Stabilization of Dispersed Phase to Static Coarsening: Polymer Blend Compatibilization via Solid-State Shear Pulverization

Andrew H. Lebovitz,[†] Klementina Khait,[†] and John M. Torkelson*,[†,‡]

Department of Chemical Engineering and Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208-3120

Introduction. Achieving compatibilization of immiscible polymer blends has been a long-standing academic and technological challenge.[1−5] Interest in compatibilization arises because synergistic properties may result when dispersed-phase particle sizes are maintained within a certain size range, usually on the order of 1 μm. As a result, a common definition for a compatibilized blend is one in which the average dispersed-phase domain size is stable to coarsening upon high-temperature annealing, also called static coarsening.[6]

The most commonly studied method for compatibilizing blends involves addition of premade block/graft copolymers[6−13] which may reduce interfacial tension at polymer−polymer interfaces[14] and provide steric hindrance to coalescence[6,15] during coarsening of the dispersed-phase structure that accompanies melt processing. This approach has severe limitations related to thermodynamics, kinetics, and availability. When added to blends, block copolymers typically phase separate into micelles with very low critical micelle concentrations,[16−18] leaving few copolymers free to migrate to interfaces, and that migration is slow because of the low diffusivity of copolymers in melts. Also, block copolymers appropriate for compatibilization are commercially available in few compositions, limiting the blends considered as practical targets for compatibilization. As a result, a recent review stated that "no polymer blend compatibilized by addition of low levels of premade block/graft copolymers has been commercialized."[1] A second approach has employed reactive compatibilization in which reactions between functionalized polymers yield interfacial block/graft copolymers. While compatibilization has been achieved by this method,[15,16,19−25] condensation-type functional-group reactions are chemically controlled rather than diffusion-controlled, leading to typically low reaction rate parameters at melt process conditions and limiting the application of this approach. The low reaction rates and necessity to modify addition-type polymers with functional groups have yielded a limited number of commercial, compatibilized blends made by this method.[2]

Here we demonstrate that immiscible blend compatibilization may be obtained via a novel, continuous process called solid-state shear pulverization.[26−29] By processing in the solid state rather than in the melt, pulverization eliminates the thermodynamic and kinetic stumbling blocks associated with conventional melt processing that often limit the efficiency and intimacy of mixing that can be achieved in immiscible polymer blends. In particular, we demonstrate for several immiscible blends that the number-average dispersed-phase diameter, D_n, of copulverized blends is stable to long-term, high-temperature annealing while coalescence of the dispersed phase is present during annealing of blends processed by twin-screw extrusion. The origin of the compatibilization achieved via pulverization, related to in-situ block copolymer formation, is also briefly discussed. (A complementary study has shown that interpolymer radical coupling leading to block copolymer formation can occur during pulverization of immiscible blends.[30,31])

Experimental Section. Two polystyrene (PS) samples were used as the matrix phase: PS101 (M_n = 101 000, M_w = 273 000, Aldrich) and PS106 (M_n = 106 000, M_w = 256 000, BASF PS158K). The dispersed phase was poly(methyl methacrylate) (PMMA) ($M_w \sim$ 120 000, Aldrich) or high-density polyethylene (HDPE) (Equistar Petrothene LM6007, melt flow index = 0.8 g/10 min). Blends (PS101/PMMA, PS106/HDPE) were copulverized using a Berstorff pulverizer operating at a screw speed of 200 rpm, with temperatures maintained below the melt or glass transitions of the components and one of two screw configurations (screw "A" and screw "B") that imposed varying degrees of shear/pressure to the materials. (Further information regarding pulverization, including description of equipment, is given in refs 26−29.) Blends were also produced via melt mixing using a Berstorff corotating twin-screw extruder (200 rpm, melt temperature of 215 °C).

