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Compatibilizing effects of block copolymer mixed with immiscible polymer blends by solid-state shear pulverization: stabilizing the dispersed phase to static coarsening

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Abstract

A continuous, industrially scalable process called solid-state shear pulverization (SSSP) leads to compatibilization of polystyrene (PS)/high-density polyethylene (HDPE) blends by addition of a commercially available styrene/ethylene–butylene/styrene (SEBS) triblock copolymer. Partial or full compatibilization is characterized by a reduction or elimination of coarsening of the dispersed-phase domains during high-temperature (190 °C), static annealing. In the case of a 90/10 wt% PS/HDPE blend, processing with 3.5 wt% SEBS block copolymer by SSSP yields a coarsening rate that is reduced by a factor of 10 (six) relative to a melt-mixed blend without copolymer (with 3.5 wt% SEBS block copolymer). Addition of 5.0 wt% SEBS block copolymer to the 90/10 wt% PS/HDPE blend during SSSP yields a reduction in coarsening rate by a factor of thirty relative to a melt-mixed blend without copolymer. With an 80/20 wt% PS/HDPE blend, pulverization with 10 wt% SEBS block copolymer yields cessation of coarsening when the average dispersed-phase domain diameter reaches 1.6–1.7 μm. The implications of these results for developing a new, technologically attractive method for achieving compatibilization of immiscible polymer blends are discussed.

Keywords: Compatibilization; Blend; Block copolymer

1. Introduction

Blending of polymers is an attractive route to produce new polymeric materials. Compared to the development of a novel homopolymer via the synthesis of a new monomer, making blends of currently available homopolymers offers significant savings in time and cost, and the blend properties may be tuned by changing the composition [1–3]. This approach is complicated by the fact that polymer blends are generally thermodynamically immiscible [4]. Thus, a major goal in the field of polymer blends is the compatibilization of immiscible blends.

One definition of a compatibilized blend that relates to the thermodynamic nature of immiscible blends is that the dispersed phase is stabilized against coarsening during high temperature, static annealing [5]. A quantitative measure of the extent of compatibilization is provided by the coarsening rate constant, K, resulting from characterization of the coarsening of the number-average dispersed-phase particle diameter, D_n, as a function of annealing time, t:

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

Eq. (1) is based on theoretical expectations of coarsening involving coalescence and/or Ostwald ripening [6–8]. In the context of Eq. (1), the closer the blend is to being fully compatibilized, the closer the value of K will be to zero.

More than a dozen compatibilization strategies have been investigated, many without significant scientific or technological success [1–3]. One approach that has yielded some commercial success is reactive compatibilization in which a block or graft copolymer is formed in situ at the interfacial regions of the immiscible blend by reaction of condensation-type functional groups [9–13]. This strategy

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relies on block or graft copolymer at interfacial regions providing steric hindrance [5,14] to coalescence of the dispersed phase, often with a significant reduction in the interfacial tension [15]. Such an approach is not limited to step-growth polymers as long as the polymers are chemically modified with condensation-type functional groups. For example, reactive blending leading to compatibilization has been demonstrated in polystyrene (PS)/poly(methyl methacrylate) (PMMA) and PS/polyethylene (PE) blends, in some cases resulting in sub-micron dispersed phase particles at 20% dispersed-phase content [16,17]. Besides the need to modify addition-type polymers with condensation-type functional groups, this approach is also limited by the fact that most condensation reactions have very low reaction rate parameters [18] as they are chemically controlled (possess a significant activation barrier to reaction) rather than diffusion controlled (lack a significant activation barrier) [19].

Another compatibilization strategy is the addition of pre-made block or graft copolymer during melt mixing of immiscible blends [5,14,20–26]. This approach has both thermodynamic and kinetic limitations. At low copolymer concentration, melt mixing leads to most copolymers being wasted in micelles (block copolymers often have a very low critical micelle concentration in homopolymer [27]) instead of locating at the interface. Furthermore, the diffusion of free copolymers to the interface is slow. Thus, while there have been many studies of this approach, some yielding compatibilization in small scale mixing as with a MiniMax mixer [5,14], a review by Koning et al. [1] concluded that this strategy has not been commercially successful.

We have had recent success in demonstrating that a novel process called solid-state shear pulverization (SSSP) can be used to compatibilize PS/PMMA and PS/PE blends [28,29]. Unlike traditional melt mixing, SSSP is a mechanochemical method by which to blend polymers in the solid state [30–33] or to make well dispersed polymer nanocomposites [33,35]. The SSSP method has the advantages over other mechanochemical methods, such as cryogenic ball milling [36–38] and pan milling [39], of being a continuous process and possessing a wide range of process tunability. Additionally, in comparison to other mechanochemical methods, SSSP is a relatively mild process in that it neither significantly alters the molecular structure of crystallizable polymers such as HDPE or polypropylene [31,40,41] nor leads to extraordinarily large levels of chain scission [28–30,40,42], unlike cryogenic mechanical milling [43,44]. In particular, our earlier SSSP studies demonstrated that, within error, the value of the coarsening constant K was zero in appropriately pulverized blends that underwent subsequent static annealing [28] and that the compatibilization originated with the in situ formation of block copolymer [29]. The block copolymer resulted from coupling of polymer radicals that are formed from low levels of chain scission that can accompany SSSP [29].

