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Polymer Blend Compatibilization by Gradient Copolymer Addition during Melt Processing: Stabilization of Dispersed Phase to Static Coarsening

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Introduction. It has long been appreciated that blending of immiscible polymers can allow for synergistic tunability of material properties.[1−5] However, compatibilization of immiscible blends remains an academic and technological challenge. As optimal properties often rely on an average dispersed-phase diameter less than several microns, the stabilization of the dispersed phase domain size against coarsening, taken as the definition[6] of compatibilization, is key to processing immiscible blends. Many compatibilization strategies have been tested,[1] most involving methods that theoretically lead to a reduction in interfacial tension[7] and/or to steric hindrance against coalescence.[6] These strategies include the addition of premade block,[8−12] tapered block,[13] graft,[14] and random[15,16] copolymers during melt processing. The use of added block/graft copolymers has led to compatibilization in selected small-scale studies but has not been commercialized, due in part to the very low critical micelle concentration[5,17,18] (cmc) that prevents sufficient copolymer from reaching blend interfacial regions during melt processing. Random copolymer addition typically leads to encapsulation of the dispersed phase and thus does not lead to compatibilization even in small-scale studies.[15] A strategy that has seen some commercial success is reactive compatibilization, resulting in the in situ production of block or graft copolymer at the blend interfaces during melt processing.[1,19,20] Reactive processing by solid-state shear pulverization (SSSP) has also yielded compatibilization.[21−23]

The advent of nitroxide-mediated controlled radical polymerization[24] and atom-transfer radical polymerization[25] has led to the production of a new class of copolymer called gradient copolymers[26−33] that possess a gradual change in composition along the chain length. Gradient copolymers may also be made by ring-opening metathesis polymerization.[34] Theoretical studies[35,36] indicate that gradient copolymers dispersed in homopolymer have much higher cmcs and exhibit broader interfacial coverage than block copolymers of the same composition, suggesting that gradient copolymers may be effective blend compatibilizers. The simplicity of controlled radical polymerization also makes gradient copolymers attractive for academic studies and technological application.

Here we demonstrate for the first time that compatibilization of an immiscible blend can be achieved via the addition of gradient copolymer during melt processing. By comparing several blend systems in terms of the evolution of the number-average dispersed phase diameter, D_n, of melt mixed samples after static annealing, we show that coarsening can be eliminated or suppressed upon melt mixing by addition of gradient copolymer to the blend.

Experimental Section. Two polystyrene (PS) samples were used in this study: PSa (M_n = 26 600, M_w/M_n = 1.09, Pressure Chemical) and PSb (bimodal molecular weight distribution: M_{n1} = 36 900, M_{w1}/M_{n1} = 1.88, M_{n2} < 2000, Scientific Polymer Products). Poly(methyl methacrylate) (PMMA) (M_n = 16 200, M_w/M_n = 1.84, Scientific Polymer Products) and poly(*n*-butyl methacrylate) (PnBMA) (M_n = 97 700, M_w/M_n = 2.27, Aldrich) were the dispersed phases. Styrene (S), methyl methacrylate

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(MMA), and *n*-butyl methacrylate (nBMA) (Aldrich) were deinhibited with inhibitor remover (Aldrich) and dried over CaH_2. Gradient copolymers of S/MMA (SgradMMA) and S/nBMA (SgradnBMA) were made using alkoxyamine 29, 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane,[37] as unimolecular initiator.

Semibatch polymerization involved addition of MMA or nBMA to an initially all S reaction mixture, which was purged with N_2 for 30 min prior to polymerization. SgradMMA (M_n = 37 700, M_w/M_n = 1.63[38]) and SgradnBMA (M_n = 94 300, M_w/M_n = 1.47[38]) were obtained after 8 h at 93 °C and 5 h at 105 °C, respectively. Low conversion (<5%) S/MMA random copolymer (SranMMA) was synthesized by batch, bulk copolymerization at 80 °C for 15 min using AIBN (Aldrich) as initiator (M_n = 36 600, M_w/M_n = 1.90). (For details on copolymer synthesis and proof of the gradient structure of SgradMMA, see Supporting Information.) Copolymers were characterized after several cycles of dissolution/precipitation with tetrahydrofuran (THF)/methanol, followed by drying under vacuum at elevated temperature. Gel permeation chromatography (GPC) was used to determine the molecular weights (MWs) of all copolymers and PS samples relative to PS standards using THF as eluent (Waters Breeze instrument). The MWs of PMMA and PnBMA were measured using GPC and a universal calibration curve using appropriate Mark−Houwink parameters.[39,40] The styrene mole fraction (F_S) of each copolymer was obtained via ^{1}H NMR (Varian Inova 500 MHz spectrometer) spectroscopy with $CDCl_3$ as solvent: F_S = 0.59 for both SgradMMA and SranMMA and F_S = 0.79 for SgradnBMA.

