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Block copolymer compatibilization of cocontinuous polymer blends

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Abstract

The effect of block copolymers on the cocontinuous morphology of 50/50 (w/w) polystyrene (PS)/high density polyethylene (HDPE) blends was investigated using symmetric polystyrene–polyethylene block copolymers (PS–PE) with molecular weights varying from 6 to 200 kg/mol. The coarsening rate during annealing was compared to the Doi–Ohta theory. An intermediate molecular weight PS–PE, 40 kg/mol, showed remarkable results in reducing the phase size and stabilizing the blend morphology during annealing. Mixing small amounts of 6, 100 or 200 kg/mol PS–PE in the blend did not reduce the phase size significantly, but did decrease the coarsening rate during annealing. In stabilizing the morphology, 6 kg/mol PS–PE was inferior to 100 and 200 kg/mol. The existence of an optimal molecular weight block copolymer is due to a balance between the ability of the block copolymer to reach the interface and its relative stabilization effect at the interface.

Keywords: Copolymer; Cocontinuous; Polystyrene–polyethylene block copolymers

1. Introduction

The primary motivation for blending immiscible polymers is to create materials with combinations of properties superior to the components [1,2]. However, immiscible polymer blends have the disadvantage that they are not thermodynamically stable [3]. Therefore, post-mixing processing such as molding or annealing can dramatically affect the blend morphology. The change in morphology may reduce or eliminate the benefits achieved by blending. To address this challenge, the morphological stability of immiscible polymer blends is often improved by adding a block copolymer, pre-made or generated in situ by reaction, which preferentially locates at the polymer–polymer interface [4,5]. The addition of such compatibilizers can lead to more stable, finer scale morphologies by reducing the effective interfacial tension [6–10] and slowing phase coarsening [11–14].

Blending two immiscible polymers near 50/50 composition leads to a cocontinuous morphology. In addition to stabilizing this morphology, a goal of adding block copolymer to cocontinuous polymer blends is to expand the composition range of cocontinuity. Several studies have investigated the effect of block copolymer on the boundaries of the region of cocontinuity [15–19]. In each case, the addition of block copolymer caused the region of cocontinuity to narrow, contradictory to the desired results. This result is surprising because the addition of block copolymer is expected to reduce the effective interfacial tension and thereby promote the formation of elongated domains, making cocontinuous morphologies easier to generate. Previous research has shown that systems with low interfacial tension tend to form cocontinuous morphologies over a wider composition range than those with high interfacial tension [20,21]. One possible cause of the narrowing of the region of cocontinuity is the effect of block copolymer on the coalescence of domains. Lyu et al. have shown that the addition of block copolymer to polystyrene/polyethylene (PS/PE) blends reduces coalescence and stabilizes droplet morphologies [13]. These effects

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favor the formation of droplet morphologies over cocontinuous morphologies and may thus cause the region of cocontinuity to narrow.

The effect of block copolymers on the morphological stability of cocontinuous polymer blends during annealing has also been investigated [11,14,22–24]. Mekhilef et al. found that the addition of styrene–(ethylene-*co*-butene)–styrene (SEBS) triblock copolymer slowed the coarsening of cocontinuous morphologies in 50/50 PS/PE blends compared to neat blends [11]. Yuan and Favis investigated the effect of annealing on 50/50 and 60/40 PS/poly(L-lactide) (PLLA) blends [23,24]. The addition of PS–PLLA diblock copolymer slowed the domain growth compared to neat blends. Harrats et al. investigated the stabilizing effect of pure (PS–PE) and tapered (PS–PS/PE–PE) block copolymers on the morphology of 80/20 PS/PE blends [22]. The tapered block copolymer included a middle block that gradually changed composition from pure PS to pure PE. Although, the pure block copolymer retarded the coarsening of the morphology, the domains still showed some increase in size. The tapered block copolymer provided superior stabilization of the blend morphology compared to the pure block copolymer as evidenced by essentially no change in the morphology during annealing. The better performance of the tapered block copolymer was attributed to the gradual composition change in the middle of the polymer chains, which better matched the composition at the interface between the homopolymers. Harrats et al. also found that tapered block copolymers provided better stabilization during annealing than pure triblock copolymers [14]. The superior performance of tapered block copolymers compared to the triblock copolymers was attributed to the existence of fewer conformational constraints at the interface.