Here we demonstrate even greater applicability of SSSP for blend compatibilization involving the co-pulverization of commercially available block copolymer with a polymer blend of interest. This new compatibilization strategy simplifies the method of compatibilizing blends via SSSP by neither requiring that certain levels of chain scission be achieved during SSSP nor requiring that SSSP yield minimum levels of block copolymer by interpolymer radical coupling. By using SSSP to mix the block copolymer with the blend, we also overcome the kinetic limitations (requiring free block copolymer to diffuse to interfacial regions during melt processing) and thermodynamic limitations (the very low critical micelle concentrations observed in the melt state for block copolymer in homopolymer) that limit the effectiveness of the melt mixing approach to achieve compatibilization.

2. Experimental

Polystyrene (BASF PS 158K, with $M_n = 106{,}000$ g/mol and $M_w = 256{,}000$ g/mol, as determined by gel permeation chromatography) was used as the blend matrix. High-density polyethylene (HDPE) (Equistar Petrothene LM6007, with melt flow index = 0.8 g/10 min) was used as the dispersed phase. A commercially available (Aldrich), styrene/ethylene–butylene/styrene (SEBS) triblock copolymer was used as the compatibilizing agent for the PS/HDPE blend. According to Aldrich, this triblock copolymer contains 28 wt% styrene units and has a value of $M_w = 118{,}000$ g/mol, suggesting that on average each styrene end block is ∼16,000–17,000 g/mol in molecular weight.

All blends (90/10 and 80/20 wt% PS/HDPE, with and without added copolymer) were processed by SSSP. Unlike some recently described single-screw pulverizers [45,46], the apparatus used in all SSSP studies employed here is a commercially available twin-screw pulverizer (Berstorff) which is essentially a modification of a twin-screw melt extruder. It should be noted that the SSSP process conditions employed in the current study differ from those employed in Ref. [28] in which in situ compatibilization of PS/HDPE blends (identical to those in terms of starting materials and compositions) was achieved without added copolymer. The pulverization conditions employed in the present study are ‘milder,’ e.g. the SSSP screw design has been adjusted to yield somewhat less chain scission than observed in Ref. [28]. Evidence of this comes from analysis by gel permeation chromatography of the molecular weight of the PS in the blend before and after pulverization. In the present study, in the case of the 90/10 wt% PS/HDPE blend, the PS M_n is reduced 33% by pulverization while in Ref. [28] there was a 43% reduction in PS M_n due to pulverization. (Chain scission leading to polymer radical formation during SSSP is a prerequisite for compatibilization originating with in situ block copolymer formation due to interpolymer radical coupling reactions at blend interfaces). For further information on the SSSP equipment and operating parameters, see Refs. [28–34]. Gel permeation chromatography (GPC) was done using equipment and procedures described in Ref. [29].

For comparative purposes, the blends without added copolymer were also made by twin-screw extrusion at 210 °C while two of the blends with added copolymer were also made by melt mixing but using a MiniMax mixer, also at 210 °C. Three steel balls were added to the MiniMax mixing cup in order to achieve optimal mixing [47].

In order to obtain samples for static annealing studies, the particulate product from the SSSP process was processed in a single-screw melt extruder. Static annealing was done using a differential scanning calorimeter (MettlerToledo 822e DSC) at 190 °C and annealing periods ranging from 10 to 480 min. A Hitachi S3500N scanning electron microscope was used to observe the morphology; the accelerating voltage was set at 10 kV to prevent charging problems. Microscopy samples were prepared by first cutting samples with a razor blend and then coating with a 3 nm gold layer using a Cressington 208HR high resolution coater. Number-average particle diameters were calculated using Scion Image Beta 4.0.2 image analysis software employing a minimum of several hundred particles per annealed sample.

3. Results and discussion

Fig. 1 shows the effects of 240 min of static annealing at 190 °C on the morphologies of two 90/10 wt% PS/HDPE blends that were made by melt mixing, in one case without added SEBS triblock copolymer and in another with 3.5 wt% SEBS triblock copolymer. In both cases, substantial coarsening of the dispersed phase is observed, indicating that the MiniMax melt mixing of the blend with added triblock copolymer is ineffective in providing more than weak stabilization against coarsening.

