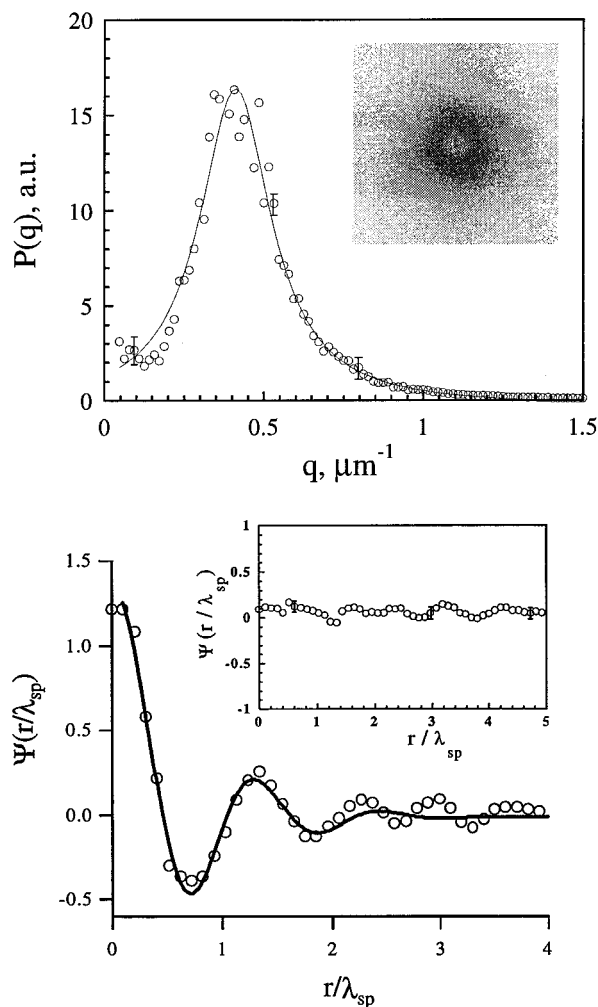


Figure 4. Height analysis of an intermediate-stage phase-separated film as in Figure 3. (a, top) Radial average $P(q)$ of 2-d FFT (inset) of entire image shown in Figure 2. Solid line is a Lorentzian functional form fit to obtain the peak position, q^* , representing the average phase separation scale. The $P(q)$ data are in arbitrary units. (b, bottom) Radial averaged normalized height variation $\Psi(r/\lambda_{sp})$ about a representative target pattern [circled area in Figure 2; see eqs 1 and 2 for definition of $\Psi(r/\lambda_{sp})$]. Height data are expressed in units of the average film thickness, and the radial coordinate is given in units of λ_{sp} . Solid line fit is the linearized CHC model prediction $\Psi_{CHC}(r/\lambda_{sp})$ for the composition wave pattern where the scale parameters of the Bessel and Gaussian functions have been adjusted for a best fit. Comparison between height data and theory assumes that the height variations of the film directly reflect composition variations. This assumption can only be approximately true. Moreover, the linearized CHC theory¹⁹ is strictly applicable to very short times so only a qualitative agreement should be expected. Inset shows the radial averaged normalized height variation for a random position within the film removed from the vicinity of the target patterns (i.e., the “spinodal background”).

difference is then normalized by h_{av} so that $\Psi(r)$ is dimensionless.

