Anomalous Phase Inversion in Polymer Blends Prepared by Cryogenic Mechanical Alloying

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Received July 5, 2000

Recent efforts have demonstrated that solid-state processing methods, such as cryogenic mechanical alloying (CMA)[1] and solid-state shear pulverization (S^3P),[2] offer alternative strategies for producing highly dispersed multicomponent polymer blends. By their very nature, these processes yield fine powders, which must be subsequently consolidated or melt-processed to form objects. While nanoscale dispersion of one polymer within the matrix of another has been achieved without compatibilizing agents in binary blends produced by CMA,[1] the morphological characteristics of such blends can be compromised when the blends are consolidated at elevated temperatures due to the inherent immiscibility of the polymers. If chemical coupling between molecules of one or more polymer species occurs during CMA, this shortcoming might be alleviated to a major extent, and unique blend morphologies might be preserved. In several of the CMA blends examined thus far, no evidence of chemical coupling between different polymer species has been observed, in which case phase coarsening typically ensues during consolidation. In this work, we report on our observation of anomalous phase inversion in binary blends composed of poly(methyl methacrylate) (PMMA) and poly(ethylene-*alt*-propylene) (PEP) prepared by CMA and consolidated under quiescent conditions at temperatures above the glass transition temperature (T_g) of PMMA.

Since the entropy of mixing in polymer blends is often vanishingly small, polymer−polymer interactions tend to dominate the phase behavior of such blends, with the result being that most polymer pairs are immiscible.[3−6] Commonly observed morphologies generated during the course of phase separation in binary polymer blends include dispersed spheroidal or ellipsoidal domains of the minority component within a matrix of the majority component, as well as interpenetrating and bicontinuous networks.[7,8] Phase inversion occurs when the minority component becomes the continuous phase and the majority component is dispersed.[9] This phenomenon, which is generally observed under melt−shear conditions, normally depends on blend composition and the viscosities of the polymer components.[10−14] Adedeji et al.[15] have also shown that phase inversion can occur in compatibilized blends exhibiting exothermic interfacial mixing. In the absence of exothermic mixing, Jordhamo et al.[11] report that the tendency for a binary blend to undergo phase inversion can be predicted from the empirical expression $\eta_A\phi_B/\eta_B\phi_A = X$. Here, η_i and ϕ_i (i = A or B) represent the steady-shear viscosity and volume-fraction composition of component i. According to this relationship, phase A is continuous if $X < 1$, phase B is continuous if $X > 1$, and a co-continuous morphology develops when $X \sim 1$. In this work, phase inversion is observed in PMMA/PEP blends of fixed composition and relatively invariant viscosity ratio, prepared by CMA and consolidated at elevated temperatures.

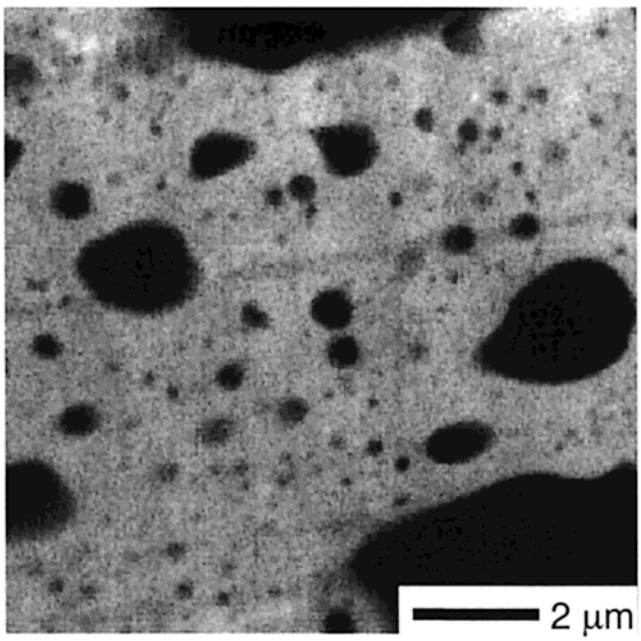

Figure 1. Representative NEXAFS image of a 75/25 PMMA/PEP blend cryomilled for 8 h and consolidated at 125 °C, revealing that the PEP forms discrete domains within the continuous PMMA matrix. The image was acquired at 288.0 eV (PEP appears dark relative to PMMA).