Although, there have been a number of studies of the effect of block copolymers on cocontinuous polymer blends, the effect of block copolymer molecular weight on the morphology has not been investigated. In this study, we investigated the effect of block copolymers of varying molecular weight on the morphology of 50/50 (w/w) PS/PE blends using SEM with image analysis. The morphology change during annealing was also studied. For the block copolymer observed to be the most efficient in compatibilization, we examined the effect of concentration of the block copolymer.

2. Experimental section

2.1. Materials

Key properties of the polymers used in these experiments are shown in Table 1. PS and HDPE (Dow 4452N, density = 0.95 g/cc) were supplied by the Dow Chemical Company. Viscosities of the homopolymers were measured using a parallel plate rheometer (ARES, Rheometric Scientific Inc.) at 170 °C. Symmetric PS–PE diblock copolymers with nominal molecular weights of 6, 40, 100 and 200 kg/mol (hereafter referred to as 6k, 40k, 100k and 200k PS–PE) were also used in these experiments. PS–PE block copolymers were prepared by first synthesizing polystyrene–polybutadiene block copolymers (PS–PBD) by anionic polymerization in cyclohexane at 40 °C. Under these conditions, the butadiene adds primarily in a 1, 4 fashion. Upon selective hydrogenation, a nearly linear polyethylene block is obtained. Details of the anionic polymerization and catalytic hydrogenation methods are described elsewhere [13,25–27]. The PS homopolymer and the PS part of the block copolymers are atactic.

2.2. Blend preparation

Blends were prepared by mixing the components in a Haake batch mixer (HBI System 90, Thermo Electron Co.) equipped with roller blades. Antioxidant (Irganox 1010, Ciba) was added at 0.2 wt% to the blends to reduce degradation. The blend composition was 50/50 (w/w) PS/PE. In the blends containing PS–PE diblock copolymers with different molecular weights, the loading was 1% by weight. To study the effect of block copolymer concentration, blends containing 0.1 and 0.3% 40k PS–PE were prepared. The materials were added simultaneously and mixed at 50 rpm (maximum shear rate = 48 s^{-1}) at a temperature of 170 °C for 10 min. The blends were then removed and quenched in liquid nitrogen within 1 min.

2.3. Annealing

After quenching the blends prepared in the mixer, several samples with ~2 mm thickness were annealed under quiescent conditions under a nitrogen atmosphere at 170 °C for various time intervals. These samples were quenched using liquid nitrogen to freeze the annealed morphology.

2.4. Scanning electron microscopy and image analysis

Samples were prepared for scanning electron microscopy (SEM, JEOL 6500) by cryo-microtomy at −120 °C using a glass knife to generate clean and flat surfaces. Contrast between the phases was achieved by immersing each sample in toluene for 2 min to remove the PS at the surface. The samples were then coated with 50 Å of platinum and imaged at 5 kV using SEM.

Since the size scale of the domains and depth of field in the micrographs made it difficult to accurately detect the interface using automated methods [28,29], the phase boundaries were manually traced for this analysis. The program Scion Image (Scion Corporation, Frederick, MD) was then used to determine the perimeter and area of the phase domains in each image. The total amount of interface perimeter per unit area in each image was calculated from

Table 1
Molecular weight and rheological data at 170 °C for blend components

Material	M_n (kg/mol)	M_w/M_n	η at 0.1 s^{-1} (Pa s)	η at 50 s^{-1} (Pa s)	η at 100 s^{-1} (Pa s)
PS	61	<1.1	3000	1800	1300
HDPE	18	5	3400	1300	1000
PS–PE 6k	3–3	<1.1			
PS–PE 40k	20–20	<1.1			
PS–PE 100k	50–50	<1.1			
PS–PE 200k	100–100	<1.1			

these results. For each set of conditions, between 5 and 15 images were analyzed to determine the average perimeter per unit area.

3. Results

SEM micrographs of 50/50 PS/PE blends without PS–PE diblock copolymer prepared at 50 rpm are shown in Fig. 1. The series of images shows the effect of annealing after the blends were mixed in the batch mixer. A dramatic change in the size scale of the blends is seen between the samples quenched after mixing and after 10 min of annealing. Further annealing of this blend causes additional coarsening of the blend morphology; however, the cocontinuous morphology is retained.

The effect of block copolymer on the morphology can be seen in Figs. 2 and 3. For ease of comparison of the block copolymers with different molecular weights, the magnification is kept constant at 1000× and 200× for Figs. 2 and 3, respectively. The addition of 1% 6k, 100k or 200k PS–PE did not have a substantial effect on the blend morphology after mixing compared to the blend with no PS–PE as shown in Fig. 2. However, the 40k PS–PE reduced the phase size significantly. A comparison of the morphologies after 15 min of annealing (Fig. 3) shows that all of the PS–PE block copolymers slowed the coarsening of the blend morphology during annealing. Based on the phase size, the 40k PS–PE is the most effective for suppressing coarsening, followed by the 100k PS–PE.