Annealing of samples was done using Izod impact bars (0.32 cm thick) injected molded from powder made by pulverization or from pellets produced by melt mixing via twin-screw extrusion. Bars were fitted into a mold covered with aluminum foil and metal plates in a compression press maintained at 190 °C for 10, 60, 120, 240, or 480 min.[32] A Hitachi S3500N scanning electron microscope (SEM), with a 10 kV accelerating voltage, was used to observe blend morphology. SEM samples were prepared by fracturing the bars perpendicular to the flow direction; the fracture surface was coated with a 3.5 nm layer of gold (Cressington 208HR high-resolution coater) in order to minimize sample charging effects due to the electron beam. D_n was determined by characterizing 140−950 particles per sample using Scion Image Beta 4.0.2 image analysis software. Gel permeation chromatography (GPC), calibrated with monodisperse PS standards and tetrahydrofuran as solvent, was used to characterize molecular weight (MW).

Results and Discussion. Figure 1 compares the morphology observed for 90/10 wt % PS106/HDPE blends processed via twin-screw extrusion or pulverization and annealed at 190 °C for 0, 240, or 480 min. The unannealed, melt-mixed sample exhibits a fine dispersion of HDPE particles with D_n of 0.9 μm. However, there is a major increase in D_n with increasing annealing time. In contrast, with the PS106/HDPE blend made via pulverization using screw B, D_n remains stable to annealing at a value of 1.0−1.1 μm.

Figure 2 quantifies the impact of annealing on D_n in the 90/10 wt % PS106/HDPE blends. For the blend made

† Department of Chemical Engineering.
‡ Department of Materials Science and Engineering.
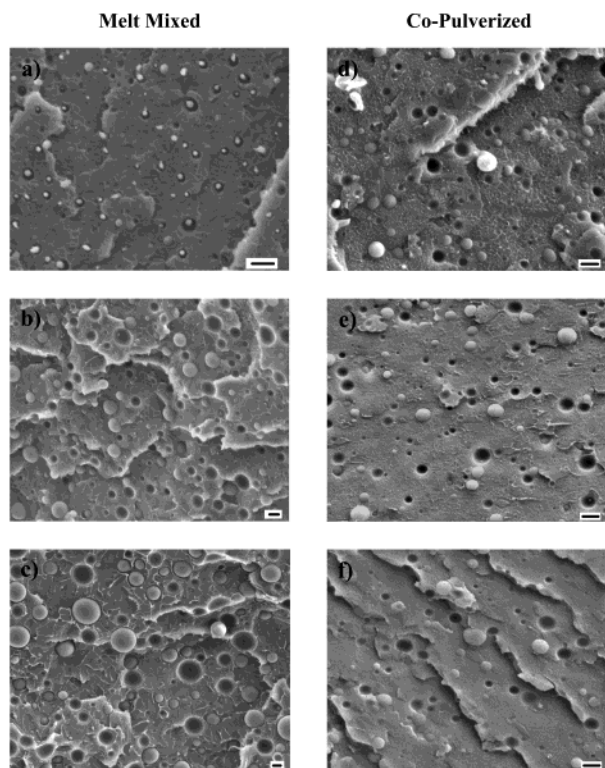* To whom correspondence should be addressed: e-mail j-torkelson@northwestern.edu.

Melt Mixed   **Co-Pulverized**

Figure 1. SEM comparison of a 90/10 wt % PS/HDPE blend prepared by melt mixing via twin-screw extrusion and annealed at 190 °C for (a) 0, (b) 240, and (c) 480 min with the same blend prepared by solid-state shear pulverization (screw B) and annealed at 190 °C for (d) 0, (e) 240, and (f) 480 min. Size bar = 3.0 μm in all micrographs. (Note: size bar is substantially reduced with annealing for melt-mixed blends but is invariant with annealing for copulverized blends.)
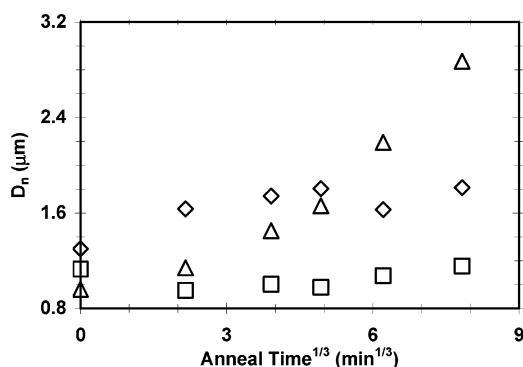

