Internal Phase Separation Drives Dewetting in Polymer Blend and Nanocomposite Films

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ABSTRACT: We present experimental results showing that roughening in polymer blend films is driven by the underlying phase-separated morphology. To control morphology and stability, nanoparticles (NP) are added to poly(methyl methacrylate) (PMMA):poly(styrene-ran-acrylonitrile) (SAN) (50:50) films having a thickness of 550 nm. These PMMA:SAN films undergo symmetric wetting with PMMA layers at the surface and substrate and separate into PMMA-rich (A) and SAN-rich (B) coexisting phases. Three varieties of NP are investigated and either partition into A (NP_A) or segregate weakly (NP_w) or strongly (NP_s) to the interface between A and B. Using scanning force microscopy, the surface roughness is monitored for films containing up to 20 wt % NP. Whereas rupture is observed in neat blends and blends with NP_w or NP_A, stable films are produced by the addition of only 2 wt % NP_s. Although capillary fluctuations fail to predict roughening, a novel model based on the Laplace pressure produced by the internal morphology agrees with experimental results. For neat blends and blends with NP_A, long wavelength fluctuations exhibit universal scaling with roughness \( \lambda \propto R^{1/4} \). Although the origin of this coupling is unknown, we propose that spinodal decomposition during initial phase separation may trigger the long wavelength fluctuations. By identifying the driving force for roughening in nanocomposite films, we can better understand and control high-performance coatings containing incompatible components and functional inorganic additives.

Introduction

Liquid film stability on solid substrates underlies many technologically important processes ranging from paint gloss to the resolution of inkjet printers. Although most coatings are technologically important processes ranging from paint gloss to the resolution of inkjet printers. Although most coatings are multicomponent and multiphase, roughening and rupture mechanisms are not understood. For single-layer1–11 homogeneous films, capillary fluctuations produced by long-range van der Waals forces1,4,6–8,11 or external stimuli, e.g., electric field,3,5,10 can destabilize films, whereas the Laplace pressure, which resists interfacial deformation, can stabilize the films. For polymer blends undergoing phase separation, Hoppe et al.12 found that the rupture time \( t_r \) and the periodicity of fluctuations at rupture \( \lambda_{f,i} \) scaled linearly with film thickness \( d \). In these experiments, the driving force for destabilization was unclear. Recently, Clarke13,14 suggested that lateral compositional fluctuations, due to phase separation, destabilize polymer blend films.

Before investigating roughening in polymer blend films, the structural evolution proceeding rupture must be understood. For A/B blends where A wets the free surface and substrate, three distinct stages of evolution are observed after a critical quench.15 The early stage is characterized by rapid growth of wetting layers concurrent with the formation of a three-dimensional (3D) bicontinuous structure in the midlayer.16 At the onset of the intermediate stage, this 3D structure evolves into discrete, circular domains of A that span the B midlayer.17 In the late stage, long wavelength (order 10 \( \mu m \)) interfacial fluctuations cause the film to rupture.18 The origin of these fluctuations is unknown. These previous studies of A/B blends provide the starting point for understanding the mechanism of roughening in liquid films.

In this paper, we provide experimental evidence that the Laplace pressure induced by a phase-separated structure provides the driving force for roughening and rupture in neat polymer blend (A/B) films and those containing nanoparticles (NP). The NP systems are designed to either partition into A (NP_A) or weakly (NP_w) or strongly (NP_s) segregate to the interface between phases. During phase separation, roughened films display periodic, lacey structures, similar to a spinodal dewetting pattern. Whereas NP_w inhibit roughening more than NP_A, NP_s prevent film rupture at concentrations as low as 2 wt %. The periodicity of fluctuations scales with roughness as \( \lambda \propto R^{1/4} \) for neat blends and blends containing NP_A, whereas scaling breaks down for blends containing NP that segregate to the interface, namely NP_w and NP_s.