Fig. 4(a) shows the plot of perimeter per area versus time for the neat blend and the blends with 1% 40k PS–PE. Note that assuming the sample is isotropic, the perimeter per area is equal to interfacial area per unit volume, or the specific interfacial area, Q. The amount of interface in the blend with no PS–PE reduces rapidly from 0.22 to 0.03 μm^{-1} in 10 min. The morphology changes little after about 10 min of annealing. This behavior may result because the phase size approaches a size limit resulting in pinch-off or other mechanism, causing phase coarsening to slow. Blends

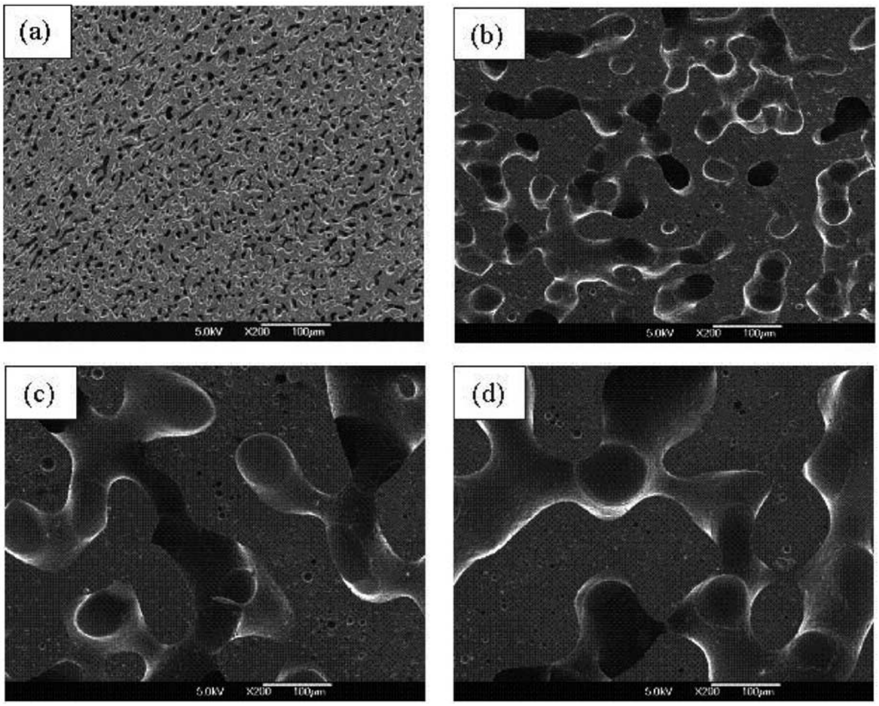

Fig. 1. SEM micrographs of neat 50/50 PS/PE blends after mixing at 50 rpm for 10 min at 170 °C followed by annealing for (a) 0 min, (b) 10 min, (c) 15 min and (d) 25 min at 170 °C. (Scale bar = 100 μm).