$$\Psi(r/\lambda_{sp}) \equiv [h(r) - h_{av}]/h_{av} \quad (1)$$

The average vanishes for large r where r is the radial distance from the center of the target pattern. The linearized Cahn–Hilliard–Cook (CHC) theory indicates that Ψ should be approximated as a Gaussian decay function multiplied by a Bessel function of index zero in the case of a two-dimensional circular wave pattern.¹⁹ This functional form is shown in Figure 4b where the

scale parameters of the Gaussian and Bessel functions have been adjusted to fit the data. The functional form of the fit is given by

$$\Psi(r/\lambda_{sp}) = \Psi(r=0) \exp[-\delta_1 z^2] J_0(z),$$

$$z = (\delta_2 r/\lambda_{sp} - R_0) \quad (2)$$

where the decay parameter of the Gaussian equals $\delta_1 = 0.0125$, the scale parameter of the Bessel function J_0 equals $\delta_2 = 5.38$, $\Psi(r=0) = 1.34$, and R_0 is the fitted value of the particle radius, $R_0 = 82$ nm. We observe that the first minimum of the phase separation pattern occurs for values of r/λ_{sp} close to 1 and infer that the scale of a ring of the target pattern is comparable to the overall scale of phase separation. Thus, the modulation of the phase separation process has the qualitative characteristics of a circularly symmetric wave in the plane of the film with the amplitude decaying away from the source of the perturbation. (J_0 is an eigenfunction of the Laplacian in two dimensions and describes the amplitude of an ideal circularly symmetric wave.) The fitted particle radius R_0 is comparable to the average particle radius $R_0 \approx 100$ nm as measured by scanning optical microscopy. Note that the AFM height data only indirectly reflect the compositional variations within the film and that the linearized theory is strictly limited to the early stage of phase separation so that only a qualitative agreement between experiment and theory should be anticipated.

As a control measurement, the radial average of height fluctuations normalized by the average film height was taken for random positions within the film, relatively far removed from any filler particle. A representative radial average is shown as an inset to Figure 4b. Only small random fluctuations are observed, indicating that the height pattern is radially isotropic in the "background" phase separation pattern. We also observed that the target patterns persist longer in the larger bright regions shown in Figure 2 where presumably there are aggregates of filler particles. This general tendency is consistent with the simulations discussed in the next section.

Simulations of the perturbation of phase separation by filler particles have indicated that the target composition wave patterns in dilute filler dispersions persist up to a point where the background phase separation scale λ_{sp} becomes larger than the size of the filler particles. Experimentally, the target patterns are observed to be a transient stage of the phase separation process, disintegrating toward later stages of phase separation. The extent to which the filler particles perturb the film morphology in the late stage of phase separation is then examined. The AFM data in Figures 2 and 3 correspond to intermediate-late stage phase separation where the spinodal decomposition pattern is actively breaking up through a process driven by hydrodynamic flow. In a late stage of phase separation the film pattern consists of droplets of the PS-rich phase surrounded by the PVME-rich matrix phase on the silicon substrate. Figure 5a illustrates the late stage morphology (methanol washed) corresponding to 100 min annealing at 145 °C. The morphology of the filled film is contrasted with the structure of the *unfilled* films under the same conditions of temperature and film thickness in Figure 5b. We observe that the film morphology in this very late stage appears essentially identical to Figure 5a, apart from the absence of filler