Melt blend compositions were fixed at 80/20 wt % PS/PMMA and 85/15 wt % PS/PnBMA with a 5 wt % copolymer addition with respect to total weight (blend and copolymer). Samples (1 g) of each powdery mixture were melt processed in a cup-and-rotor mixer (Atlas Electronic Devices MiniMAX molder) for 10 min at 120 rpm rotor speed and with three steel balls in the cup to optimize mixing.[6] The blending temperature was set at 180 °C (PS/PMMA) or 165 °C (PS/PnBMA). Samples were removed by spatula and quenched in liquid N_2. Each sample was annealed at 180 °C by differential scanning calorimetry (Mettler-Toledo DSC 822e) with a N_2 atmosphere. All samples were fractured at room temperature and dipped into acetic acid (PS/PMMA) or 2-propanol (PS/PnBMA) to remove the dispersed phase. A 3 nm layer of gold was sputter-coated onto the sample surface, and the morphology was observed using a Hitachi S3500N scanning electron microscope with a 20 kV accelerating voltage. A total of 250−480 particles per sample were analyzed using Scion Image Beta 4.0.2 software to determine D_n.

Results and Discussion. Figure 1 shows the morphology of three PSa/PMMA blend systems before and after static annealing at 180 °C for 240 min. The 80/20 wt % PSa/PMMA blends (Figure 1a,b) and the 77/18/5 wt % PSa/PMMA/SranMMA blends (Figure 1c,d) coarsen substantially after annealing. The existence of nonspherical particles as well as the nonrandom distribution of particles in Figure 1c, which are absent in Figure 1d after coarsening, is consistent with the results on a similar PS/PMMA/SranMMA system by Lee et al.,[15] who reported particle encapsulation by SranMMA and rapid coalescence during annealing. Thus, although thin-film "sandwich" studies[41] indicate that placement of a S/MMA random copolymer at the interface of PS and PMMA films can reinforce the interface, random copolymer addition during melt processing of a polymer blend is not a viable compatibilization strategy. In contrast, the 77/18/5 wt % PSa/PMMA/SgradMMA blend (Figure 1e,f) exhibits both a much smaller $D_n(0)$ value, consistent with a reduced interfacial tension, and an absence of coarsening.

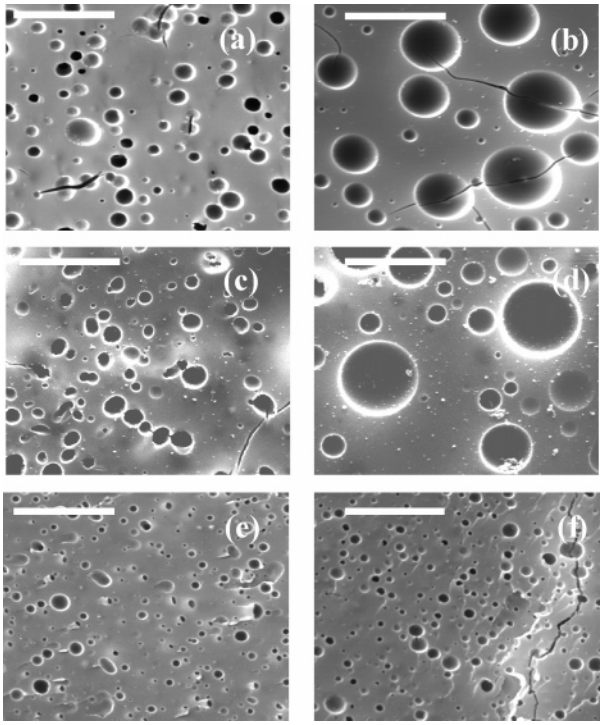

Figure 1. Scanning electron micrographs of PS/PMMA blend sets before and after annealing for 240 min at 180 °C: 80/20 wt % PSa/PMMA blend before (a) and after (b) annealing, 77/18/5 wt % PSa/PMMA/SranMMA blend before (c) and after (d) annealing, and 77/18/5 wt % PSa/PMMA/SgradMMA blend before (e) and after (f) annealing. Note: both SranMMA and SgradMMA are 59 mol % S and 41 mol % MMA. Size bar = 10 μm in all micrographs.