Figure 2. Effect of annealing time at 190 °C on D_n for a 90/10 wt % PS/HDPE blend prepared via ($\triangle$) melt mixing by twin-screw extrusion, ($\diamond$) pulverization (screw A), and ($\square$) pulverization (screw B).

by twin-screw extrusion, D_n grows from 0.9 to 2.9 μm after an 8 h anneal. The data between 60 and 480 min show D_n growing roughly as $t^{1/3}$, where t is annealing time, expected for coarsening by coalescence and/or Ostwald ripening.[33,34] At shorter annealing times, the growth rate is less than $t^{1/3}$, which may be due in part to the finite time needed to achieve a 190 °C temperature in the bars used in the annealing studies. (Thermocouple placement in the sample holder indicated that ~3 min is needed to achieve thermal equilibration.) In contrast, little or no coarsening was observed in the copulverized blends. For the blend made with screw A, at most only a small increase in D_n from ~1.3 to ~1.6 μm is observed in the first 10 min of annealing after
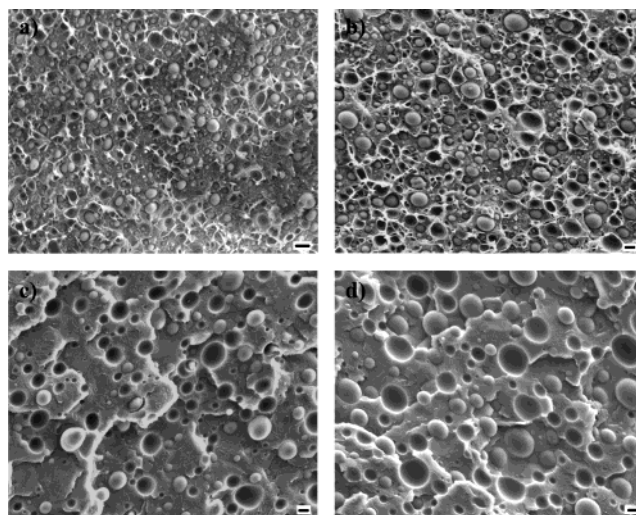

Figure 3. SEM comparison of a 70/30 wt % PS/PMMA copulverized blend that was annealed at 190 °C for (a) 0 and (b) 240 min and of an 80/20 wt % PS/HDPE copulverized blend that was annealed for 190 °C for (c) 0 and (d) 240 min. Size bar = 3.0 μm in each micrograph.

Table 1. Effect of Annealing Time on D_n for PS/PMMA and PS/HDPE Pulverized Blends

system	anneal time (min)	D_n (μm)
70/30 wt % PS/PMMA	0	1.8
	10	2.0
	60	2.1
	120	2.0
	240	2.0
80/20 wt % PS/HDPE	0	3.8
	10	3.5
	60	3.9
	120	3.8
	240	3.6

which there is little or no growth in D_n. For the copulverized blend made using screw B (a higher shear screw design) the initial D_n value is slightly reduced compared with the sample made using screw A and remains constant at 1.0−1.1 μm at all annealing times, indicating achievement of a fully compatibilized blend.