Details regarding the PMMA and PEP homopolymers employed in this study have been provided earlier[1] and are not reproduced here. Blends composed of 75/25 w/w PMMA/PEP were prepared by adding predetermined quantities of the homopolymers, as well as steel ball bearings (10/1 w/w bearings/polymer), to a steel vial that was inserted in a SPEX 8000 mill configured to operate at ca. −180 °C. The mill and its operation at cryogenic temperatures are discussed elsewhere.[1] After cryomilling was performed for a time t_m, the resultant powders were inserted into a mold capable of holding 12 specimens and annealed above the T_g of PMMA under specified conditions in a Carver press. Annealing was conducted under quiescent conditions, and two series of blends were prepared for investigation. Powders were annealed for 15 min at temperatures ranging from 150 to 200 °C in the first series. Those in the second series were annealed at 150 °C for times (t_a) up to 1 h. The annealed samples were quenched to ambient temperature in water and subsequently sectioned at −100 °C to produce specimens for near-edge X-ray absorption fine structure (NEXAFS) microscopy. General details

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10.1021/ma001151p CCC: $20.00
Published on Web 02/16/2001

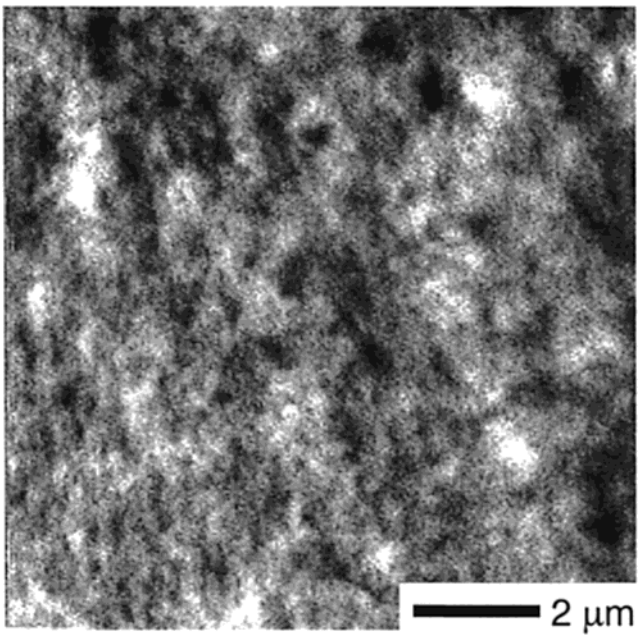

Figure 2. NEXAFS image of the 75/25 PMMA/PEP blend cryomilled for 10 h and consolidated at ambient temperature, demonstrating the "as-milled" morphology of the blend under these conditions.

and advantages of NEXAFS microscopy,[16,17] as well as its use in this work,[1] are provided elsewhere. Images were collected at a photon energy of 288.0 eV so that PEP appears dark relative to PMMA. Melt-shear viscosities of as-received and milled PMMA and PEP were measured as a function of shear rate at 150 °C with a Rheometrics Mechanical spectrometer (RMS-800).

