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Communications to the Editor

Novel Strategy for Polymer Blend Compatibilization: Solid-State Shear Pulverization

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Polymer blend compatibilization has been studied for decades.[1−5] Industrial interest centers on creating blends with the combined properties of the components or less expensive blends by combining costly and inexpensive polymers with limited property reduction; academic interest focuses on the causes of the incompatibility of immiscible blends as well as compatibilization strategies. One strategy[1] involves the addition of premade block/graft copolymers, either to reduce interfacial tension or to provide steric effects hindering coalescence during coarsening of the dispersed-phase structure that accompanies melt processing.[6−12] This method has several problems, including those of thermodynamics (when mixed with homopolymers, block copolymers phase separate into micelles with a low critical micelle concentration, leaving few copolymers free to migrate to an interface), kinetics (copolymer diffusion through polymer to an interface is slow), synthesis (block/graft copolymers do not exist commercially for most blends of interest), and economics (block copolymers are costly). Thus, despite hundreds of related research studies,[13] reportedly no polymer blend compatibilized by addition of low levels of premade block/graft copolymers has been commercialized.[1] Another strategy[1] involves reactive compatibilization in which reactions between functionalized polymers yield block/graft copolymers at interfaces. Although some polymers, e.g. nylon, naturally contain functional groups at chain ends, most must be functionalized prior to reactive compatibilization. While compatibilization may be achieved in this manner,[10,14−18] slow reaction rates at melt processing conditions usually make this method impractical for use.[19−21]

Here we employ a novel method, solid-state shear pulverization (S^3P), to compatibilize a polypropylene (PP)/polystyrene (PS) blend without adding premade copolymers or conventional functional groups. S^3P is done at temperatures below the melt transition (semicrystalline polymers) or glass transition (amorphous polymers). Polymer pellets or flakes undergo compression and high shear/extensional conditions, resulting in fragmentation/fracture into a fine powder without melting.[22−24] (The compressive/shear forces in S^3P are not unlike those in mechanical alloying,[25−30] used for decades to intimately mix metals from immiscible components and to produce microstructures of nanometer-scale grain size.) Depending on S^3P conditions, chain scission may occur, yielding highly reactive free radicals at chain ends. Radical combination at interfaces and in highly mixed regions may yield block copolymers[31] like those achieved with reactive compatibilization during melt mixing of functionalized polymers.

S^3P was done with a Berstorff PT-25 pulverizer which is a modified twin-screw device (25 mm screw diameter, $L/D = 26$). Cooling coils surround the barrel to maintain low barrel temperature (0−10 °C). Feed rate, screw rpm, and shear/compression conditions may be controlled to optimize mixing and powder output. Typical conditions included a 300 rpm screw speed and feed rates giving average residence times of ~3 min. References 22 and 32 give details on the S^3P process. An Atlas Electric Devices Co. 4 cm^3 capacity Laboratory Mixing Molder ("mini-max mixer"[33]) and an injection molder were used for melt mixing.

Recycled PS and PP came from Maine Plastics (North Chicago, IL). PS was also made by free radical polym-

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Table 1. Effect of Pulverization on Molecular Weight (PS) or Melt Flow Rate (PP, g/10 min): Indications of Chain Scission

polymer	process condition	M_n	M_w	melt flow rate[a]
virgin PS	prior to pulverization	10 500	19 000	
virgin PS	post-pulverization	9 000	18 000	
recycled PS	prior to pulverization	110 000	205 000	
recycled PS	post-pulverization	58 000	78 000	
recycled PP	prior to pulverization			6.6 ± 0.3
recylced PP	post-pulverization (low shear)			6.9 ± 0.3
recycled PP	post-pulverization (high shear)			12 ± 2
recycled PP	prior to pulverization			37 ± 4
recycled PP	post-pulverization (low shear)			39 ± 2
recycled PP	post-pulverization (high shear)			67 ± 8
recycled PP	prior to pulverization			19 ± 1
recyceld PP	post-pulverization (high shear)			29 ± 1
recycled PP	prior to pulverization			0.53 ± 0.03
recycled PP	post-pulverization (high shear)			1.00 ± 0.08

[a] At 230 °C with a 2.16 kg load, following ASTM D-1238.

