A COMPOSITION-MORPHOLOGY MAPPING OF PARTICLE-FILLED POLYMER BLENDS UP TO HIGH FILL FRACTION

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Abstract

This study explores the effects of particulate filler on the morphology of two immiscible high-molecular-weight thermoplastic polymers across a wide range of composition. Blends of polyisobutylene (PIB) and polyethylene oxide (PEO) with silica particle loadings of up to 30 vol% were studied. The silica particles have a strong affinity for PEO, and hence the effects of particles on the morphology depend on whether or not there is sufficient PEO to engulf the particles. We observe two morphologies that are qualitatively different from those seen in particle-free polymer blends: one in which particles are bonded together by small menisci of PEO, and the other in which a highly-filled particles-in-PEO phase percolates throughout the sample. Other morphologies in filled blends resemble droplet-matrix or cocontinuous morphologies in corresponding unfilled blends. Overall, particles have major effects on the morphology when the polymer preferred by the particles (PEO) is in a minority, but only modest effects when the preferred polymer is in a majority.

Introduction

Immiscible homopolymers are often blended together to realize blends with improved mechanical, electrical, or transport properties [1-3]. In many such applications, the morphology of the polymer blend plays a critical role in determining the properties of the blend, and hence there has been much research on structure development in such blends. This includes mapping out the relationship between morphology and composition, the effect of the relative viscosity or elasticity of the constituents on phase continuity, and exploiting compatibilizers to modify the morphology. [4-6] In this paper, we are concerned with polymer blends that are filled with a solid particulate species. The central question motivating this paper is: how does a particulate filler affect the morphology of an immiscible polymer blend?

Much of the literature on particle-filled polymer blends has been summarized in excellent reviews [7, 8]. Most of the existing research has focused on situations in which the particulate filler is present at a low volume fraction, usually less than 5 vol%. Even at these relatively dilute loadings, remarkable effects have been noted: morphological stabilization (i.e. morphology remaining stable for extended periods under molten conditions) [9], an improvement in dispersion (i.e. a finer-scale morphology) [10], and changes in phase continuity induced by filler [11]. Studies at filler loadings exceeding 5 vol% are uncommon [12, 13], and each of these covers only a narrow range of blend compositions. A comprehensive study of particle effects across the entire composition space remains missing.

In this paper we map the composition-morphology relationship in particle-filled blends of two immiscible thermoplastic homopolymers, with a focus on the “fully-wetting situation”, i.e. the particles have a strong affinity for one of the two polymers. The goal of this paper is to explore, for the first time, the composition-morphology relationship across a wide range of compositions using a single set of materials.

The materials were selected to permit clean interpretation of the results: the particles are spherical and non-porous, the two polymers have roughly equal viscosity and one of them can be selectively dissolved for structural characterization by SEM.

Materials and Methods

Experiments used polyisobutylene (PIB BASF Oppanol B-15, \(M_w \approx 75000\) g/mol), polyethylene oxide (PEO Dow Polyox N-10, \(M_w \approx 10^5\) g/mol) and fused silica particles (Industrial Powders SS1205). These particles are polydisperse with sizes in the 0.5 to 5 \(\mu\)m range and the mean diameter is 2 \(\mu\)m.

Blends were prepared using a Brabender Electronic Plasti-Corder model EPL-V5501. It operates on the counter rotation of two roller blades, which induces strong shear forces for efficient mixing of the blends. The maximum mixer capacity with the roller blades installed is 60 mL. The composition is specified by the three volume fractions denoted \(\phi_{\text{PIB}}\), \(\phi_{\text{PEO}}\), and \(\phi_{\text{p}}\). Note of course that \(\phi_{\text{PIB}} + \phi_{\text{PEO}} + \phi_{\text{p}} = 1\). This study examines particle volume fractions of \(\phi_{\text{p}} = 0, 10, 20, \) and 30%, and the PEO:PIB ratios are varied from 4:96 to 88:12. The PIB/PEO/silica ternary blends were prepared in a two-step procedure. The PIB and PEO were first mixed together at 95 °C at a mixing speed of 92 rpm for 5 mins. A small test sample of PIB/PEO blends was taken out of the mixer for later characterization. Then, silica particles were added, also in small increments, and blending continued for 5 mins at same speed. After recovering and cooling the blends, samples were washed with octane to remove the PIB. The
residue (PEO and particles) were examined by Scanning Electron Microscopy (SEM-JEOL JSM6510).