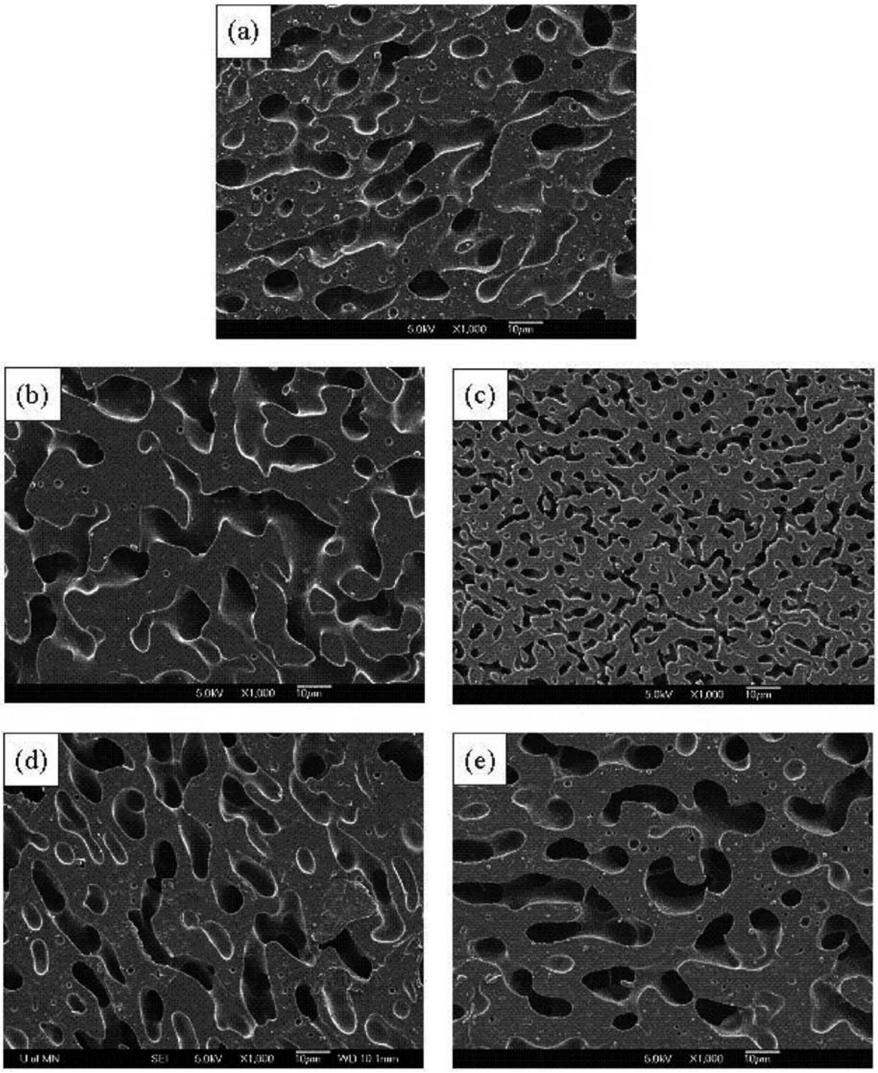

Fig. 2. SEM micrographs of 50/50 PS/PE blends with 1% PS–PE block copolymers after mixing at 50 rpm for 10 min at 170 °C: (a) no block copolymer, (b) 6k, (c) 40k, (d) 100k and (e) 200k PS–PE. (Scale bar $= 10$ μm).

containing 1% 40k PS–PE show an initial specific interfacial area twice that of the neat blend and the slowest change during annealing. The amount of interface is reduced by only about 25% after 55 min of annealing (Fig. 4(a)). For the blends with other block copolymers, the perimeter per area as a function of time is plotted in Fig. 4(a). For the blend with 1% 6k PS–PE, the change in the specific interfacial area is slower than the neat blend; however, after 30 min of annealing, the morphology of this blend closely resembles that of the neat blend. The 100k PS–PE shows an initial change similar to 6k PS–PE, but appears to stabilize the morphology at $Q \approx 0.09\ \mu\text{m}^{-1}$ after 4 min of annealing. The morphology of the blend with 200k PS–PE also shows the same initial change as that of the 6k and 100k PS–PE then stops coarsening after 9 min ($Q \approx 0.06\ \mu\text{m}^{-1}$).

The Doi–Ohta theory for complex interfaces can be adapted to annealing of cocontinuous polymer blends [30]. This theory was derived for a 50/50 (v/v) mixture of Newtonian fluids with equal viscosity. Vinckier and Laun used the Doi–Ohta theory to derive an equation for the coarsening rate of cocontinuous blends under quiescent conditions [31]:

$$\frac{1}{Q} = \frac{1}{Q_0} + c_1 \frac{\Gamma}{\eta} t \tag{1}$$

where Q_0 is the specific interfacial area at zero annealing time, c_1 is a kinetic constant for size relaxation, Γ is the interfacial tension, η is the viscosity (3000 Pa s for this blend). This equation was used to fit the experimental data to obtain $c_1\Gamma/\eta$, which represents the coarsening rate.

Fig. 5 is a plot of $1/Q$ versus time for blends without PS–PE and blends with 1% PS–PE of various molecular weights. With the exception of the blend with 40k PS–PE, $1/Q_0$ values are in the range of 5–6 μm. The blend with 40k PS–PE has a $1/Q_0$ of 2 μm, indicating its superior reduction