After CMA and powder consolidation at elevated temperatures, the 75/25 PMMA/PEP blends generally exhibit clear signs of phase coarsening in which the PEP forms discrete macroscale dispersions within a PMMA matrix. Figure 1 displays a representative NEXAFS image acquired from such a blend that was subjected to CMA for 8 h and consolidated at 125 °C (just above the PMMA T_g after milling). Similar, and often more pronounced, phase coarsening is observed[1] in blends prepared by CMA at shorter t_m. As anticipated from polymer mobility considerations,[18] the rate at which phase coarsening proceeds is strongly dependent on the consolidation temperature, increasing significantly with increasing temperature. If the blend displayed in Figure 1 is annealed at 200 °C, for example, discrete PEP domains measuring in the 100 μm range develop.[1]

The morphology of the 75/25 PMMA/PEP blend cryomilled for 10 h and consolidated at 25 °C (far below the PMMA T_g) and 780 MPa is presented in Figure 2. This image resembles previous images of "as-milled" blends[1] and confirms that the PEP is reasonably well-dispersed within the PMMA matrix prior to consolidation. During quiescent consolidation at temperatures above the PMMA T_g, the blend morphology dramatically transforms. Figure 3 shows a series of NEXAFS images collected from blends cryomilled for 10 h and annealed for 15 min at three different temperatures (in °C): 150 (part a), 175 (part b), and 200 (part c). In Figure 3a, small discrete domains of PMMA, measuring on the order of 500 nm within a semicontinuous PEP matrix, identify the onset of phase inversion. As the temperature is increased to 175 °C (Figure 3b), the PMMA domains increase in size relative to those in Figure 3a, and begin to measure about 1−2 μm across. Further growth of the PMMA domains at 200 °C is evident in Figure 3c. Comparison of Figure 3c with images such as the one presented in Figure 1 reveals that the 75/25 PMMA/PEP blends subjected to CMA for 10 h respond to high-temperature annealing much differently than those cryomilled for up to 8 h.

To follow the kinetics of this surprising phenomenon, we next examine the second series of blends in which the consolidation temperature is 150 °C and t_a is systematically varied. The images provided in Figure 4 have been acquired from blends annealed for different t_a (in min)—1 (part a), 2 (part b), 5 (part c) and 30 (part d)—prior to quenching. Note that Figure 3a constitutes an intermediate blend in this series (t_a = 15 min). Close examination of the images in Figure 4 provides insight into the mechanism by which PEP evolves into the continuous phase after originating as discrete domains within PMMA. In Figure 4a, the PEP forms domains closely resembling those in Figure 1 after 1 min of annealing. Large PEP domains persist in the blend as t_a is increased to 2 min (Figure 4b), but the PMMA matrix appears to contain numerous small PEP elements. As t_a is increased to 5 min, the large PEP domains appear less distinct than those seen in previous images, and discrete PMMA domains similar to those seen in Figure 3a emerge. As t_a is increased further from 15 (Figure 3a) to 30 (Figure 4d) min, the PMMA domains become increasingly more distinct, the PEP domains appear to dissolve, and a continuous PEP matrix forms. Images of the blend at t_a = 60 min do not differ noticeably from Figure 4d and suggest that this