Figure 3 and Table 1 provide details regarding the achievement of compatibilization via pulverization using higher dispersed-phase content blends: 70/30 wt % PS101/PMMA (using screw A) and 80/20 wt % PS106/HDPE (using screw B). For both blends, D_n is essentially constant (maximum variation of ~15%) over a 4 h anneal at 190 °C.[35] The compatibilization shown in Figure 3 and quantified in Table 1[35] is not observed in blends produced by twin-screw extrusion in which D_n grows over a 4 h anneal by factors of 4.0 and 4.3 in the PS101/PMMA and PS106/HDPE blends, respectively. These results underscore the utility of pulverization in yielding compatibilization even at high dispersed-phase contents where fast coalescence rates may be otherwise expected. They also show that compatibilization can be achieved via pulverization over a range of D_n values; the pulverized 80/20 wt % PS106/HDPE blend has a D_n value almost a factor of 4 greater than the 90/10 wt % blend made with the same screw, but both systems are compatibilized.

Compatibilization of copulverized blends originates from in-situ block copolymer formation. While the blends studied here are not designed to prove in-situ block copolymer synthesis, another study[30] has been done on a moderate MW PS/very high MW PMMA

system with labels originally on the PS chains. After pulverization, labels were found via fluorescence-detection GPC to be attached to very high MW chains. This can occur via chain scission during pulverization followed by radical−radical combination leading to block copolymer formation at interfaces or in regions of interpolymer mixing. Chain scission, a prerequisite for in-situ block copolymer formation, was found in the PS106/HDPE pulverized blends. In the 80/20 wt % blend, copulverization with screw A (screw B) reduced the PS M_n and M_w by 20% (33%) and 38% (49%), respectively; in the 90/10 wt % blend, coppulverization with screw A (screw B) reduced the PS M_n and M_w by 33% (43%) and 46% (48%), respectively. Almost no scission occurred in extruded blends. (It must be noted that there was *no cross-linking* of PS in the pulverized PS/HDPE or PS/PMMA blends; pulverized PS blends from this and previous studies yield complete PS dissolution in appropriate solvents.[26,27,30,36−39] Thus, cross-linking of PS, which has been reported after exposure to radiation[40] or intense, batch mechanical milling,[41] cannot explain the stabilization of dispersed-phase domain size to static annealing observed in immiscible PS blends processed via solid-state shear pulverization.[42])

The very small growth in D_n achieved at short annealing time in the 90/10 wt % PS106/HDPE pulverized blend (Figure 2, screw A) and in the 70/30 wt % PS101/PMMA blend (Figure 3 and Table 1, screw A) may be rationalized to result from a small fraction of initial particles having insufficient interfacial block copolymer to be stable to coalescence.[35] Upon coalescence with another particle, the level of interfacial block copolymer may be sufficient to prevent further coalescence. This is consistent with comments by Macosko and co-workers,[6] who noted that compatibilization requires only that blend interfaces have enough copolymer to provide sufficient steric hindrance to prevent coalescence.

Besides investigating further how process parameters and blend composition affect the ability of solid-state shear pulverization to achieve blend compatibilization[36] via in-situ block copolymer formation,[30] the relative abilities of pulverization and twin-screw extrusion to achieve particular dispersed-phase domain sizes are also under study.[37,38] Comparison with other methods for achieving compatibilization via in-situ radical−radical recombination reactions yielding block copolymers, as may occur in sonication,[43,44] batch mechanical alloying,[41,45−48] and a novel process[49,50] using melt mixing of polymers made by nitroxide-mediated controlled radical polymerization, is underway.

References and Notes

(1) Koning, C.; Van Duin, M.; Pagnoulle, C.; Jerome, R. *Prog. Polym. Sci.* **1998**, *23*, 707.

(2) Majumder, B.; Paul, D. R. In *Polymer Blends*; Paul, D. R., Bucknell, C. B., Eds.; Wiley: New York, 2000; Vol. 1, p 539.

(3) Litmanovich, A. D.; Plate, N. A.; Kudryavtsev, Y. V. *Prog. Polym. Sci.* **2002**, *27*, 915.

(4) Molau, G. E. *J. Polym. Sci., Part A* **1965**, *3*, 4235.

(5) Willis, J. M.; Favis, B. D. *Polym. Eng. Sci.* **1988**, *28*, 1416.