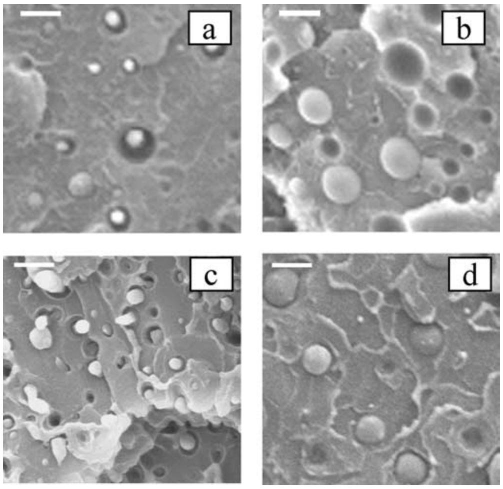

Fig. 1. Scanning electron micrographs of a 90/10 wt% PS/HDPE blend prepared by twin screw extrusion without addition of SEBS triblock copolymer and statically annealed at 190 °C for (a) 0 min and (b) 240 min. The same blend prepared by MiniMax mixing with 3.5 wt% SEBS triblock copolymer and statically annealed at 190 °C for (c) 0 min and (d) 240 min. Size bar = 2.0 μm in all micrographs.

Fig. 2 shows the effects of 240 min of static annealing at 190 °C on the morphologies of three 90/10 wt% PS/HDPE blends that were made by SSSP, in one case without added SEBS triblock copolymer and in the other cases with 3.5 and 5.0 wt% SEBS triblock copolymer, respectively. The initial values of the average HDPE particle diameters are similar in all three cases, ranging from 0.41 to 0.49 μm, which in turn are similar to the initial value of the average particle diameter in the blend that was melt mixed with 3.5 wt% added SEBS triblock copolymer (0.51 μm) (Table 1). Comparison of the morphologies of the three samples in Fig. 2 indicates that there is a significant trend toward stabilization of the dispersed phase particle size against coarsening with added SEBS triblock copolymer in the samples made by SSSP and that the trend is greater with greater triblock copolymer addition.

Fig. 3 plots the coarsening data for all six samples of the 90/10 wt% PS/HDPE blends investigated in this study. Within a reasonable level of error, most samples follow the trend expected from Eq. (1), with D_n^3 scaling linearly with annealing time. The coarsening rate decreases in the following order: melt mixed with no added SEBS copolymer, melt mixed with 3.5 wt% SEBS copolymer,

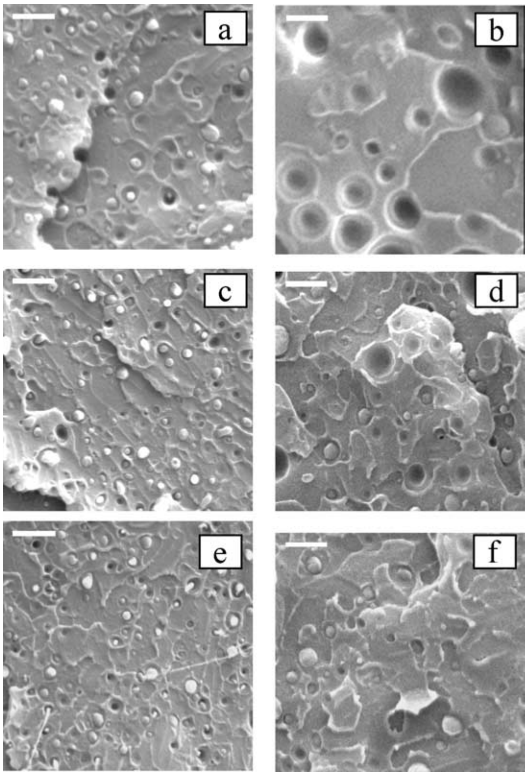

Fig. 2. Scanning electron micrographs of a 90/10 wt% PS/HDPE blend prepared by SSSP: without copolymer and statically annealed at 190 °C for (a) 0 min and (b) 240 min; with 3.5 wt% SEBS triblock copolymer and statically annealed at 190 °C for (c) 0 min and (d) 240 min; with 5 wt% SEBS triblock copolymer and statically annealed at 190 °C for (e) 0 min and (f) 240 min. Size bar = 2.0 μm in all micrographs.

Table 1
Initial average dispersed-phase particle diameter and coarsening constant (static annealing at 190 °C over 480 min) of 90/10 and 80/20 wt% PS/HDPE blends as a function of mixing process and added SEBS triblock copolymer

PS/HDPE	Addition of SEBS	$D_n(0)$[a] (μm)	Coarsening constant K (μm^3/min)	Correlation coefficient r[b]
90/10	Twin screw, 0%	0.82 ± 0.03	0.037	0.998
90/10	MiniMax, 3.5%	0.51 ± 0.03	0.022	0.988
90/10	SSSP, 0%	0.49 ± 0.01	0.0081	0.876
90/10	SSSP, 2%	0.45 ± 0.01	0.0071	0.993
90/10	SSSP, 3.5%	0.42 ± 0.02	0.0039	0.972
90/10	SSSP, 5%	0.41 ± 0.02	0.0012	0.977
80/20	Twin screw, 0%	1.29 ± 0.04	0.90	0.986
80/20	MiniMax, 10%	0.82 ± 0.02	0.021	0.986
80/20	SSSP, 10%	0.42 ± 0.01	[c]	[c]

[a] Uncertainties in $D_n(0)$ values were calculated by randomly removing 20% of the particle diameters used in the determination of $D_n(0)$. The uncertainties include the range of calculated $D_n(0)$ values from three or four tries.