Results and Discussion

The following discussion is split into three sections: the first on particle-free blends, the next on particle effects on the morphology and last, on particle effects on phase inversion. While a large number of samples were studied, only a few (illustrated in a ternary composition diagram in Fig. 1) are shown in detail in this paper.

Particle Free Blends

Before discussing effects of particles on the morphology, Fig. 2 first presents the morphological changes with composition in the absence of particles. When PEO is in a small minority, it forms the dispersed phase comprising roughly round drops with a size of a few microns (Fig. 2a). With increasing PEO loading, the PEO drops grow in size with spherical and non-spherical shapes. This is attributable to a sharp increase in capillary forces. At 56% PEO (Fig. 2c), the sample no longer disintegrates completely in octane, and the PEO phase remains completely un-fragmented. The PIB phase of this sample is continuous as well which is termed as co-continuous morphology. With further increase in PEO content, the PIB loses continuity and becomes large and non-spherical at high PEO content (Fig. 2d), and small and nearly spherical when the PIB is dilute (not shown).

In summary, the particle-free blends show behavior that is consistent with that expected from the literature: (1) the minority phase tends to form the dispersed phase; (2) phase inversion appears when the two polymers have comparable volume fractions; (3) the morphology appears co-continuous at phase inversion; (4) the size of the dispersed phase increases greatly approaching phase inversion from either side; and finally, (5) the dispersed phase becomes increasingly elongated near phase inversion on either side.

![Figure 1](image1.png)

Figure 1. The compositions of the blends from Figs. 2, 3, and 5 represented on a ternary composition diagram.

Particle Effects on Morphology

Fig. 3 illustrates the effects of adding 10 vol% particles to the blends in Fig. 2. Fig. 3a corresponds to a regime of composition space where the PEO volume fraction (3%) is much less than the particle fraction (10%). Despite the superficial resemblance of Fig. 2a to Fig. 3a, these two morphologies are completely different. In Fig. 2a, the round particles visible are the solidified PEO drops, whereas in Fig. 3a, a majority of the round particles are silica.

![Figure 2](image2.png)

Figure 2. SEM images of particle-free samples with the PIB/PEO/particle ratios listed at the top right of each image. The triangular composition diagram of Fig. 1 shows the four compositions

From the appearance of Fig. 3a, the particles appear to be bound together by small menisci of PEO. This is analogous to the structure of a sand castle which owes its strength to small water menisci that bind together sand grains [14]. Adopting the terminology from the literature on wet granular materials, we call this morphology the funicular morphology, i.e. a morphology in which a single meniscus binds together multiple particles by capillary forces. It is noteworthy that such a morphology has no analog in particle-free polymer blends nor in filled polymers (where particles are dispersed into a single homopolymer). Such a morphology appears only when particles and a small amount of the preferentially-wetting polymer are both dispersed together.

For the compositions in Figs 3b, c and d, the PEO fraction greatly exceeds the particle fraction. Since the PEO is completely wetting towards the particles, when it is in large excess, it completely engulfs the particles and hence a silica+PEO combined phase is formed. For the composition PIB/PEO/silica= 70/20/10 (Fig. 3e), one obtains a standard droplet-matrix morphology: the dispersed consists of round drops of PEO which themselves contain the particles. At higher PEO loadings than that, the changes in morphology with composition are now qualitatively similar to those in Figs 2b, c, and d although there are some differences. Fig. 3b consists of a highly elongated dispersed phase, which resembles Fig. 2b, but with a modest increase in the size of the dispersed phase, i.e. particles induce coarsening, at least at 10% loading. Indeed we have noted previously that addition of particles...
can sometime accelerate drop coalescence in polymer blends [15].