Table 2. T_g's of PS or PS-Rich Phase in PP/PS Blend

material	T_g (°C)	T_g (°C) after 2 h anneal at 190 °C
PS standard	100	
recycled PS	100	
PP/PS blend, injection molded	95	
PP/PS blend, mini-max mixed	93	100
PP/PS blend, pulverized	90	90
PP/PS blend, pulverized and injection molded	90	

Table 3. Percent Crytallinity of PP Homopolymer and PP in PP/PS (25/75 wt %) Blends Processed under Various Conditions

	% crystallinity		
material	before erasing thermal history[44]	after erasing thermal history[45]	after 2 h anneal at 190 °C[46]
PP homopolymer pre-pulverization	53 ± 3	53 ± 2	
PP homopolymer post-pulverization	48 ± 2	49 ± 2	
PP in injection molded blend		54 ± 3	
PP in mini-max mixed blend		39 ± 3	48 ± 2
PP in post-pulverized blend		29 ± 2	32 ± 3

erization. Differential scanning calorimetry (DSC, Perkin-Elmer DSC7) gave glass transition temperatures, T_g (10 °C/min heating rate, onset method), and percent crystallinity (heat of fusion of 100% crystalline PP = 165 J/g[34]). Characterization included melt flow rate (Kayness model 7050 melt indexer; ASTM D-1238), gel permeation chromatography (Waters 810; tetrahydrofuran), and scanning electron microscopy (SEM). SEM samples were cryogenically fractured in liquid N_2 as described in ref 35. Specimens were sputtered with a 40 nm layer of gold (Anatech Ltd. Hummer VII; Ar atmosphere). Micrographs are secondary electron images (JEOL JXA-840 scanning electron microscope; 5 kV accelerating voltage).

It was first necessary to gain a qualitative understanding of factors affecting chain scission during S^{3}P. Table 1 shows molecular weight (MW) averages or melt flow rates (which increase with decreasing MW) for homopolymers processed via S^{3}P and indicates that polymer type, MW, and shear conditions are key to scission. With low-shear S^{3}P, PS below its bulk entanglement MW (~31 000)[36] does not exhibit a significant reduction in MW and thereby experiences little scission. However, high-MW PS shows a major reduction in MW and hence substantial scission from S^{3}P. This suggests that while unentangled chains undergo "pullout" upon transformation of pellets or flakes into powder, entangled chains may undergo scission during S^{3}P. In contrast, with PP, high shear is needed for scission. At low shear conditions similar to those used for PS, PP melt flow rates are the same prior to and after S^{3}P. However, when PP is subjected to high shear, melt flow rate nearly doubles, indicating significant scission.

Thus, with high shear, PP and PS can be pulverized to yield chain scission and formation of free radicals that may serve as functional groups for reactive compatibilization.[31] This fact, combined with results of a study[32,37] showing that copulverization of blends of extreme viscosity ratio (and difficult to melt mix) leads to efficient mixing, indicates that S^{3}P may be used in reactive compatibilization. To test this, a model blend (25/75 wt %) of PP (melt flow rate of 19 g/10 min at 230 °C with a 2.16 kg load)/PS ($M_n = 110\ 000$) was studied, and the PP crystallinity and PS-rich phase T_g were analyzed. Given the difference in T_g of pure PP (~−15 °C) and pure PS (100 °C), mixing of low levels of PP into the PS-rich phase is evidenced by a reduction in T_g of the PS-rich phase relative to that of pure PS. Likewise, mixing of PS into the PP-rich phase (with the mixing of PP into the PS-rich phase) reduces PP crystallinity relative to that of pure PP.

T_g values are listed in Table 2. (See ref 38 for thermograms.) Virgin and recycled PS have T_g's of ~100 °C. Dry mixing the PP/PS blend followed by injection molding yields a PS-rich phase T_g of ~95 °C, with a broadening of the transition relative to homopolymer, indicating a small degree of mixing of PP into the PS-rich phase. Upon melt mixing with the mini-max mixer, the PS-rich phase has $T_g \sim 93$ °C, indicating somewhat better mixing. In the pulverized PP/PS blend, the PS-rich phase T_g is 90 °C, and the transition is broadened further than in the melt-mixed blends. The same behavior is observed for a PP/PS blend that is pulverized and then injection molded. The 10 °C reduction in T_g of the PS-rich phase relative to that of homopolymer shows that S^{3}P leads to more intimate mixing than melt processing.[39]

Table 3 gives PP crystallinity for various process conditions. Independent of S^{3}P, neat PP crystallinity is ~50%. This indicates that chain scission, which accompanies S^{3}P as shown by increases in melt flow rate, occurs predominantly in amorphous regions of semicrystalline polymers. Since S^{3}P does not alter neat PP crystallinity, the mixing achieved via S^{3}P may be monitored via crystallinity. The injection molded blend has a PP crystallinity of ~50%, suggesting little PP/PS mixing. In contrast, upon blending via the mini-max mixer the PP crystallinity reduces to ~40%, consistent with some mixing. In the pulverized blend, the PP crystallinity reduces to ~30%, indicating greater mixing.