[b] While other studies that report values of coarsening constants generally do not provide correlation coefficients for those values, we note that the quality of our data is comparable to that found in Refs. [6,65–70].

[c] Sample essentially ceased coarsening at annealing times greater than 120 min.

SSSP with no added SEBS copolymer, and then SSSP with 2.0, 3.5, and 5.0 wt% added SEBS copolymer, respectively. Two other points are also noteworthy. First, the coarsening rate is much lower in the blend with no added copolymer processed by SSSP than in the blend with 3.5 wt% added copolymer processed in a MiniMax mixer. This difference may be due to the in situ production of a very small level of interfacial block or graft copolymer via SSSP in the blend lacking added block copolymer. (It is not possible in the present study to prove in situ block copolymer formation during SSSP using the approach described in Ref. [29] due to the fact that HDPE does not dissolve in any solvent that can be used via room-temperature GPC. However, the same physics associated with in situ block copolymer in Ref. [29] is applicable in the present study. Furthermore, there are measurable levels of chain scission during SSSP, a prerequisite for interpolymer radical coupling leading to block copolymer formation. Thus, we believe it is reasonable to suggest that a small level of in situ block copolymer formation is possible during SSSP of the systems considered in the present study). While the copolymer produced via SSSP is insufficient to yield a fully compatibilized blend, it may nevertheless provide a reduction in coarsening relative to a melt mixed blend in which no copolymer is produced in situ. Second, the coarsening rate for the blend with 5.0 wt% added SEBS copolymer processed by SSSP is nearly zero.

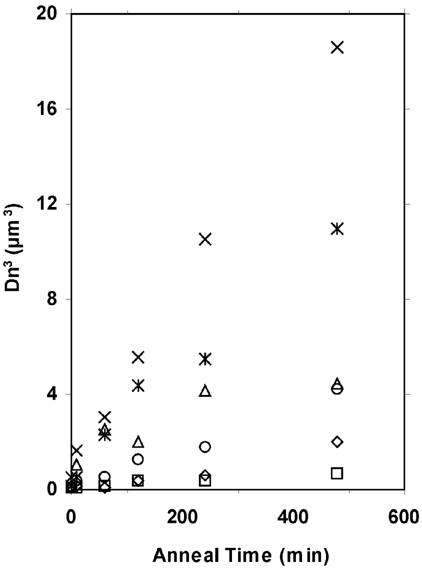

Fig. 3. Effect of static annealing time at 190 °C on D_n^3 for a 90/10 wt% PS/HDPE blend prepared via (×) twin screw extrusion without copolymer, (*) MiniMax with 3.5 wt% SEBS triblock copolymer, (△) SSSP without copolymer, (○) SSSP with 2 wt% SEBS triblock copolymer, (◇) SSSP with 3.5 wt% SEBS triblock copolymer, and (□) SSSP with 5 wt% SEBS triblock copolymer.

Table 1 provides a quantitative comparison of the initial dispersed-phase particle diameters and coarsening rate constants for the 90/10 wt% blend systems shown in Fig. 3. While there is substantial similarity among all the values of $D_n(0)$ except for the melt-mixed PS/HDPE blend without added SEBS triblock copolymer, which is somewhat larger than the other values, there are dramatic differences in the values of K obtained in the various 90/10 wt% blends. While addition of 3.5 wt% SEBS copolymer in the melt-mixed blend reduces the value of K by about one-third from 0.037 to 0.022 μm^3/min, this is a minor change in comparison to those observed in the various blends processed by SSSP. Even the blend made by SSSP without added copolymer exhibits a value of $K = 0.0081$ μm^3/min that is reduced by almost 80% relative to that of the melt-mixed blend without added copolymer.

The observation that the pulverized blend without added copolymer shows a greater trend toward compatibilization than the melt mixed blend with added copolymer is likely associated with the following: although the pulverization of this sample was not optimized to yield the required interfacial block copolymer for full compatibilization as was done in Ref. [28], the in situ production of even a very small amount of block copolymer in the blend made by SSSP can contribute substantially toward stabilization of the dispersed-phase domain size against coarsening. However, the addition of the SEBS triblock copolymer in the 90/10 wt% blend made by SSSP contributes to a quantitatively significant improvement in compatibilization. In the case of the blend made by SSSP with 3.5 wt% added SEBS copolymer, the value of K is reduced to 0.0039 μm^3/min. In the blend made by SSSP with 5.0 wt% added SEBS copolymer, the value of K is reduced further to

0.0012 μm^3/min, ∼3% of that of the blend made by melt mixing without any added copolymer. While it might be tempting to declare the blend made by SSSP with 5.0 wt% added copolymer to be fully compatibilized, a fairer statement would be to declare it nearly fully compatibilized, as there is a measurable difference in the values of D_n(0 min) (=0.41 μm) and D_n(480 min) (=0.88 μm). Nevertheless, this is the most dramatic suppression of coarsening that has been reported in the literature by addition of commercially available copolymer to a PS/HDPE blend.

