Self-Regulated Structures in Nanocomposites by Directed Nanoparticle Assembly

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ABSTRACT

Adding surface-modified silica nanoparticles (NPs) to polymer blend films, we demonstrate that directed interfacial segregation of NPs stabilize either three-dimensional (3D) interpenetrating or 2D discrete structures at high and low volume fractions of NPs, respectively. A simple interfacial energy argument provides a general guideline for predicting whether the NPs are directed to the interface between phases or into one phase. The final morphology and domain size can be predicted from the volume fraction of NPs, film thickness, and NP size.

Nanoparticles (NPs) added to organic films provide a promising method to enhance the properties of optoelectronic devices, chemical and biological sensors, and nanoreactors. Whereas organic materials have been typically used to organize NPs, recent studies show that the NPs themselves can drive structural transitions in water−oil emulsions and block copolymers. A self-regulating, stable structure is highly desirable for many applications. For example, a mesoscale, bicontinuous structure of interpenetrating n-type and p-type polymers provides optimal performance for photovoltaic and light-emitting devices; unfortunately, lifetime can be severely reduced by phase coarsening that occurs during device operation. Here, depending on NP loading and surface chemistry, the addition of NPs to a phase-separating polymer blend film produces extremely stable, self-regulating structures. If NPs partition into one phase, the structural evolution slows down, but phase coarsening continues resulting in a roughened film. However if NPs are driven to the interface between phases, stable discrete or bicontinuous structures form at low and high NP loading, respectively, and film rupture is prevented. The interfacial segregation of NPs can be justified by minimizing the system free energy. Finally, we propose general guidelines for using NPs to produce stable bicontinuous structures in multiphase systems.

Before the effect of NPs can be investigated, structural evolution in the neat polymer blend must be understood. Previously, films containing deuterated poly(methyl methacrylate) (dPMMA) and poly(styrene-ran-acrylonitrile) (SAN) at the critical composition, 50:50, were found to undergo three distinct stages of evolution. An early stage is characterized by a three-dimensional (3D) bicontinuous structure as well as wetting of dPMMA at the free surface and substrate. With the onset of the intermediate stage, the 3D structure evolves into discrete, 2D dPMMA domains that span the SAN midlayer. In the late stage, the film ruptures because of interfacial fluctuations. In this paper, we demonstrate that NPs driven to the interface regulate the formation of either the 2D or 3D structures.

The dPMMA and SAN (33 wt % AN), from Polymer Source and Monsanto, respectively, had weight average molecular weights \( M_w \) and polydispersities (PDIs) of 106000 and 1.20 and 118000 and 2.24, respectively. The radii of gyration are 11.6 and 9.5 nm, respectively. This blend exhibits a lower critical temperature of \( 160 \) °C. At 195 °C, the coexisting compositions are nearly pure dPMMA and SAN. MSTs are monodisperse, colloidal silica NPs (MBK-ST, Nissan Chemical), with a 22 nm diameter and a surface of methyl and hydroxyl groups. P2Ks are 18 nm in diameter, having a silica core (DMAC-ST, Nissan Chemical) with a shell of grafted PMMA brushes with a chlorine end group \[ \text{Si} \left( \text{CH}_2 \right)_n \text{OOC} \left( \text{CH}_3 \right)_2 (\text{MMA})_x \text{Cl} \; (x \approx 18) \]. The \( M_w \) and grafting density of the PMMA are 1800 (PDI = 1.18) and 0.7 chains/nm², respectively. These NPs are stable up to 200 °C as confirmed by thermal gravimetric analysis. The dPMMA/SAN (50:50) and NPs were mixed in methyl isoamyl ketone (MIAK), spun-cast on silicon, and dried at 120 °C in a vacuum for 24 h. The film thickness values ranged from 550 to 3000 nm. Samples were annealed on a hot stage (Mettler FP-82, Mettler Toledo) at 195 °C in argon.
The NP dispersion throughout the film was determined by focused ion beam (FIB) etching and scanning electron microscopy (SEM) (FEI Strata DB235), as schematized in Figure 1a. First, to reduce sample charging, Au/Pd coatings (nanometers) were deposited on the films. Second, Ga$^+$ ions (30 keV and 10 to 1000 pA) etched a trench ($10 \mu m \times 10 \mu m$) through the film and into the substrate. Third, samples were tilted by $52^\circ$ and then imaged by scanning electron microscopy (SEM) (2 keV). Parts b and d of Figure 1 show that MST and P2K, respectively, are homogeneously distributed in the as-cast films. Note that P2K is mainly individual NPs, whereas MSTs form small aggregates ($\sim 100$ nm). MSTs are directed into the dPMMA phase (Figure 1c) upon annealing, whereas P2Ks decorate the interface between SAN and dPMMA (Figure 1e).