Whether coarsening occurs by coalescence and/or Ostwald ripening, the value of D_n is expected to depend on annealing time, t, as follows:[42−44]

$$D_n^3(t) = D_n^3(0) + Kt \qquad (1)$$

where K is the coarsening constant. Coarsening data for the blends systems in Figure 1 are plotted in Figure 2 according to this relationship. It is noteworthy that the 77/18/5 wt % PSa/PMMA/SranMMA blend shows a higher coarsening rate at the early stage of annealing than that of the 80/20 wt % PS/PMMA and then nearly levels off at a value of D_n^3 = 6.9 μm^3 (D_n = 1.9 μm). This effect is presumably due to an initially fast coalescence between the encapsulated PMMA particles followed by a slower coarsening in the presence of well-established SranMMA layers covering the coalesced particles.[15] In contrast, the 77/18/5 wt % PSa/PMMA/SgradMMA blend shows an invariance of domain size with annealing, with D_n in the range 0.60−0.65 μm. The conclusion that the blend containing the SgradMMA is fully compatibilized is reinforced by a comparison of K values: K = 0.020 μm^3/min for the 80/20 wt % PS/PMMA blend while K is reduced by more than 2 orders of magnitude in the blend containing the SgradMMA to a value of 0.00018 μm^3/min. The latter value may be taken to be zero within error.

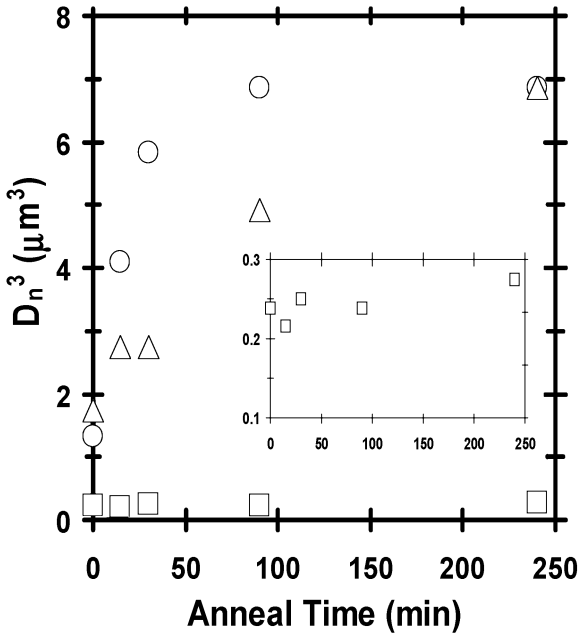

Figure 2. Effect of annealing time at 180 °C on D_n^3 for PS/PMMA blend sets shown in Figure 1: 80/20 PSa/PMMA blend (triangles), 77/18/5 PSa/PMMA/SranMMA blend (circles), and 77/18/5 PSa/PMMA/SgradMMA blend (squares). The inset is a magnification of the 77/18/5 wt % PSa/PMMA/SgradMMA blend results showing the absence of significant coarsening.

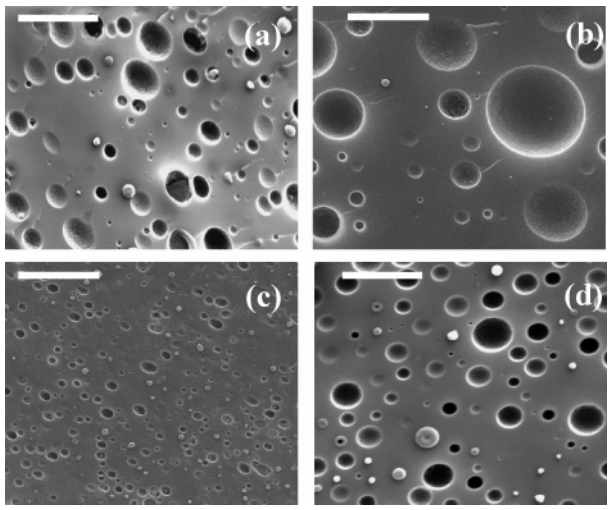

Figure 3. Scanning electron micrographs of PS/PnBMA blend sets before and after annealing for 240 min at 180 °C: 85/15 wt % PSb/PnBMA before (a) and after (b) annealing and 81/14/5 wt % PSb/PnBMA/SgradnBMA before (c) and after (d) annealing. Note: SgradnBMA is 79 mol % S and 21 mol % nBMA. Size bar = 10 μm in all micrographs.