Experimental Methods

Deuterated poly(methyl methacrylate) (A) and poly(styrene-ran-acrylonitrile) (B), from Polymer Sources and Monsanto, respectively, have weight-average molecular weights (\( M_w \)) and polydispersities (PDIs) of 106 000 and 1.20 and 118 000 and 2.24, respectively. This blend exhibits a lower critical temperature of \( \sim 160^\circ C \). At 195 \(^\circ C \), the coexisting compositions are nearly pure A and B.15 The three NP have distinct surface functionalities that control their segregation behavior. NP_A are colloidal silica particles (Nissan Chemical) with a diameter of 22 nm and a surface with methyl and hydroxyl groups.19,20 NP_w and NP_s, denoting weakly and strongly segregating particles, have a silica core (Nissan Chemical) with a slightly smaller diameter (15 nm). These NP’s are grafted with PMMA brushes having \( M_w \)’s of 23 700 and 2100, respectively. As discussed in ref 21, NP_s distribute throughout phase A, NP_w are found in phase A and at the A/B interface, and NP_s locate only at the A/B interface. The A/B blend (50/50) and NP’s...
were mixed in methyl isoamyl ketone, spun-cast on silicon, and dried at 120 °C in a vacuum for 24 h. The film thickness was $d = 550$ nm. Films were annealed on a hot stage (FP-82, Mettler Toledo) at 195 °C in argon. The surface and midlayer morphologies were characterized using a Dimension 3000 SFM (Veeco Inc.) driven in tapping mode. To reveal the interface morphology of B, A was removed by exposing films to 2.85 MeV He$^{2+}$ ions and then rinsing with acetic acid.$^{15-18}$

Results

Roughening was evaluated by following the evolution of the surface and interface morphology. As an example of the image analysis procedure, Figure 1 shows the surface and the midlayer morphology of a film with 2 wt % NP$_w$ after a 24 h anneal. First, the topography of the surface is projected as a 3D image, as shown in Figure 1a. The surface fluctuation wavelength $\lambda_s$ is determined by measuring the mean diameter of the area for each high region. Using SPIP software (Image Metrology Inc.), a watershed segmentation algorithm$^{22}$ then divides the image into regions as shown in Figure 1b. The same cutoff values are used for surfaces having a similar roughness. As roughness increases, larger cutoff values are required to remove high-frequency noise. Partly imaged regions near the edge are omitted as shown in Figure 1c. From this image, $\lambda_s$ is determined from the mean diameter of a circle having the same area as the original irregularly shaped region. For the internal or midlayer morphology shown in Figure 1d, the correlation length $\xi$ between A domains (dark) was determined from the dominant wavevector, $k_{\text{max}}(t)$, by converting the image into reciprocal space by a fast-Fourier transform and using $\xi(t) = 2\pi/k_{\text{max}}(t)$.

Surface roughening and rupture can be slowed down or even prevented by the addition of NP as dramatically illustrated in Figure 2. Figure 2a shows that neat blend films are extremely rough and exhibit a root-mean-square (rms) roughness ($R_q$) of 506 nm after 72 h. Upon adding 5 wt % NP$_A$ or NP$_w$, films are smoother as shown by parts b and c of Figure 2, respectively.

With respect to the neat blend, the $R_q$ values are lower, 223 and 167 nm, respectively, even though films are annealed for a longer time, 120 h. However, the addition of 5 wt % NP$_A$ or NP$_w$ does not prevent rupture. In contrast, films with 5 wt % NP$_s$ are remarkably stable and very smooth ($R_q = 7$ nm) as shown by Figure 2d. As shown below, the driving force for film roughening can be understood by analyzing $R_q$ and $\lambda_s$.

Figure 3 shows how $R_q$ evolves with time for the neat blend (closed triangles) and blends containing 2–20 wt % NP. By observing that hazy (rough) films display $R_q$ values $>100$ nm, a rupture time $\tau$ is empirically defined by $R_q(t_\tau) = 100$ nm. Applying this definition to Figure 3a, $\tau$ is $\approx 14$ h for neat blends and $\approx 24$, $\approx 36$, and $\approx 76$ h for 2, 5, and 10 wt % NP$_A$, respectively. The increase in $\tau$ with NP$_A$ loading is attributed to an increase in the viscosity of the A phase, as previously described.$^{23}$ Whereas films containing 2 and 5 wt % NP$_A$ rupture after $\approx 50$ and $\approx 60$ h, respectively, the addition of 10 and 20 wt % NP$_A$ produces stable films for at least 120 h, as shown in Figure 3b. Remarkably, film stability is achieved by the addition of only 2 wt % NP$_s$ as shown in Figure 3c. This result is consistent with our recent observation that the internal phase structure can be pinned by jamming of NP$_s$ at the interface.$^{21}$