To determine the internal structure of films with thickness $d = 550$ nm, dPMMA was removed by exposing samples to 2.0 MeV He$^+$ and then immersed in acetic acid. The remaining SAN phase was imaged by atomic force microscopy (AFM) (Dimension 3000, Veeco Instruments) in tapping mode. Figure 2a represents a typical intermediate stage morphology of a neat blend, which has nearly circular dPMMA domains (dark) imbedded in a SAN matrix (light). Upon addition of 5 wt % and 10 wt % MST and annealing for 24 h, parts b and c of Figure 2 show that domain shape is nearly circular, as in the neat system, but domain diameter decreases as MST concentration increases. Similar behavior was observed for macroscopic nanoparticles in oligomer blends. However, after 24 h, a striking structural transition from discrete to bicontinuous is observed upon adding P2K. At 5 wt % (Figure 2d), the domain shape becomes irregular, whereas for 10 wt % (Figure 2e) a bicontinuous structure is observed, suggesting a structural pinning during the early stage.

The domain growth dynamics is quantified by the correlation length, $\xi(t) = 2\pi/k_{\max}(t)$, where $k_{\max}(t)$ is the dominant wave vector determined from the fast Fourier transform of the internal morphology in parts a–e of Figure 2. For neat blends and low NP loadings, a coalescence model captures domain growth. Figure 2f shows $\xi$ plotted against $t^{1/3}$ for the neat blend and blends with NPs. Upon addition of 5 wt % MST, domain growth slows down relative to the neat blends. At 10 wt %, however, domain growth ceases and $t^{1/3}$ scaling breaks down in agreement with theory. As discussed below, at long times both the neat blends and blends with MST rupture, preventing further observation of domain growth. Films containing P2K, on the other hand, exhibit a pinned structure with $\xi$ of 1700 and 950 nm at 5 and 10 wt %, respectively, suggesting that domain size and shape are self-regulated and stabilized by directing NPs to the interface.

After the intermediate stage, films can rupture because of long-range fluctuations between the wetting and middle layers. Parts a and b of Figure 3 show that films without and with 5 wt % MST, respectively, rupture after 72 h and exhibit root-mean-square roughness values ($R_q$) of 506 and 269 nm. In contrast, Figure 3c shows that films with 5 wt % of P2K are remarkably stable and have a very small $R_q$ of 9 nm. Figure 3d plots $R_q$ with time to distinguish between rough and stable films. Because a “rough” film appears opaque due to diffuse scattering of light, a phenomenological relationship $R_q(t) = 0.2d$ is used to define the rupture time or $t_r$. These values are 15, 40, and 60 h for 0, 5, and 10 wt % MST, respectively. On the other hand, films containing 5 and 10 wt % P2K do not rupture and remain smooth ($R_q < 10$ nm for 120 h). This stabilization is particularly striking because the annealing $T$, 195 °C, is far above the glass transition temperature of the SAN.
transition $T$, $\sim$110 °C, and well into the two-phase region (i.e., 35 °C above critical $T$).\textsuperscript{15} Whereas the NPs (MST) that segregate into the dPMMA phase slow roughening, probably by enhancing viscosity,\textsuperscript{14} directing NPs (P2K) to the interface between phases produces a smooth, stable film.

The broad significance of these novel studies requires understanding why MST NPs partition into one phase whereas P2K NPs are stable at the dPMMA/SAN interface. Whereas the former case is attributed to the affinity of dPMMA to the hydroxyl-terminated silica,\textsuperscript{14} the latter case requires understanding why P2K at the dPMMA/SAN interface is trapped at a free energy minimum. For spherical NPs, Pieranski\textsuperscript{25} showed that NP will be positioned at the A/B interface if

$$|\sigma_{A/NP} - \sigma_{B/NP}| < \sigma_{A/B}$$


Figure 2. AFM images (20 μm) of the internal structure of films without NPs (a) and with 5 (b) and 10 wt % (c) MST and 5 (d) and 10 wt % (e) P2K. The dPMMA was removed as described in the methods section. Films were annealed for 10 (a) or 24 h (b–e). The domain correlation length $\xi$ is plotted against $t^{1/3}$ in (f). For both MST and P2K, the addition of NPs reduces domain size. With increasing P2K concentration, a discrete (d) to bicontinuous (e) structural transition is observed. Note the pinning of $\xi$ at 1700 and 950 nm for 5 and 10 wt % P2K, respectively.

Figure 3. Surface AFM images (100 μm) of films without NP (a), and with 5 wt % MST (b), and 5 wt % P2K (c) after 72h. RMS roughness values are 506, 269, and 9 nm, respectively. The roughness values are plotted against time in (d). Legends follow Figure 2f. Here, films containing P2K exhibit remarkable stability, whereas films with MST eventually rupture and become macroscopically rough.

$$\Delta E_{int} = \frac{\pi R^2}{\sigma_{A/B}} |\sigma_{A/NP} - \sigma_{B/NP} + \sigma_{A/B}|^2$$

where $R$ is the NP radius. The contact angle of water, $\theta$, on dPMMA and P2K is used to determine $\sigma_{dPMMA/P2K}$ and $\sigma_{SAN/P2K}$, respectively. The Cl end group increases the surface energy of P2K, as indicated by an increase in $\theta$ from 70° to 84° for PMMA and P2K films, respectively. At 195 °C, $\sigma_{dPMMA/SAN}$ is 0.9 mJ/m$^2$\textsuperscript{15} and $\sigma_{dPMMA/P2K}$ and $\sigma_{SAN/P2K}$ are 0.6 and 1.0 mJ/m$^2$, respectively.\textsuperscript{27} With these values in eq 2, $\Delta E_{int}$ is $7.1 \times 10^{-20}$ and $4.8 \times 10^{-19}$ J when the A phases
Oil/water emulsions were stabilized with silica particles by directed interfacial segregation of P2K. Utilizing structures based on stable, bicontinuous phases, the effect of R on interfacial segregation can be readily understood. For R ≈ 10 nm, NPs will be trapped at the phase boundary when eq 1 is satisfied. However, for small NPs (i.e., R < 2.5 nm), strong interfacial segregation is not expected.