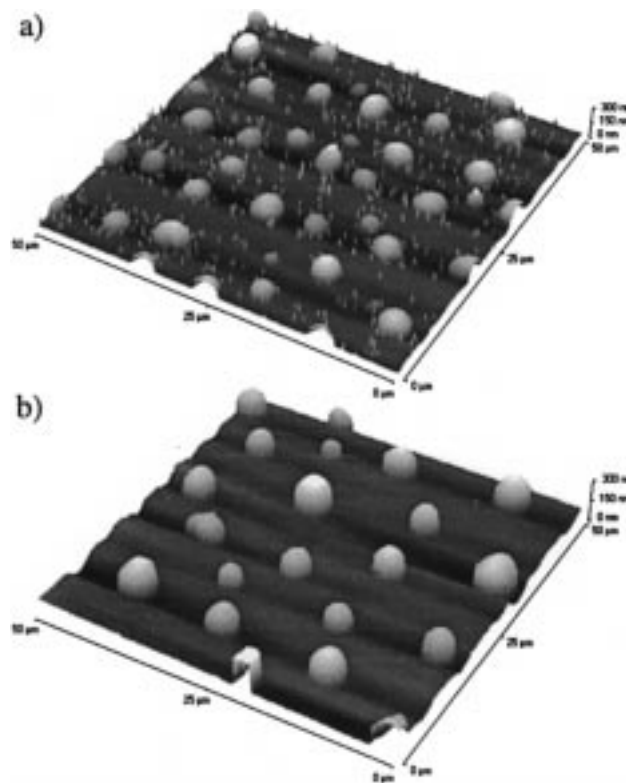


Figure 5. AFM topography of final late stage phase separation of a filled PS/PVME polymer blend following the breakup of spinodal phase separation pattern. (a) Film containing fillers annealed for 100 min at 145 °C and then washed in methanol to enhance contrast. (b) The phase separation pattern in (a) is similar to the blend film without filler in this stage. Note that the extended darker regions following the droplets in the background planar section of the surface are artifacts induced by the large droplets during the AFM scanning process.

particles exposed on the washed regions of the film. The droplets are fairly circular with or without filler.

Although the images of Figure 5 show little perturbation of the phase separation pattern in the very late regime of coarsening, there are perturbations to the droplets in the early stage of droplet breakup. At the beginning of the late stage regime the droplets become highly distorted by the filler particles. This interesting transient droplet distortion phenomena is separate from the target pattern phenomena emphasized in the present paper and will be considered in a subsequent paper. We note however that little change in the phase separation coarsening kinetics is seen in our filled films relative to the unfilled films.

The enrichment of the PS to the silica particles in the film makes it difficult to judge the magnitude of the silica core region R_0 of the target patterns directly. The relatively large scale of a few of the surface features in the filled phase separating blend images suggested to us that some of the silica particles are actually small particle aggregates. We gain some insight into this problem by washing away the remaining PS-rich phase with toluene. This second washing leads to a surface with only randomly distributed silica particles remaining (Figure 6a). The particle density, size, and distribution not too different from what was present initially in as-cast films (Figure 1). Thus, we infer that the silica particles are not segregated to any polymer phase during the phase separation process, but instead are immobilized at the silicon surface in a random distribution. A line profile (Figure 6b) of the AFM data in Figure