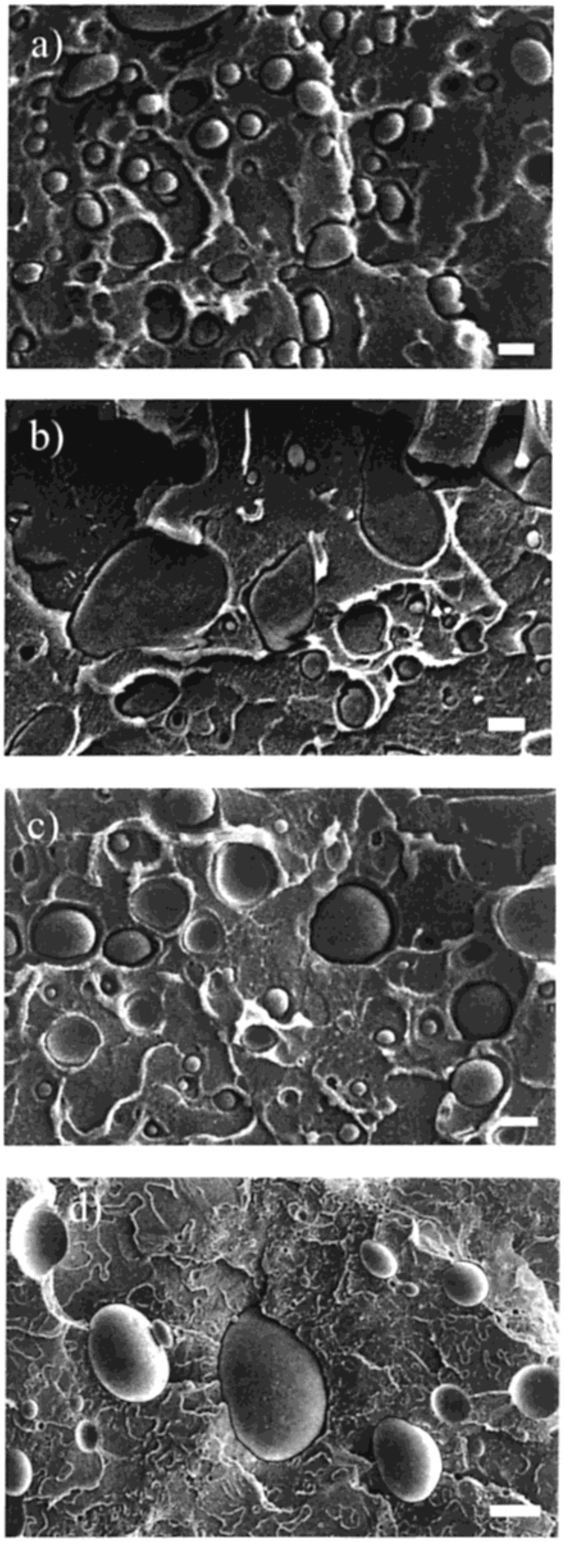

Figure 1. Scanning electron micrographs of a 25/75 wt % PP/PS blend after (a) S^3P processing[47] or (b) melt mixing. Note the generally smaller dispersed-phase diameters in the pulverized blend associated with more intimate mixing. After annealing the blends for 2 h at 190 °C, little coarsening is observed in the (c) pulverized blend while significant coarsening of dispersed-phase diameters is observed in the (d) melt-mixed blend. (Size bar = 1 μm for (a), (b), and (c); size bar = 10 μm in (d).)