Figures 3 and 4 compare the effects of static annealing at 180 °C and the presence of SgradnBMA on the initial morphology and coarsening characteristics of PSb/PnBMA blends. The value of $D_n(0)$ is reduced (0.81 μm vs 1.9 μm) in the blend containing the SgradnBMA, consistent with a reduction in interfacial tension. However, in contrast to the results in the PS/PMMA system given in Figures 1 and 2, only a substantial reduction rather than an elimination of coarsening is achieved upon addition of the SgradnBMA to the PSb/PnBMA system. (Although the data in Figure 4 do not fit very well to eq 1, determinations of K values reveal that $K = 0.22\ \mu m^3$/min for 85/15 wt % PSb/PnBMA blend while $K = 0.025\ \mu m^3$/min for the 81/14/5 wt % PSb/PnBMA/SgradnBMA blend.) This effect may be associated with two effects. First, as the SgradnBMA is 79 mol % S, it is significantly less likely to be located at the blend interface than in the case of the 59 mol % SgradMMA. Thus, there may be too little interfacial gradient copolymer to suppress coalescence in the PSb/PnBMA blend. Second, as compared to the 80/20 PSa/PMMA blend, the value of K is more than an order of magnitude greater in the PSb/PnBMA blend. Thus, the PSb/PnBMA blend is inherently much less compatible under the conditions of study than the PSa/PMMA blend.

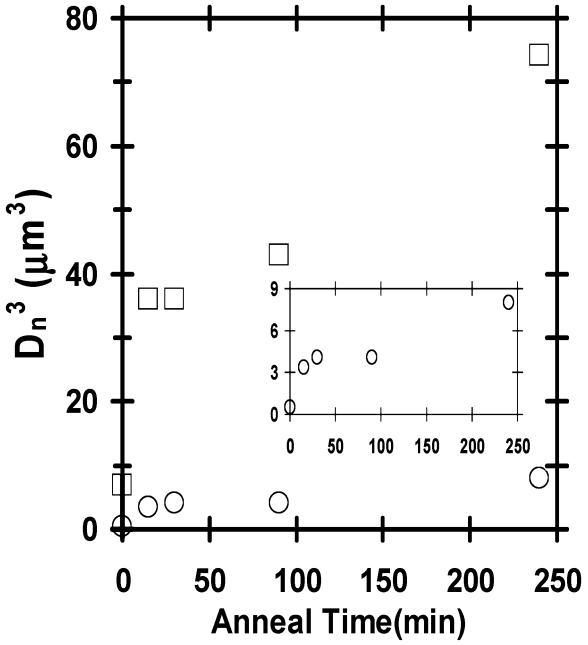

Figure 4. Effect of annealing time at 180 °C on D_n^3 for PS/PnBMA blend sets shown in Figure 3: 85/15 wt % PSb/PnBMA (squares) and 81/14/5 wt % PSb/PnBMA/SgradnBMA (circles). The inset is a magnification of 81/14/5 wt % PSb/PnBMA/SgradnBMA blend results.

This study has demonstrated that gradient copolymer addition is a viable strategy for compatibilization of melt-processed polymer blends. The results of this investigation strongly suggest that the success of this strategy depends significantly on the overall composition of the gradient copolymer as well as details regarding the inherent incompatibility of the blends. Study of the applicability of this compatibilization strategy to other immiscible blends, comparison of this strategy to approaches involving reactive compatibilization by interpolymer radical coupling via SSSP[21−23] or melt processing of blends containing polymers made by controlled radical polymerization,[45] and further syntheses and characterization of gradient copolymers in the bulk state, solutions, and blends are underway.

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Supporting Information Available: Experimental details on copolymer syntheses of SgradMMA, SranMMA, and SgradnBMA. This material is available free of charge via the Internet at http://pubs.acs.org.

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