![Image](25x420 to 294x681)

Figure 3. SEM images of samples with 10 vol% particles. The PIB/PEO/particle ratios are listed at the top right of each image. The triangular composition diagram in Fig. 1a shows the compositions of the samples.

At even higher PEO loadings (Figs. 3c and 3d) there are no changes in phase continuity as compared to the particle-free samples.

Fig. 3 omitted one interesting range of compositions, viz. when \( \phi_p \approx \phi_{PEO} \). Under these circumstances, there is just sufficient PEO to engulf all the particles and form a combined particles+PEO phase. The internal particle filling fraction of the combined phase is

\[
\phi_{combined}^p = \frac{\phi_p}{\phi_p + \phi_{PEO}}
\]

(1)

Clearly, if \( \phi_{PEO} \) is comparable to or slightly lower than \( \phi_p \), \( \phi_{combined}^p \) can be higher than 0.5, perhaps even as high as 0.7. At such high filling, the combined phase is internally-jammed, i.e. its rheology is expected to resemble that of a paste (e.g. possessing a high yield stress) rather than a molten polymer (e.g. being viscous or viscoelastic). Such solid-like behavior has a large effect on the morphology. To illustrate this, Fig. 4 compares two blends with compositions in the vicinity of \( \phi_p \approx \phi_{PEO} \).

Fig. 4a has \( \phi_p = 0.1 \) and slightly less PEO than the particles (\( \phi_{PEO} = 0.06 \)) such that there is barely sufficient PEO to engulf all the particles. As per equation 1, the combined phase has \( \phi_{combined}^p = 0.625 \). At this extremely high value of particle loading, one may therefore expect the combined phase to be highly solid-like. Indeed the dispersed phase appears non-spherical and highly irregular due to particles protruding from its surface. We believe that the non-spherical shapes appear because of the yield stress of the highly concentrated dispersed phase; due to this yield stress, interfacial tension forces are not sufficient to enforce spherical shaped aggregates. Thus the aggregates retain whatever shapes they achieved during the mixing process.

Following the literature on wet granular materials [16], such aggregates were dubbed “capillary aggregates” [17]. Capillary aggregates, do not coalesce readily, both due to their high yield stress, and because the protruding particles hinder contact of the molten PEO that is on the interior of the aggregates [17]. In contrast, if \( \phi_p \ll \phi_{PEO} \), (eg. Fig. 3b), the dispersed phase can coalesce like “normal” liquid drop.

![Image](58x65)  

Figure 4. SEM images of samples with roughly equal PEO and particle loading which shows different morphologies. The PIB/PEO/particle ratios are listed at the top right of each image.

Similar to Fig. 4a, Fig. 4b also has a PEO loading slightly less than the particle loading so that a highly filled combined phase is formed. But in Fig. 4b, the particle loading is much higher than in Fig. 4a. Now the capillary aggregates are found to connect with each other and form a percolating (i.e. space-filling network). Such a capillary aggregate network appears to be a new kind of bicontinuous morphology.

We also examined the effect of particles at \( \phi_p = 0.3 \), which is a much higher loading than in Fig. 3. These results are shown in Fig. 5. We observed funicular aggregates a low PEO loading (Fig. 5a), followed by capillary aggregate networks (Fig. 5b), and phase inversion into a PEO-continuous structure (Fig. 5d). Figs. 3 and 5 taken together suggest that the greatest effects of particles appear when \( \phi_{PEO} < \phi_p \). In contrast, at \( \phi_{PEO} > \phi_p \), particle effects were modest.

**Particle Effects on Phase continuity and Inversion**

From Figs 2, 3 and 5, it is clear that particles can affect which phase is the continuous phase and hence we examined phase inversion in detail. A combination of image analysis and solvent extraction using octane was used to judge phase continuity. The samples were then classified (Fig. 6) into one of four categories using the following criteria.
PIB-continuous (filled blue circles): The samples disintegrated when immersed in octane (i.e. removing PIB).
PEO-continuous (filled black squares): The samples remained intact in octane.
Cocontinuous (hollow green triangles): The samples remained nearly intact in octane and the interface appeared smooth.
Capillary aggregate network (hollow green diamonds): The samples remained intact in octane and the interface appeared rough with particles protruding out.