Figure 4 shows how $\lambda_s$ evolves with time for the neat blend and blends containing 2–20 wt % NP. Initially, all films are smooth ($R_q \approx 5$ nm), and no periodic fluctuations are observed. For the shortest annealing time, 1 h, all samples have similar $\lambda_s$ values, ca. 8 nm. For blends with NP$_A$, $\lambda_s$ monotonically increases as time increases and, after 120 h, approaches 21, 22, and 20 nm for 2, 5, and 10 wt % loadings, respectively. As shown in Figure 3a, $R_q$ increases in a similar manner before reaching $\approx 321$, $\approx 228$, and $\approx 206$ nm at 120 h, respectively. On the other hand, for blends with NP$_w$, $\lambda_s$ values are shorter and reach only $\approx 13$, $\approx 12$, and $\approx 9$ nm, respectively, consistent with the much smaller $R_q$ values of $\approx 11$, $\approx 8$, and $\approx 5$ nm shown in Figure 3c. However, for blends containing 20 wt % NP$_w$,
between 24 and 120 h, $\lambda_s$ increases from 12 to 18 $\mu$m. However, $R_q$ is nearly invariant, only increasing slightly from 9 to 13 nm, suggesting that the wavelength and local roughness are de-coupled. This observation is discussed later.

**Discussion**

Capillary fluctuations along the interface between the wetting and midlayer is a potential driving force for film roughening. In the layered structure A/A:B/A/substrate, deformation along the A/A:B interface can dominate roughening because the interfacial tension ($\sigma_i = 0.9$ mJ/m$^2$) is much less than the surface tension ($\sigma_s = 27.4$ mJ/m$^2$)\textsuperscript{15}. If a long-range van der Waals force produces interfacial fluctuations, $\lambda_s$ and $\sigma_i$ are given by

$$
\lambda_s = 4\pi d^2(\sigma_s / \sigma_i)^{1/2} \quad \text{and} \quad \sigma_i = (48\eta \pi^2 \sigma_s / d^2)^{1/2}
$$

where $\sigma_s$ and $\eta$ are the Hamaker constant and viscosity, respectively.\textsuperscript{1} Using literature and measured values for $\sigma_s \approx 10^{-19}$ J and $\eta \approx 4.0 \times 10^{-3}$ Pa s,\textsuperscript{6,24} respectively, and the $d$ value for the entire film, 550 nm, $\lambda_s$ and $\sigma_i$ are 169 years and 530 $\mu$m, respectively. Clearly these predictions are inconsistent with the experimental results in Figure 3, which indicate $\lambda_s \approx 1$ day and $\sigma_i \approx 10$ $\mu$m. Here, we present a new model that is consistent with the phase-separated morphology prior to rupture and attributes film rupture to the Laplace pressure produced by the internal structure in the midlayer.

In our system, the Laplace pressure can stabilize or destabilize the film. The stabilizing Laplace pressure results from the surface curvature ($\psi P_s$), which comes from long-range fluctuations along $x$ and $z$ directions (cf. Figure 5), namely, $\psi P_s = \sigma_i \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \left( \frac{\lambda_s}{\xi} \right)^2$ and $\psi P_i = \sigma_i \left[ \frac{4R_q}{d^2 - R_q^2} \left( \frac{\lambda_s}{\xi} \right)^2 \right]$ (2)

For $\Delta P_i > \Delta P_s$, B flows from depressed to elevated regions as illustrated by the arrow below Figure 5b. This flow amplifies the long-wavelength fluctuations and increases film roughness. In this treatment, the flow of B will decrease the amount of B in the thin region (B phase shrinks) and increase B in the thick region (expands). Conversely, A domains will expand and shrink within the thin and thick regions, respectively.
tested by determining whether respectively. Because of the higher curvature of the B phase in thin wavelength fluctuations. Black and gray corresponds to A and B phases, exerts a Laplace pressure that destabilizes the film by amplifying long-wavelength fluctuations in film thickness facilitate rupture. The internal structure film thickness that depict the late stage morphology evolution where (a, b) Two sequential cartoons of the internal structure and Figure 5.

Figure 5. (a, b) Two sequential cartoons of the internal structure and film thickness that depict the late stage morphology evolution where fluctuations in film thickness facilitate rupture. The internal structure exerts a Laplace pressure that destabilizes the film by amplifying long-wavelength fluctuations. Black and gray corresponds to A and B phases, respectively. Because of the higher curvature of the B phase in thin regions \((r_2 < r_1)\), the Laplace pressure is greater in the thin regions \((P_s > P_m)\). Thus, B flows from depressed to elevated regions because of the internal Laplace pressure gradient \((\Delta P_s)\), resulting in amplification of long-wavelength fluctuations. Evidence for this mechanism is presented by the SFM image \((40 \mu m \times 40 \mu m)\) of the midlayer for a blend with 5 wt % NP, after 72 h (c). Here, the light and dark regions correspond to high and low points, respectively, whereas the black circles are A domains (etched). Note that the B phase is continuous, although B appears discrete in (a) and (b). The same gray and black color schemes are used in (a), (b), and (c). \(R_q, \lambda_s, \xi\) are 134.6 nm, 23.7 \(\mu m\), and 2880 nm, respectively.