Fig. 4 shows the effects of 240 min of static annealing at 190 °C on the morphologies of three 80/20 wt% PS/HDPE blends, one made by melt mixing without added SEBS copolymer, and the other two made with 10 wt% added SEBS copolymer but processed by different methods, either melt mixing or SSSP. The melt-mixed 80/20 wt% PS/HDPE blend without added copolymer shows tremendous coarsening, much more so than in the melt mixed 90/10 wt% blend without added copolymer. This effect is expected given that the larger concentration of dispersed phase particles in the blend with 20 wt% HDPE will lead to much higher rates of coalescence that relies on interparticle contacts occurring via Brownian motion. Both of the 80/20 wt% PS/HDPE blends with the 10 wt% added SEBS copolymer exhibit much less coarsening than the blend without added copolymer.

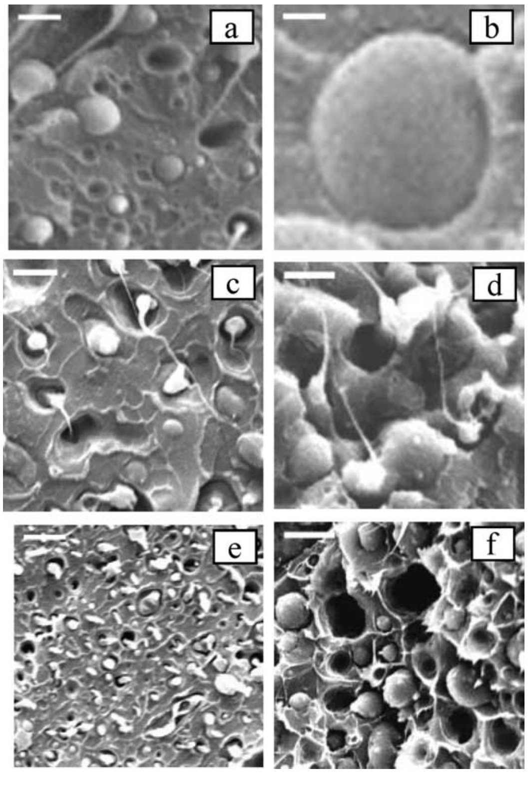

Fig. 4. Scanning electron micrographs of an 80/20 wt% PS/HDPE blend prepared via twin screw extrusion without copolymer and annealed at 190 °C for (a) 0 min and (b) 240 min, via MiniMax mixing with addition of 10 wt% SEBS triblock copolymer and annealed at 190 °C for (c) 0 min and (d) 240 min, via SSSP with addition of 10 wt% SEBS triblock copolymer and annealed at 190 °C for (e) 0 min and (f) 240 min. Size bar = 2.0 μm in all micrographs. (Note: due to the extremely high coarsening rate exhibited by the 80/20 wt% PS/HDPE prepared via twin screw extrusion without copolymer, coarsening data were taken for that sample using much lower magnification micrographs than that shown in (b) above).

Fig. 5 provides a quantitative comparison of the coarsening data for the three 80/20 wt% PS/HDPE blend systems. The data from the two samples made by melt mixing may be fit reasonably well to Eq. (1), although the blend with the 10 wt% added SEBS triblock copolymer must, because of its reduced coarsening, be plotted on a separate scale to reveal the approximate linearity of the data. The coarsening rate constants for these two samples are given in Table 1. The value of K increases by nearly a factor of 25 in the melt mixed 80/20 wt% blend ($K=0.90$ μm^3/min) compared to the 90/10 wt% blend ($K=0.037$ μm^3/min), both lacking copolymer. Interestingly, the coarsening rate constant in the melt-mixed 80/20 wt% blend with 10 wt% SEBS copolymer ($K=0.021$ μm^3/min) is reduced by more than a factor of 40 relative to the melt-mixed 80/20 wt% blend without copolymer and yet is nearly identical to that of the melt-mixed 90/10 wt% blend with 3.5 wt% added copolymer.