Thermal analysis was also used to test compatibilization. If phase compositions achieved during S^3P are stable to annealing at temperatures high relative to the PP melt transition and PS T_g, this would be consistent with compatibilization. When the blend processed via the mini-max mixer is annealed at 190 °C for 2 h, the PS-rich phase T_g reverts to 100 °C and the PP crystallinity to ~50%. Thus, the annealing method is sufficient for the phases in a noncompatibilized blend to evolve to pure PS and PP compositions. In contrast, after annealing the pulverized blend the PS-rich phase T_g remains at 90 °C and the PP retains ~30% crystallinity, showing that phase compositions are stable; i.e., the blend is compatibilized.

While this proof-of-principle study shows that this process is capable of compatibilizing blends, much investigation is needed to understand and optimize this approach. Issues to be addressed more fully include the development of morphology in S^3P-processed blends relative to that in melt-processed systems. Figure 1 shows morphologies obtained in the S^3P-processed and melt-mixed PP/PS blends. Pulverization leads to PP dispersed-phase diameters often ~1 μm or smaller while considerably larger PP dispersed-phase diameters are seen in melt-mixed blends.[40] Consistent with the conclusion from T_g and crystallinity studies that compatibilization accompanies pulverization, the S^3P-processed blend exhibits little coarsening of dispersed-phase microstructure upon annealing as compared to the noncompatibilized, melt-mixed blend. Controlling blend morphology and compatibilization via the S^3P process and understanding the molecular-scale mechanisms behind the compatibilization will be key foci of future work. It will also be important to compare compatibilization and intimate mixing achieved in the continuous, short-residence time, near-ambient-temperature S^3P process with those attained via batch, cryogenic, mechanical alloying, such as ball milling studies of blends done at <-180 °C with duration up to 10 h.[41,42] Other studies, including characterization of block copolymer formed during S^3P, investigation of which blends may easily allow for compatibilization via S^3P, comparison of the applicability of S^3P to virgin blends versus commingled plastic waste (addressing rational design of polymeric resins as well as recycling[43]), and scale-up to a commercial-size, 60 mm diameter-screw S^3P device, are underway.

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References and Notes

(1) Koning, C.; Van Duin, M.; Pagnoulle, C.; Jerome, R. *Prog. Polym. Sci.* **1998**, *23*, 707.
(2) Paul, D. R. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. II, pp 35–62.
(3) Ajii, A.; Utracki, L. A. *Polym. Eng. Sci.* **1996**, *36*, 1574.
(4) Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1984**, *24*, 525.
(5) Xanthos, M. *Polym. Eng. Sci.* **1988**, *28*, 1392.
(6) Molau, G. E. *J. Polym. Sci., Part A* **1965**, *3*, 4235.
(7) Macosko, C. W.; Guegan, P.; Khandpur, A. K.; Nakayama, A.; Marachel, P.; Inoue, T. *Macromolecules* **1996**, *29*, 5590.
(8) Milner, S. T.; Xi, H. W. *J. Rheol.* **1996**, *40*, 663.
(9) Sundararaj, U.; Macosko, C. W. *Macromolecules* **1995**, *28*, 2647.
(10) Beck Tan, N. C.; Tai, S. W.; Briber, R. M. *Polymer* **1996**, *37*, 3509.
(11) Kim, J. R.; Jamieson, A. M.; Hudson, S. D.; Manis-Zloczower, I.; Ishida, H. *Macromolecules* **1998**, *31*, 5383.
(12) Jorzik, U.; Wolf, B. A. *Macromolecules* **1997**, *30*, 4713.