(6) Macosko, C. W.; Guegan, P.; Khandpur, A. K.; Nakayama, A.; Marechal, P.; Inoue, T. *Macromolecules* **1996**, *29*, 5590.

(7) Sundararaj, U.; Macosko, C. W. *Macromolecules* **1995**, *28*, 2647.

(8) Ramic, A. J.; Stehlin, J. C.; Hudson, S. D.; Jamieson, A. M.; Manas-Zloczower, I. *Macromolecules* **2000**, *33*, 371.

(9) Eastwood, E. A.; Dadmun, M. D. *Macromolecules* **2002**, *35*, 5069.

(10) Milner, S. T.; Xi, H. W. *J. Rheol.* **1996**, *40*, 663.

(11) Thomas, S.; Prudhomme, R. E. *Polymer* **1992**, *33*, 4260.

(12) Wang, Y. B.; Hillmeyer, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2755.

(13) Creton, C.; Kramer, E. J.; Brown, H. R.; Hui, C. Y. *Adv. Polym. Sci.* **2002**, *156*, 53.

(14) Hu, W. C.; Koberstein, J. T.; Lingelser, J. P.; Gallot, Y. *Macromolecules* **1995**, *28*, 5209.

(15) Adedeji, A.; Lyu, S.; Macosko, C. W. *Macromolecules* **2001**, *34*, 8663.

(16) Maric, M.; Macosko, C. W. *J. Polym. Sci., Part B: Polym. Phys.* **2002**, *40*, 346.

(17) Major, M. D.; Torkelson, J. M.; Brearley, A. M. *Macromolecules* **1990**, *23*, 1711.

(18) Shull, K. R.; Kramer, E. J.; Hadziioannou, G.; Tang, W. *Macromolecules* **1990**, *23*, 4780.

(19) Scott, C. E.; Macosko, C. W. *Polymer* **1994**, *35*, 5422.

(20) Triacca, V. J.; Ziaee, S.; Barlow, J. W.; Keskkula, H.; Paul, D. R. *Polymer* **1991**, *32*, 1401.

(21) Yashin, V. V.; Spontak, R. J. *AIChE J.* **1998**, *44*, 416.

(22) Beck Tan, N. C.; Tai, S. W.; Briber, R. M. *Polymer* **1996**, *37*, 3509.

(23) Xanthos, M.; Dagli, S. S. *Polym. Eng. Sci.* **1991**, *31*, 929.

(24) Oyama, H. T.; Inoue, T. *Macromolecules* **2001**, *34*, 3331.

(25) Liu, N. C.; Xie, H. Q.; Baker, W. E. *Polymer* **1993**, *34*, 4680.

(26) Furgiuele, N.; Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Macromolecules* **2000**, *33*, 225.

(27) Furgiuele, N.; Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Polym. Eng. Sci.* **2000**, *40*, 1447.

(28) Ganglani, M.; Torkelson, J. M.; Carr, S. H.; Khait, K. *J. Appl. Polym. Sci.* **2001**, *80*, 671.

(29) Khait, K.; Torkelson, J. M. *Polym.-Plast. Technol. Eng.* **1999**, *38*, 445.

(30) Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Macromolecules*, in press.

(31) Low-to-moderate levels of chain scission accompanying pulverization lead to polymeric radical formation. Interpolymer radical coupling at interfacial regions or in regions of significant blend-component mixing can yield block copolymer. Repeated fragmentation and remixing of blend components enhance the likelihood of heteropolymer radical coupling during *solid-state* shear pulverization. For more details, see ref 30.