In contrast, the sample with the 10 wt% added SEBS triblock copolymer that was processed by SSSP shows initial growth in the dispersed-phase particle size with static annealing followed by stability in average particle size at 1.6–1.7 μm after 120 min static annealing. While the cause of this effect is not yet certain, it is possible to rationalize the effect as being associated with a level of interfacial block copolymer achieved during SSSP that upon initial static annealing is insufficient to yield a fully compatibilized

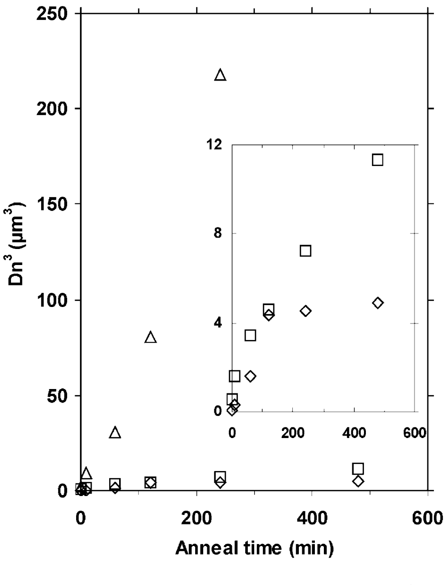

Fig. 5. Effect of static annealing time at 190 °C on D_n^3 for an 80/20 PS/HDPE prepared via (△) twin screw extrusion without copolymer, (□) MiniMax mixing with 10 wt% SEBS triblock copolymer, and (◇) SSSP with 10 wt% SEBS triblock copolymer.

blend. However, upon coalescence of dispersed-phase particles, there is an accompanying reduction in interfacial area while there may be little or no loss in interfacial copolymer. At a sufficient coverage of the interfacial regions by copolymer (at sufficient annealing time), there may be a cessation of coarsening due to steric hindrance effects from the interfacial copolymer.

The cessation of coarsening after about 120 min of static annealing indicates that the styrene end blocks in the added copolymer are of sufficient molecular weight (estimated to average ~16,000–17,000 g/mol) to allow for blend compatibilization via SSSP. Studies by Macosko and co-workers [5,11] indicate that the styrene block lengths in the SEBS block copolymer employed in the present study may be less than optimal for achieving blend compatibilization by steric hindrance effects. The very weak compatibilization effect observed in our melt-mixed blends with added block copolymer further supports this point. Thus, it is important to stress that the strategy of achieving blend compatibilization by block copolymer addition during SSSP is technologically attractive as it may be possible to employ a range of commercially available block copolymers that would have very limited compatibilization effects if added to a blend during melt processing.

The underlying cause for the later-stage cessation of coarsening observed in the 80/20 wt% PS/HDPE blend with 10 wt% SEBS copolymer but not in the 90/10 wt% PS/HDPE blend with 5 wt% SEBS copolymer is as yet unknown. However, it may be due to the lower ratio of copolymer to interfacial area in the 90/10 wt% PS/HDPE blend system naturally resulting in a lower interfacial coverage by copolymer. Further investigation will be needed to confirm this hypothesis.

We should also note that the chain scission that can accompany SSSP processing of polymer blends cannot by itself explain or contribute significantly to the substantial reduction in coarsening observed in the present study in the SSSP-processed samples relative to samples made by melt mixing. There are several reasons for this. Coarsening of these blends occurs by one or a combination of two mechanisms, coalescence and Ostwald ripening [6–8,48]. In the case of coalescence, the coarsening rate constant, K, is inversely proportional to matrix (PS) zero-shear-rate viscosity, η_0 [6,48]. In the current study, the PS matrix is of sufficiently high molecular weight, M, that it is entangled, meaning that $\eta_0 \sim M^{3.0-3.4}$ [49]. Thus, any reduction in M due to SSSP-induced chain scission would result in a major increase in K. In the case of Ostwald ripening, $K \sim D\gamma$ [6, 48]. Here D is the diffusion coefficient of the dispersed-phase polymer through the polymer matrix while γ is the interfacial tension. In the case of an entangled polymer system, $D \sim M^{-2.0-2.4}$ [50,51] while γ generally exhibits relatively little effect of molecular weight when entangled [15,52–54]. Hence, in the absence of other effects such as in situ block copolymer formation, any reduction in molecular weight due to SSSP-induced chain scission would lead to an enhanced K value based on Ostwald ripening. Thus, regardless of the coarsening mechanism, chain scission in the absence of other effects should lead to an increase in the coarsening rate, exactly the opposite of what is observed in the present study.

An intriguing but not fully understood result from the present study concerns the fact that 90/10 wt% PS/HDPE blend processed via SSSP resulted in substantially less coarsening than in either the melt-mixed 90/10 wt% PS/HDPE blend or the melt-mixed 90/10 wt% PS/HDPE with 3.5 wt% SEBS copolymer. Earlier we suggested that this result may be explained by a small level of in situ block copolymer formation accompanying the SSSP process. While we cannot unequivocally prove that copolymer was formed during SSSP of the 90/10 wt% PS/HDPE blend, we have done the following experiment that offers support for the suggestion that block copolymer was formed in situ. We added the product of the pulverized 90/10 wt% PS/HDPE blend to tetrahydrofuran (THF), allowing the separation of the soluble PS from the insoluble HDPE. The recovered, dried PS was added to virgin HDPE in a 90/10 ratio and melt mixed via a MiniMax. We then did static annealing studies and compared the results to those of the static annealing studies of the 90/10 wt% PS/HDPE blend made by twin-screw extrusion and the 90/10 wt% PS/HDPE blend made by SSSP. The data, shown in Fig. 6, reveal that the 90/10 wt% PS/HDPE blend made by MiniMax of PS (recovered from pulverized blend) with virgin HDPE had a K value of 0.041 μm^3/min (correlation coefficient $r = 0.999$), about 10% greater than that of 90/10 wt% PS/HDPE blend made by twin-screw extrusion and nearly a factor of five greater than that of the 90/10 wt% PS/HDPE blend made by SSSP.