(13) According to www.webofscience.com, there are more than 600 articles published since 1987 in the refereed research literature with a combination of the keywords *poly* and *blend* and *copolymer*. Over 500 references are found under the same circumstances using the keyword *compatibilization*.
(14) Scott, C. E.; Macosko, C. W. *Polym. Eng. Sci.* **1995**, *35*, 1938.
(15) Wildes, G.; Kesskula, H.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 71.
(16) Yashin, V. V.; Spontak, R. J. *AIChE J.* **1998**, *44*, 416.
(17) O'Shaughnessy, B.; Sawhney, U. *Macromolecules* **1996**, *29*, 7230.
(18) Legros, A.; Carreau, P. J.; Favis, B. D.; Michel, A. *Polymer* **1994**, *35*, 758.
(19) Scott, C. E.; Macosko, C. W. *Polymer* **1994**, *35*, 5422.
(20) Scott, C. E.; Macosko, C. W. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 205.
(21) Oromehie, A. R.; Hashemi, S. A.; Meldrun, I. G.; Waters, D. N. *Polym. Int.* **1997**, *42*, 117.
(22) Wolfson, S. A.; Khait, K.; Dienst, M. *Mod. Plast.* **1994**, *71*, 63.
(23) Khait, K.; Torkelson, J. M. *Polym.-Plast. Technol. Eng.* **1999**, *38*, 445.
(24) Ahn, D. C.; Khait, K.; Petrich, M. A. *J. Appl. Polym. Sci.* **1995**, *55*, 1431.
(25) Suryanarayana, C.; Froes, F. H. *Adv. Mater.* **1993**, *5*, 96.
(26) Benjamin, J. S. *Metall. Trans.* **1970**, *1*, 2943.
(27) Gilman, P. S.; Benjamin, J. S. *Annu. Rev. Mater. Sci.* **1983**, *13*, 279.
(28) Gaffet, E.; Abdellaoui, M.; Malhouroux-Gaffet, N. *Mater. Trans., JIM* **1995**, *36*, 198.
(29) Koch, C. C. *Mater. Sci. Eng. A* **1998**, *244*, 39.
(30) Koch, C. C. *Annu. Rev. Mater. Sci.* **1989**, *19*, 121.
(31) In a recent compatibilization study, production of block copolymers has been inferred to occur via reaction of polymeric free radicals formed from chain scission due to high-intensity ultrasonication of dilute solutions of polystyrene with other polymers. See: Price, G. J.; West, P. J. *Polymer* **1996**, *37*, 3975.
(32) Furgiuele, N.; Lebovitz, A. H.; Khait, K.; Torkelson, J. M. *Polym. Eng. Sci.*, submitted.
(33) Orr, C. A.; Adedeji, A.; Hirao, A.; Bates, F. S.; Macosko, C. W. *Macromolecules* **1997**, *30*, 1243.
(34) Lieberman, R. B.; Barbe, P. C. In *Encyclopedia of Polymer Science and Engineering;* Mark, H. F., Menges, G., Bikales, N. M., Overberger, C. G., Kroschwitz, J. I., Eds.; Wiley: New York, 1985; Vol. 13, p 464.
(35) Gonzalez-Montiel, A.; Keskkula, H.; Paul, D. R. *Polymer* **1995**, *36*, 4621.
(36) Graessley, W. W. *Polymer* **1980**, *21*, 258.
(37) Furgiuele, N.; Khait, K.; Torkelson, J. M. *Polym. Mater. Sci. Eng.* **1999**, *81*, 125.
(38) Furgiuele, N.; Khait, K.; Torkelson, J. M. *ACS Div. Polym. Chem. Inc., Polym. Prepr.* **1999**, *40* (2), 752.
(39) Additional evidence of the efficient mixing of polymer blends afforded by S^3P is provided in refs 32 and 37 which discuss mixing polymers of extreme viscosity ratio; such systems cannot be mixed in any short-residence-time melt processing operation.
(40) 92/8 wt % PS/polyethylene (PE) blends of extreme viscosity ratio that were processed via S^3P have yielded some PE dispersed-phase diameters of 200−300 nm. See ref 32.
(41) Smith, A.; Spontak, R. J.; Ade, H.; Smith, S. D.; Koch, C. C. *Adv. Mater.* **1999**, *11*, 1277.
(42) Smith, A. P.; Bai, C.; Ade, H.; Spontak, R. J.; Balik, C. M.; Koch, C. C. *Macromol. Chem. Rapid Commun.* **1998**, *19*, 557.
(43) La Mantia, F. P. *Macromol. Symp.* **1998**, *135*, 157.
(44) To measure the percent crystallinity without erasing the thermal history, the sample was heated from 100 to 190 °C at a rate of 5 °C/min.
(45) Each sample had the same thermal history, achieved via the following temperature program: heat from 100 to 190 °C at 5 °C/min, hold at 190 °C for 1 min, cool from 190 to 100 °C at 5 °C/min, hold at 100 °C for 1 min, and heat from 100 to 190 °C at 5 °C/min. The percent crystallinity of the sample was measured using the final heating curve.
(46) To measure percent crystallinity after annealing, samples were held at 190 °C for 2 h, cooled from 190 to 100 °C at 5 °C/min, and heated from 100 to 190 °C at 5 °C/min.
(47) The pulverized powder was injection molded to form a piece that was then cut to size for evaluation by scanning electron microscopy.

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