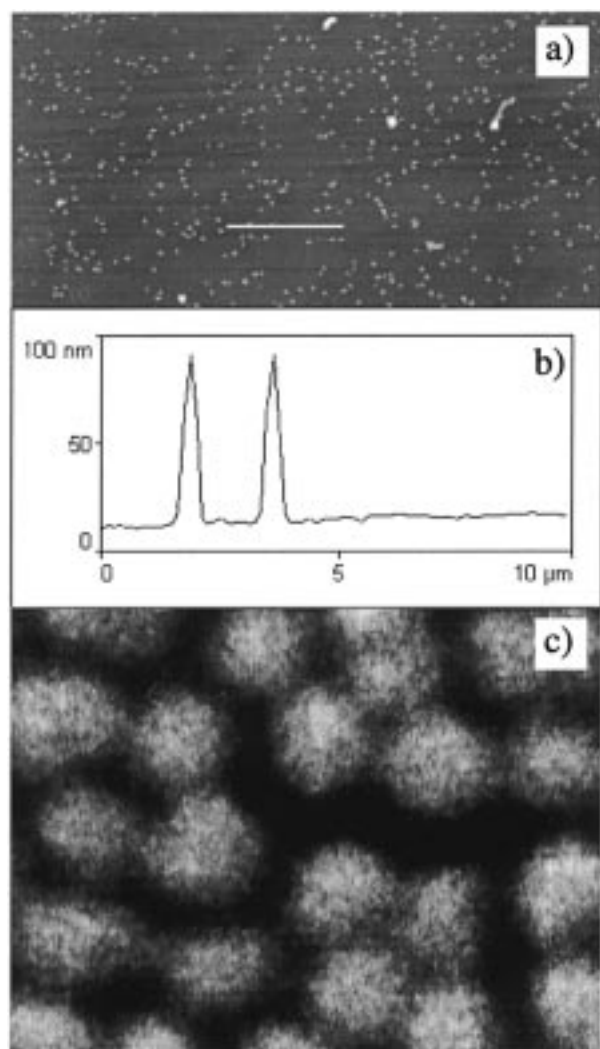


Figure 6. Methanol and toluene "double-washed" film. (a) The AFM image film shown in Figure 4 is washed with toluene to dissolve the residual polystyrene, leaving the filler particles on the substrate. (b) Line profile of "double-washed" film indicating height and width of a filler particles. (c) SEM image of the isolated silica particles, cast directly from a toluene solution onto a silicon wafer. Silica particles are nearly $0.1\ \mu\text{m}$ in diameter (image width is $0.5\ \mu\text{m}$).

6a shows two representative surface features due to the presence of the silica filler. In general, there is a distribution in the sizes of the silica features in the washed blend films, and we find that the average peak in Figure 6a has a full width at half-maximum (fwhm) of about $0.3\ \mu\text{m}$. These widths are somewhat larger than the fwhm apparent from the line profile of Figure 1. This is because Figure 1 only measures the protrusion of the silica bead above the film surface. (Accordingly, the "bead" height in Figure 1 is only 20 nm.) The dimensions are nevertheless larger than the dimensions of individual silica beads ($\approx 0.1\ \mu\text{m}$) measured by SEM, as shown in Figure 6c. The bright features in Figure 6a apparently correspond to a mixture of isolated and small clusters of silica particles that are essentially fixed in place. Notably, the modeling of filled blend phase separation¹⁹ assumes that the particles are fixed in space. Different phenomena can be expected in late stage phase separation if the particles are free to move and thus to segregate to the phase that is energetically favorable or to segregate to the interface between the coexisting phase leading to a slowing down of the phase

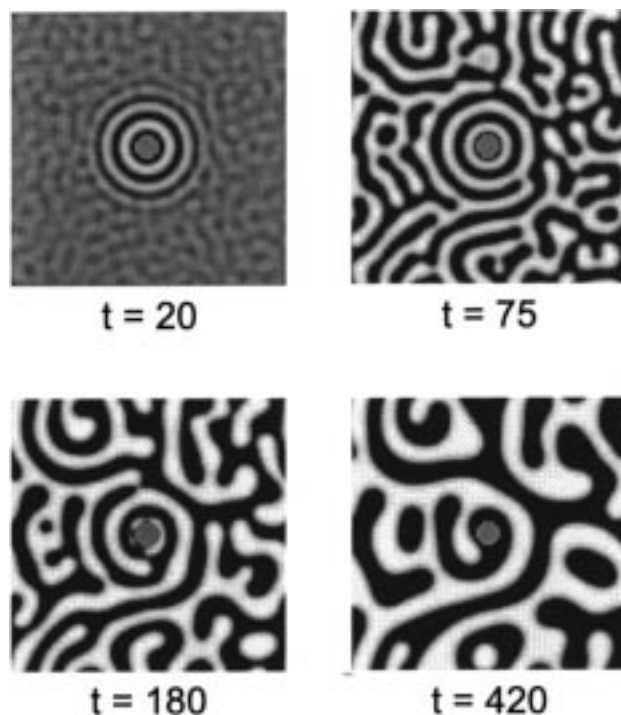


Figure 7. Illustrative Cahn-Hilliard-Cook simulation of the influence of filler particles on polymer blend phase separation in a critical composition blend. Calculations are performed in two dimensions for a relatively deep quench into the two-phase region and for a surface interaction that enriches one of the components to the filler boundary. The phase separation patterns (a) and (b) correspond to the intermediate stage phase separation regime. Note that the target pattern in (b) fragments as the "background" spinodal phase separation pattern coarsens to a scale larger than the filler particle (central gray region in figure).