(32) Annealing conditions were selected in order to obtain substantial coarsening of noncompatibilized, melt-mixed blends, allowing for a definitive determination of compatibilization (stabilization of average dispersed-phase domain size to annealing) in pulverized blends. The annealing temperature of 190 °C was chosen in order to avoid degradation of polymer samples during long-term annealing. The 480 min time scale associated with the coarsening experiments both allowed for substantial coarsening of melt-mixed blends and was comparable to or less than annealing times found in many other published coarsening studies. Studies employing coarsening intervals of similar or longer times include the following: Andradi, L. N.; Hellmann, G. P. *Polym. Eng. Sci.* **1995**, *35*, 693. Park, D. W.; Roe, R. J. *Macromolecules* **1991**, *24*, 5324. Stachurski, Z. H.; Edward, G. H.; Yin, M.; Long, Y. *Macromolecules* **1996**, *29*, 2131. Yu, W.; Zhou, C.; Inoue, T. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 2378.

(33) Siggia, E. D. *Phys. Rev. A* **1979**, *20*, 595.

(34) Song, S. W.; Torkelson, J. M. *Macromolecules* **1994**, *27*, 6389.

(35) In the case of the 70/30 wt % PS101/PMMA blend, there was an ∼11% increase in D_n from the unannealed case to a sample annealed for 10 min, after which the value of D_n remained constant. The small increase in D_n at short annealing times is associated with a small fraction of dispersed-phase particles coalescing, leading to a few noticeably larger particles in the annealed samples. The standard deviation in particle size increased from 0.8 μm for the unannealed sample to 1.2−1.5 μm for samples annealed for time frames ranging from 10 to 480 min. The very limited, short-time coalescence may be understood to arise from a

small fraction of initial dispersed-phase particles having insufficient block copolymer at interfacial regions to prevent initial coalescence. However, after initial coalescence, leading to greater levels of block copolymer at the interfacial regions of a coalesced particle, further coalescence may be suppressed. It is noteworthy that the two systems that exhibited this very limited, short-time coalescence were both pulverized using screw A. The blends pulverized using a higher shear screw design (screw B) did not exhibit similar effects.

(36) Lebovitz, A. H.; Torkelson, J. M., manuscript in preparation.

(37) Lebovitz, A. H.; Torkelson, J. M. *Polym. Mater. Sci. Eng.* **2001**, *85*, 530.

(38) Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Polymer*, in press.

(39) Sol−gel analysis, done by placing polymer into solvent, can yield a good qualitative determination of the presence of cross-linked polymer. If a polymer is linear or branched but not cross-linked, it will dissolve in an appropriate solvent, e.g., tetrahydrofuran, in the case of PS. However, if the polymer is cross-linked, it will swell, forming a gel, rather than dissolve.

(40) Dawes, K.; Glover, L. C. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; AIP Press: New York, 1996; p 557.

(41) Smith, A. P.; Spontak, R. J.; Ade, H. *Polym. Degrad. Stab.* **2001**, *72*, 519.

(42) It should be noted that a previous pulverization study (ref 28) indicated indirectly via rheological characterization the presence of slightly enhanced branching, but no cross-linking, in a HDPE sample after solid-state shear pulverization. However, the level of enhanced branching was too low to characterize quantitatively and was insufficient to change the properties of the polyethylene from HDPE to LDPE.

(43) Kim, H.; Lee, J. W. *Polymer* **2002**, *43*, 2585.

(44) Lebovitz, A. H.; Chen, A. C.; Gray, M. K.; Torkelson, J. M., manuscript in preparation.

(45) Smith, A. P.; Ade, H.; Balik, C. M.; Koch, C. C.; Smith, S. D.; Spontak, R. J. *Macromolecules* **2000**, *33*, 2595.

(46) Chen, Z.; Wang, Q. *Polym. Int.* **2001**, *50*, 966.

(47) Font, J.; Muntasell, J.; Cesari, E. *Mater. Res. Bull.* **1999**, *34*, 2221.

(48) Cavalieri, F.; Padella, F.; Bourbonneux, S. *Polymer* **2002**, *43*, 1155.

(49) Gray, M. K.; Kinsinger, M. I.; Torkelson, J. M. *Polym. Prepr.* **2002**, *43* (2), 112.

(50) Gray, M. K.; Kinsinger, M. I.; Torkelson, J. M. *Macromolecules* **2002**, *35*, 8261.