Figure 5. SEM images of samples with 30 vol% silica. The PIB/PEO/particle ratios are listed at the top right of each image. The triangular composition diagram in Fig. 1a shows the compositions of the samples.

We note that some points in Fig. 6 that are classified as cocontinuous were on the verge of losing continuity; they fragmented into 2-3 large pieces when immersed in octane. These samples are circled in red in Fig. 6.

It must be emphasized that the “cocontinuous” and the “capillary aggregate network” both have two percolating phases. However the ones classified as capillary aggregate networks (Fig. 5b) do not visually resemble the cocontinuous morphologies (Fig. 5c) common in the polymer blends literature, and indeed they may be stabilized by different mechanisms. Specifically, we pointed out that in analogous small-molecule systems, interfacial tension plays a destabilizing role in cocontinuous morphologies [18], i.e. induces coarsening or breakdown into a dispersed phase microstructure. In contrast, capillary aggregate networks are either unaffected by interfacial tension, or (if the liquid-liquid interface is concave) may even be stabilized by interfacial tension.

Examining Fig. 6, it appears that up to 20% particles, the regime of cocontinuity expands due to the addition of particles. More specifically, it is possible to retain continuity of PIB even when it is in a minority (e.g. the sample with a PIB:PEO:silica = 30:50:20 is cocontinuous even at 30% PIB). This trend of widening the range of cocontinuity is even more obvious if we exclude the red-circled points in Fig. 6 in which the PEO+particle phase is not robust enough to stay completely intact. However, the “right” edge of bicontinuity appears non-monotonic, i.e. at 30% particles, more PIB is needed to retain PIB phase continuity than at 20% particles. The reasons for this are not clear.

We note that the sequence of morphologies involved in phase inversion is quite different at low vs high particle fraction. Phase inversion is, by definition, a transition from a morphology in which PIB is the only continuous phase to one in which PEO is the only continuous phase. At low particle loading (lower three schematics in Fig. 6), phase inversion involves transitioning from a particles-in-drop morphology (PIB-continuous) to cocontinuous, and finally to the drops-in-suspension morphology (PEO-continuous). Qualitatively at least, the morphologies on the two sides of phase inversion are symmetric; both consist of roughly spherical drops of one phase in the other. This symmetry is lost at high particle loading because the particles-in-drops morphology does not exist (due to the presence of capillary aggregate networks). Instead the pendular/funicular aggregates are the only morphology that is PIB-continuous. Thus phase inversion proceeds as per the upper four schematics in Fig. 6: from the pendular/funicular aggregates (PIB-continuous), followed by capillary aggregate network and cocontinuous (both of which have two percolating phases), and finally to drops-in-suspension (PEO-continuous).

Figure 6. A classification of phase continuity on the ternary composition diagram. Schematic images of the four different morphologies at 30 vol% particles with particle-in-drops morphology at low particle loading are shown. [PIB: ■; PEO:□; Particles:●]
Conclusions

In summary, we have presented a comprehensive study of particle effects on the morphology of polymer blends. We show a rich diversity of morphologies, of which two are quite different from the morphologies appearing in binary polymer blends. The first is pendular aggregates in which particles are held together by menisci of the wetting polymer. The second is capillary aggregates comprising inclusions of the wetting polymer that have extremely high particle fillings. Such capillary aggregates can also join together into percolating networks – a morphology that is distinct from conventional cocontinuous microstructures.

While this paper was purely a study of composition-morphology relationships, it provides the basis for designing filled polymer blends for practical applications. For instance, applications that require a combination of good transport properties with mechanical robustness can be addressed by cocontinuous morphologies. Particles at a high loading can be employed to reinforce one phase and improve overall mechanical properties, or for instance, change the thermal or electrical conductivity of one phase using metal particles. This paper also serves as the basis for examining more complex situations, e.g. adding plate-like or rod-like particles. If such particles can also be engulfed by one phase, they would be able to induce solid-like behavior, and hence realize cocontinuous capillary aggregate networks, even at low particle loadings.

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References