separation process. This segregation tendency depends on the particle mobility (size and shape), quench depth, wetting of the particles by the polymer components, and the energetics of filler-blend mixing²⁷ so there are many situations that must be considered in future studies of phase separation in filled polymers.²⁸

Simulation of Target Pattern Formation in Phase Separating Blends. Simulations of phase separation in the present paper focus on the consequences of having geometrical heterogeneities of finite extent in a phase separating blend. The development of phase separation "target" patterns requires the conditions of ordinary spinodal pattern formation (i.e., "near" critical composition and temperatures in the two-phase region) and the existence of a heterogeneity that induces the enrichment of one polymer component. The target waves are actually a kind of spinodal pattern with its symmetry set by the shape of the filler particle boundary.

Lee et al.¹⁹ have adapted the Cahn-Hilliard-Cook (CHC) theory for phase separation²⁹ to describe blend phase separation with differently shaped filler particles. A variable polymer-surface interaction is incorporated into the filler model Lee et al.¹⁹ in a fashion similar to previous treatments of plane surfaces.⁶⁻⁸ Here we are interested in only the essential results that pertain to our measurements and the design of future studies of pattern formation in filled polymer blends undergoing phase separation.

In Figure 7 we show an illustration of the calculation from Lee et al.¹⁹ showing the influence of an isolated filler particle on the development of the phase separa-

tion pattern of a blend having a critical composition in two dimensions. The simulation corresponds to a relatively deep quench,³⁰ i.e., a high molecular weight and/or low T . The particle radius R_0 is smaller than the initial scale of phase separation. The surface interaction in the CHC model calculation shown in Figure 7 corresponds to a case where one of the polymer components forms a layer of enriched concentration near the surface of the particle.¹⁹ At an early stage of the phase separation process (Figure 7a) the filler particle creates a spherical composition wave disturbance that propagates a few "rings" into the phase separating medium. A radial average of the composition profile about the filler particle leads to an oscillatory pattern similar to Figure 4b. As the phase separation pattern coarsens to the scale of the filler particle (Figure 7b–d), the outer rings of the "target" pattern become disconnected and increasingly become incorporated into the developing "background" phase separation pattern. The time units in Figure 7 are given in terms of $(\xi^-)^2/2D_c$ where D_c is the collective diffusion coefficient¹⁹ and ξ^- is the correlation length in the two-phase region. The perturbing influence of the particle on the phase separation pattern becomes weak in a late stage of phase separation where the scale of the background phase separation pattern exceeds the scale of the central region of composition enrichment about the filler particle (the "bull's-eye" size of the target pattern). The finite size of the filler thus affects the duration of the transient circular composition waves. This pattern of behavior is similar to the findings of the previous section for the intermediate stage phase separation.

Discussion

The presence of filler particles in a phase separating fluid mixture is found to give rise to transient composition wave patterns in measurements on ultrathin polystyrene/poly(vinyl methyl ether) blend films with a small concentration of silica filler particles. The choice of filler size and film thickness was made to test recent simulations predicting transient target patterns in phase separating blends.¹⁹ The experiments and simulations correspond to the case where the filler particles are relatively small with low filler concentration, fixed in space, and preferentially enriching one polymer. The simulations indicate that composition waves are transient features so that the filler particles should have a limited effect on the late stage phase separation when the scale of phase separation becomes much larger than the size of the filler particles. Accordingly, measurements of the target patterns are limited to an intermediate–late stage of phase separation where the background "spinodal pattern" scale is bicontinuous and comparable to the scale of composition enrichment at the center of the target. The ring pattern and the surrounding spinodal pattern begin to break up by the disrupting effect of the developing spinodal phase separation process in combination with the hydrodynamic instability that generally causes the breakup of late-stage phase separation patterns in liquids.