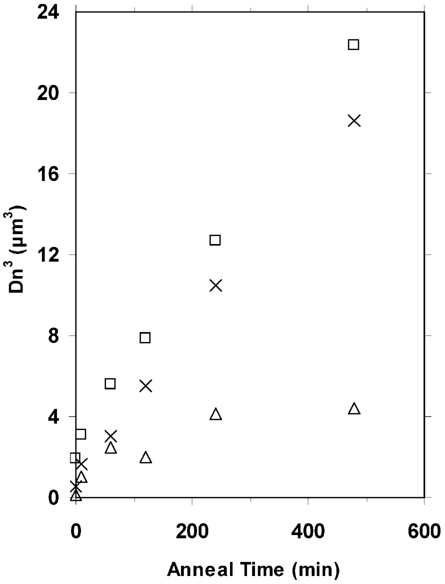

Fig. 6. Effect of static annealing time at 190 °C on D_n^3 for a 90/10 wt% PS/HDPE blend (without addition of SEBS triblock copolymer) prepared via (×) twin screw extrusion, (△) SSSP, and (□) MiniMax with PS (recovered from SSSP) and virgin HDPE.

If the melt-mixed blend made using the PS recovered from the pulverized blend contained no copolymer, we would expect that the coarsening rate would be much greater in that blend than in the 90/10 wt% PS/HDPE blend made from virgin polymer via twin-screw extrusion. That is because the M_n value of the pulverized PS is 33% lower than that of the virgin PS. Due to arguments cited above, when coarsening occurs by coalescence, such a reduction in matrix molecular weight should lead to an increase in coarsening rate by a factor of 3–4. In contrast, with coarsening by Ostwald ripening, a reduction in matrix molecular weight should yield little effect on coarsening rate as long as the matrix polymer remains entangled. Hence, unless only several percent of the coarsening is due to coalescence, an unlikely circumstance, the 10% enhancement in coarsening rate in the 90/10 wt% PS/HDPE blend made by MiniMax (of PS recovered from pulverized blend) with virgin HDPE relative to the 90/10 wt% PS/HDPE blend made by twin-screw extrusion is consistent with the presence of a very small level of copolymer in the former blend. During separation of the PS from the HDPE in THF, it would be possible for a very small amount of block/graft copolymer, possibly with a large block of PS and a shorter block/graft of HDPE, to be recovered with the PS. This very small level of block/graft copolymer could result in a reduced level of coarsening relative to the neat, virgin PS/HDPE blend made by melt mixing.

The factor of five difference in K values between the 90/10 wt% PS/HDPE blend made by MiniMax (of PS recovered from pulverized blend) with virgin HDPE and the 90/10 wt% PS/HDPE blend made by SSSP can be explained in only one way: the presence of much greater copolymer in the latter blend because much of the copolymer hypothesized to be made in situ in the pulverized blend was lost during the washing procedure to recover PS for the former blend. Any attempt to explain the effect based on molecular weight fails. The M_n values of the PS in the two blends are identical, meaning that (in the absence of in situ copolymer formation) the rates of coalescence in the two blends should also be identical. The molecular weight of the virgin HDPE in the former blend is expected to be somewhat greater (and surely is not less) than that of the latter blend, because low levels of chain scission would be expected during SSSP processing. In the absence of in situ block/graft copolymer formation during SSSP, this would mean that the latter blend made via SSSP should have a higher rate of Ostwald ripening, and thereby a higher overall rate of coarsening, than the former blend. However, this is exactly the opposite of what is observed in Fig. 6. This means that the only plausible explanation for the data shown in Fig. 6 is the formation of a low level of in situ block/graft copolymer formation during SSSP processing of PS/HDPE blends. While we do not have a reliable means to unequivocally prove this explanation to be correct by direct measurement of the presence of block/graft copolymer after SSSP, we can offer no other possible explanation for these results.

We should also note that any tendency for in situ block copolymer formation during SSSP of the blends in the current study is reduced upon addition of SEBS block copolymer. This is because the level of chain scission accompanying SSSP is significantly reduced upon addition of SEBS copolymer. This was demonstrated as follows. We added our pulverized 90/10 wt% PS/HDPE blend with 5 wt% SEBS and our pulverized 80/20 wt% PS/HDPE blend with 10 wt% SEBS to THF in order to remove the insoluble HDPE. After filtering out the HDPE, the two solutions were evaluated by GPC. We also prepared 90/5 parts by weight of PS/SEBS and 80/10 parts by weight PS/SEBS samples from virgin materials, dissolved those in THF, and evaluated those samples by GPC. Finally, we used GPC to evaluate our pure PS and our pure SEBS triblock copolymer. The PS and SEBS have peaks at dramatically different peak molecular weights, 251,000 and 107,000 g/mol (measured by GPC relative to PS standards in THF), respectively, and the SEBS is nearly monodisperse ($M_w/M_n = 1.07$) while the PS is polydisperse.