Using measured characteristics, the proposed model can be tested by determining whether \(\Delta P_s \gtrsim \Delta P_m\). For neat blends at 10 h, \(\lambda_s, R_q, \xi\) are 11 nm, 22 nm, and 2600 nm, respectively. Using eqs 1 and 2, \(\Delta P_s\) and \(\Delta P_m\) are 47 N/m² and 5700 N/m², respectively. Because \(\Delta P_s\) is about 125 times larger than \(\Delta P_m\), the internal Laplace pressure can drive B from depressed to elevated regions (i.e., arrow pointing toward +z), causing roughness amplification. For a neat bend and blends containing NP at 2, 5, and 10 wt %, \(\Delta P_s\) is consistently about 2 orders of magnitude greater than \(\Delta P_m\). Thus, experimental support for the proposed mechanism is rather extensive. In addition, the SFM image in Figure 5c provides direct evidence that B flows from low (dark) to high (light) regions. Note that A domains (dark circles) exhibit larger diameters in thin regions and smaller ones in thick regions, consistent with the sketch in Figure 5b.

For the first time, a destabilization model consistent with the underlying morphology is proposed for roughening in phase-separating polymer blend films. Nevertheless, improvements to this model are possible. For example, the curvature of the B phase in the \(x-z\) plane produces flow over a distance \(\lambda_s\). An improved model would also capture local flow of B over the distance \(\xi\), which is generated by curvature along the \(x-y\) plane defined in Figure 5c. As described in an earlier study, this curvature drives domain coalescence.17,25

Having quantified roughening using \(\lambda_s\) and \(R_q\), an investigation of coupling between these key parameters may further elucidate the origin of roughening. Figure 6 shows \(\lambda_s\) vs \(R_q\) for A/B films and those containing NP. For neat and NP blend films, a scaling relation (solid line) is observed, \(\lambda_s [nm] = 500R_q^{1/4}\), for \(R_q\) ranging from \(\sim 6\) to \(\sim 300\) nm, as shown in Figure 6. However, scaling breaks down for films containing NP that segregate to the interface, as shown in the inset of Figure 6. This result indicates that film roughening is perturbed (i.e., \(\lambda_s\) and \(R_q\) are decoupled) by NP segregation to the interface. Specifically, \(\lambda_s\) increases more rapidly than \(R_q\) as shown by the data in the inset. Qualitatively, the origin of this scaling breakdown is likely related to the prolonged film stability observed when NP locate at the interface. However, new experiments and theory are needed for a complete description.

To understand the scaling relation uncovered in Figure 6, the origin of long-range fluctuations must be known. Although a definitive answer is lacking, the recent theory by Clarke,13 which attributes film destabilization to inhomogeneities in lateral composition, may shed some light on the observed scaling behavior. In our system, we postulate that short-wavelength composition fluctuations produced by spinodal decomposition (i.e., early stage) induce the long-wavelength surface fluctuation in Figure 5. Interestingly, the initiation of a long-wavelength fluctuation by a short-wavelength fluctuation has been observed in the wrinkling of a metal layer on a polymer film28 as well as Turing and spiral waves in chemical reactions.27 We hope that our new experimental results will stimulate new theories of roughening in liquid thin films.

**Conclusion**

In this paper, film roughening is investigated in neat blends as well as those containing NP. If they segregate to the interface, NP can jam together and prevent film rupture. Although particle stabilization in emulsions is of longstanding interest, recent interest in new nanoscale materials has driven a resurgence in understanding the behavior of NP at interfaces.28 New models29 have appeared as well as the observation of interconnected glasslike structures.30 The main result of this paper is that internal phase separation destabilizes multicomponent, complex, liquid films by a morphology-driven Laplace pressure. The long-wavelength fluctuation that drives dewetting of the polymer...
blend films may be initiated by short-wavelength fluctuations resulting from spinodal decomposition. The scaling relation $s \propto R^{1/4}$ is an interesting finding that will hopefully motivate new theories of dewetting that describe polymer blend and nanocomposite liquid films. The proposed model can be extended to polymer blend films showing asymmetric wetting\textsuperscript{31} in addition to the symmetric wetting case explored in the current paper.

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**References and Notes**


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