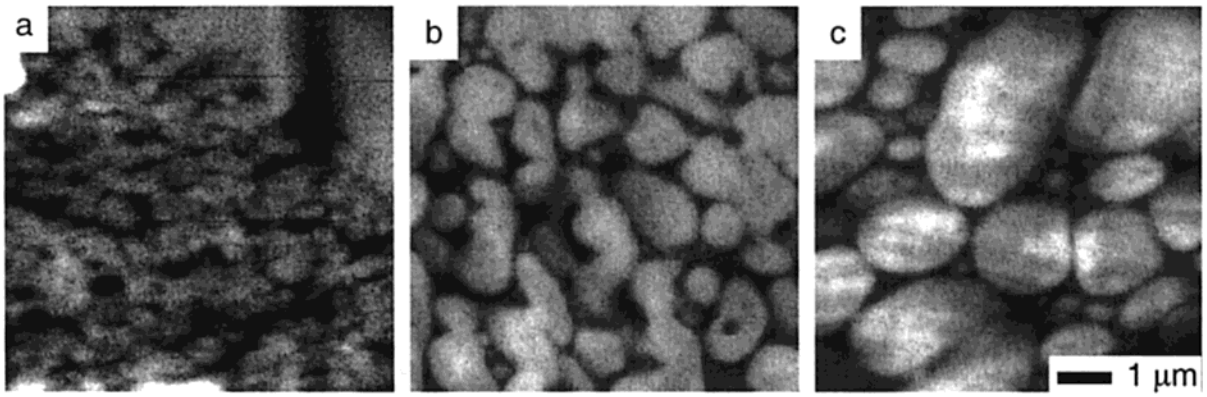

Figure 3. NEXAFS image of the 75/25 PMMA/PEP blend cryomilled for 10 h and annealed for 15 min at different consolidation temperatures (in °C): (a) 150, (b) 175, and (c) 200. As before, PMMA appears light relative to PEP.

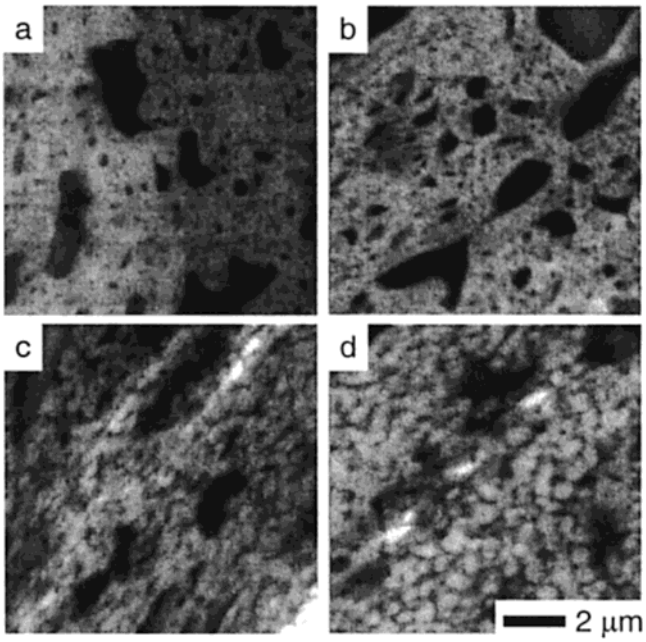

Figure 4. NEXAFS images of the 75/25 PMMA/PEP blend cryomilled for 10 h and annealed at 150 °C for different t_a (in min): (a) 1, (b) 2, (c) 5, and (d) 30.

phase inversion attains limiting behavior at a given temperature and may somehow be related to viscoelastic effects.[19]

As mentioned earlier, phase inversion is generally associated with blend composition and viscosity contrast. Since the blend composition is invariant in this study, the only other known driving force for phase inversion is the steady-shear viscosity ratio. Values of η_{PMMA}/η_{PEP} evaluated at 150 °C and a shear rate of 10^{-2} s^{-1} for PMMA and PEP as-received and after $t_m = 10$ h are about 100 and 130, respectively. On the basis of the relationship provided earlier, PEP is predicted to constitute the continuous phase in the blends examined here. It must be recognized, however, that the expression proposed by Jordhamo et al.[11] is only considered valid for viscosity ratios between 0.25 and 4 and may be inapplicable with regard to the present blends. The quiescent phase inversion observed in Figures 3 and 4 is only observed (in the absence of shear) after the blends are subjected to an extended period of CMA, and is most likely related to the accompanying CMA-induced change in molecular weight distribution of the constituent homopolymers. While the molecular driving force responsible for this phenomenon is not yet known and warrants further investigation, this result provides evidence that solid-state processes such as CMA may yield polymer blends with unexpected morphologies and properties.

Acknowledgment. X-ray microscopy data were collected using the Stony Brook NEXAFS microscope developed with financial support from the U.S. DOE (DE-FG02-89ER60858) and NSF (DBI-960-5045). Support for A.P.S. and H.A. has been provided by NSF NYI award (DMR-945-8060). We thank Dr. B.-S. Chiou for technical assistance.

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MA001151P