In both the 80/20 wt% PS/HDPE blend with 10 wt% SEBS and the 90/10 wt% PS/HDPE blend with 5 wt% SEBS, we found that SSSP led to a 16–18% reduction in M_n of the combined PS/SEBS evaluated by GPC. This compares to a 33% reduction of M_n of the PS resulting from SSSP of the 90/10 wt% PS/HDPE blend with no added SEBS. Hence, the presence of SEBS block copolymer significantly reduces the level of chain scission caused by SSSP. Furthermore, the location of both GPC peaks associated with PS and SEBS moved only very slightly toward lower molecular weight after pulverization, indicating that the observed level of chain scission in the blends is due to small levels chain scission of both the PS and SEBS. Given that the chain scission in the pulverized blends containing SEBS is roughly half that in the blends without SEBS, it is logical to conclude that any tendency for in situ block copolymer formation (caused by coupling of polymeric radicals formed by chain scission) would be reduced in the blends containing the added SEBS copolymer.

While a number of studies employing melt mixing have reportedly studied the effects of addition of commercially available SEBS triblock copolymer on the compatibilization of PS/HDPE blends [55–61], most often compatibilization in such studies is inferred from an improvement in mechanical properties, especially toughness, and/or a change in fracture mechanism [57–60] rather than from the stabilization of dispersed phase particle size. In one case, Bureau et al. [61] reported that the addition of Kraton G 1652 (an SEBS triblock copolymer with a styrene end block with a molecular weight of 7500 g/mol) to a PS/HDPE blend led to an emulsifying effect but did not result in minor phase stability. It might be argued that the lack of stabilization to coarsening in the study by Bureau et al. could be associated with the low molecular weight of the styrene end blocks, especially given the work by Macosko and co-workers [5,11] demonstrating that the block lengths in added diblock copolymers are critical to the achievement of stabilization against coarsening in polymer blends. However, the fact that our melt-mixed PS/HDPE blends with added SEBS copolymer (with longer styrene end blocks) did not yield blend compatibilization indicates that the inability of Bureau et al. to achieve compatibilization was due at least as much to the use of melt mixing as it was to choice of triblock copolymer.

Greater study of the ability to achieve compatibilization via a combination of added block copolymer and SSSP is warranted, especially regarding the optimal structure and minimum amount of the added copolymer required to obtain compatibilization. Similarly, investigation of the effect of various SSSP operating parameters, especially the screw design that is responsible for mixing during pulverization, on the ability to achieve compatibilization is warranted. The present study may be compared with another very recent study from our group demonstrating that the addition of gradient copolymers made by controlled radical polymerization combined with melt mixing of polymer blends [62] can lead to fully compatibilized blends as long as the copolymer has an appropriate gradient structure. Along with the recently proven compatibilization strategies of producing sufficient in situ block copolymer during SSSP [28,29] or twin-screw extrusion with ultrasonic treatment [63,64], our two new strategies involving the addition of block copolymer during SSSP or the addition of gradient copolymer during melt mixing [62] indicate that it may be possible to add significantly to the list of scientifically and commercially successful blend compatibilization methods.

4. Conclusions

A new method for achieving compatibilization of immiscible polymer blends has been demonstrated involving addition of commercially available triblock copolymer to blends undergoing processing via solid-state shear pulverization. Blend compatibilization was studied by observing the coarsening of dispersed-phase particles exposed to high-temperature, static annealing; the smaller the growth in average particle size with annealing, the greater the compatibilization effect. In the case of a 90/10 wt% PS/HDPE blend mixed via SSSP with 5 wt% added SEBS triblock copolymer, the coarsening constant was only 3% of that observed in a 90/10 wt% PS/HDPE blend made via melt mixing without copolymer. In the case of an 80/20 wt% PS/HDPE blend mixed via SSSP with 10 wt% SEBS triblock copolymer, coarsening ceased when the average dispersed-phase domain size was 1.6–1.7 μ. In contrast, much weaker compatibilization effects were observed when the strategy for compatibilization involved the addition of block copolymer during melt processing. The superior results achieved with SSSP are indicative of the fact that SSSP can overcome the kinetic and thermodynamic stumbling blocks that severely limit the applicability of adding block copolymer during melt processing as a strategy for blend compatibilization. Given that SSSP involves the use of a continuous, industrially scalable process that is a modification of equipment already widely used in polymer processing, the results of the present study indicate that there is some promise for the commercial application of a compatibilization strategy involving SSSP.

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