The utilization of geometrical or chemically patterned surfaces and fillers offers many opportunities for the control of the phase separation morphology and properties of blend films. Investigations of these surface-induced phase separation processes also raise many fundamental and practical issues. For example, the introduction of surface patterns^{14–18} on the filler par-

ticles could be used to impart further secondary structure into the target pattern. The surface patterns can break the symmetry of the phase separation process *within the surface*, leading to interfering composition waves. Novel "checkerboard" patterns have been predicted in simulations of phase separation near patterned substrates.¹⁴ Filler particles are an important practical example of a perturbation of phase separation by boundaries inside a fluid. In the future we will consider the influence of finite *exterior* boundaries on phase separation. It seems likely that composition waves within confined geometries should be more stable because of the decreasing surface area of the rings further from the surface. This should lead to well-developed and long-lasting perturbations of the phase separation process. The relation between boundary shape and phase separation morphology should be very interesting for this class of measurements.

Circular composition waves can also be induced by heterogeneities induced by external fields, for example, irradiation of a film leading to formation of cross-links, which can induce spherical concentration waves. Measurements of irradiated photoreactive blends of PVME and PS with a cross-linkable side group (styrene–chloromethylstyrene random copolymer) PSCMS show the formation of ring composition patterns³¹ that are reminiscent of our observations on filler blend films. Furukawa³² has interpreted these observations in terms of a model in which it is assumed that irradiation first brings the blend into the nucleation regime where droplets phase separate, followed by the entrance into the spinodal regime where the droplets act as the filler particles discussed in the present paper. This is a plausible interpretation of the qualitative origin of the patterns, but it is difficult to interpret the measurements directly since cross-linking imparts a nontrivial viscoelasticity to the polymer blend. Cross-linking also increases the molecular weight of PSCMS, and with the increased elasticity we expect a decrease in the thermal noise and thus an enhancement of the tendency to form target phase separation patterns.¹⁹ In these experiments the patterns become fixed in space once PSCMS forms a cross-linked network, facilitating the investigation of an otherwise transient pattern. The target patterns of Qui and co-workers thus seem to be qualitatively related to those found in our filled films. We expect similar patterns can be introduced by applying a variety of perturbations that likewise break the local translational symmetry of the phase separation process.

The present paper has focused on the ideal limit of dilute concentration of fillers and the local perturbation of the phase separation process induced by the filler. This is a first step toward treating highly filled blends often encountered in applications. In these highly filled blends, the distinction between interior and exterior boundaries created by the particles becomes blurred, and nonlocal perturbations of the phase separation process are anticipated. New phase-separated morphologies should also arise by varying the size and mobility of the filler particles and the depth of quench into the two-phase region. External fields can also be used to align the filler particles, providing a useful means to manipulate the large-scale phase separation morphology. These more concentrated filled polymer blends will be investigated in future work.

Conclusions

Measurements were performed on the phase separation of ultrathin polymer films with silica bead filler particles to determine the perturbation of the phase separation by filler particles. We observe the development of target composition patterns about the filler particles in our AFM measurements that have many characteristics in common with the idealized two-dimensional Cahn–Hilliard–Cook simulations of blend films with filler. The persistence of the target patterns apparently increases with particle size, and the target patterns break up when the scale of the background spinodal pattern becomes much larger than the filler particle. In the late stage of phase separation the filler particles have little influence on the film morphology, and this is also found in the simulations. More quantitative comparisons between experiment and simulations will be possible by incorporating hydrodynamic effects in the simulations.

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Note Added in Proof. A simulation study of phase separation with mobile filler particles has recently appeared [Ginzburg et al. *Phys. Rev. Lett.* **1999**, *82*, 4026]. This work indicates a substantial slowing down of the kinetics of phase separation with the addition of filler particles. We believe that deep quenches and mobile (small) particles are required to observe the kind of pinning seen in the simulations. Immiscibility of the filler in the blend components should also facilitate the accumulation of filler at the interface of the phase separating blend and the associated pinning process.

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