As previously mentioned, improved polymeric devices will utilize structures based on stable, bicontinuous phases with controlled periodicity. Figures 2d–f and 3c,d show that structural control and stabilization of a model polymer blend can be achieved by directed interfacial segregation of P2K. Oil/water emulsions were stabilized with silica particles by an “irreversible bridging” mechanism. In this mechanism, a water (oil) wetting layer containing macroscopic particles bridges oil (water) domains, and the triphase region is pinned at the contact angle. Because NPs are unable to span the wetting layer, which must be a few chains thick, irreversible bridging is unlikely in the present study. Rather, we propose that stabilization is simply determined by d, R, and NP volume fraction, $\phi_{NP}$. Because the dPMMA/SAN interface is narrow ~0.2R, P2K can assemble only up to a monolayer with area $A_{NP}$. Upon initial phase separation, the A/B interfacial area $A_{AB}$ is much larger than $A_{NP}$. As $A_{AB}$ decreases to minimize free energy, we propose that the structure stabilizes when $A_{AB} \approx A_{NP}$, namely, after P2K forms a monolayer at the dPMMA/SAN interface. For 2D hexagonally packed P2K, $A_{NP}$ normalized by film area is given by:

$$n = \frac{A_{NP}}{A_{film}} = \frac{3d\phi_{NP}}{\sqrt{2\pi R}}$$

where $n \approx 2$ and $x \approx 2d$ define the transition between the early (3D) and the intermediate (2D) stages. For P2K at 5 wt % ($\phi_{P2K} = 0.033$) and 10 wt % ($\phi_{P2K} = 0.064$), eq 3 yields $n = 1.4$ and 2.6, respectively, in agreement with the 2D and 3D structures shown in parts d and e of Figure 2e, respectively. Moreover, the $x$ values for these structures are 950 ($<x)$ and 1700 nm ($>x)$, respectively. Thus, this simple “saturation” model predicts both the structure and size of the stabilized morphology, as schematized in Figure 5.

In conclusion, directed interfacial segregation of NPs can stabilize the structure of polymer blend films and prevent film rupture, whereas NPs that partition in one or the other phase only slow growth kinetics. A simple interfacial energy argument provides a general guideline for directing NP to the interface between polymer phases, a key requirement for structure and film stability. A more sophisticated theory, for example, incorporating chain conformational entropy, is needed.

**Figure 4.** Schematic diagram of energy landscape of a single NP near the dPMMA/SAN interface. The energy barriers ($\Delta E_{int}$) to move a P2K particle initially at position (1), the dPMMA/SAN interface, to (2), the dPMMA phase, or (3), the SAN phase, are $\sim$ 11 $k_B T$ and $\sim$ 74 $k_B T$, respectively, at 195 °C.

**Figure 5.** Cross-sectional cartoons of films containing P2K. Immediately upon phase separation, the dPMMA/SAN interfacial area is large and P2K NPs are too sparse to form a monolayer as shown in (a). As phase coarsening continues, the interfacial area decreases to minimize free energy. This reduction continues until the interface becomes saturated with a monolayer of P2K. If P2K loading is high, the phase structure pins during the early stage, resulting in a stable 3D bicontinuous structure as shown in (b). However, if P2K loading is low, stabilization occurs after the early to intermediate stage transition. Thus, 2D discrete domains are stabilized as shown in (c). As described in the text, these structures can be predicted by $n$, where $n > 2$ and $n < 2$ correspond to high and low P2K loadings, respectively.
necessary to improve upon this model. For systems with NP at the interface, the final morphology, either the 3D or 2D structure, and periodicity can be predicted from the volume fraction of NP. We hope that our study will lead to a new approach for creating the next generation of polymeric electrooptic devices with tailored morphology and phase size. For example, one can now envision a polymeric solar cell containing multifunctional quantum dots that both stabilize the structure and absorb radiation.

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References
(27) The surface energy of P2K, σ, was estimated from water contact angle (θW2K) measurements on 200 nm films at 25°C, by combining Young’s equation and the geometric mean equation. Using θW2K = 84.0°, σ was ~30 mJ/m² at 25°C. Using the temperature dependence of σ, σ is ~31.4 mJ/m² at 195°C. From the surface tension values of 27.4 and 31.4 mJ/m² for dPMMA and SAN at 195°C, the interfacial energy between P2K and each polymer was 0.6 and 1.0 mJ/m², respectively.