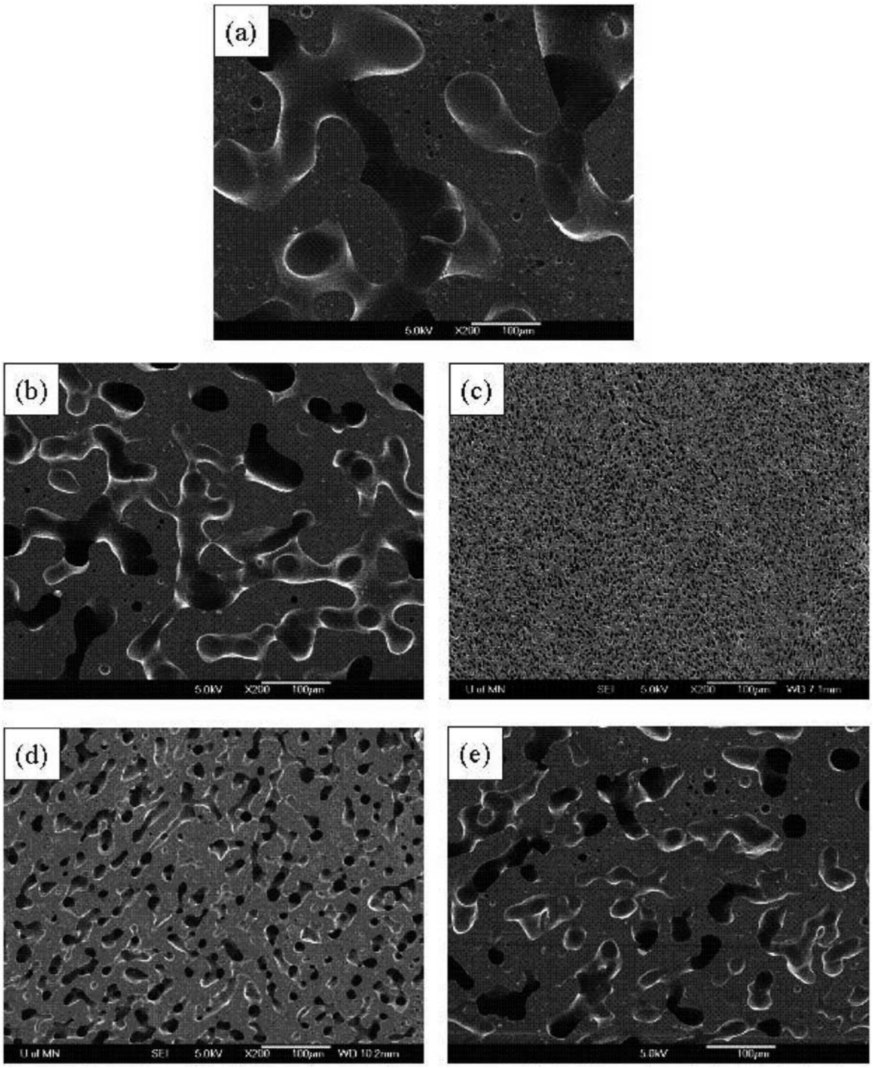

Fig. 3. SEM micrographs of 50/50 PS/PE blends with 1% PS–PE after mixing at 50 rpm for 10 min at 170 °C followed by annealing for 15 min: (a) no block copolymer, (b) 6k, (c) 40k, (d) 100k and (e) 200k PS–PE. (Scale bar = 100 μm).

of the phase size during mixing. The $c_1\Gamma$ values obtained by fitting the experimental data with Eq. (1) are summarized in Table 2. In each case, the curve fits were based on the data before morphology stabilization, i.e. the initial linear coarsening region. The $c_1\Gamma$ values shown in Table 2 indicate the efficiency of the block copolymers in slowing coarsening. For ease of comparison, the $c_1\Gamma$ values were normalized by that of the neat blend. With the exception of

Table 2
Results of fitting image analysis results to the Doi–Ohta theory and normalized interfacial coverage, Σ/Σ_{max}

Block copolymer		$c_1\Gamma$ (N/m)	Normalized $c_1\Gamma$[a]	Σ/Σ_{max}[b]	
				After mixing	After annealing[c]
	–	1.5×10^{-4}	1.0	–	–
6k	1%	6.4×10^{-5}	0.4	12.0	91.6
40k	0.1%	1.2×10^{-4}	0.8	0.3	1.0
	0.3%	6.4×10^{-5}	0.4	0.6	1.3
	1%	3.2×10^{-7}	0.002	1.1	1.2
100k	1%	6.2×10^{-5}	0.4	1.8	3.2
200k	1%	5.1×10^{-5}	0.3	1.0	3.0

[a] $c_1\Gamma$ was normalized with that of the blend with no block copolymer.

[b] Assumes all block copolymer is at the interface.

[c] Σ was calculated based on the specific interfacial area after coarsening was suppressed.

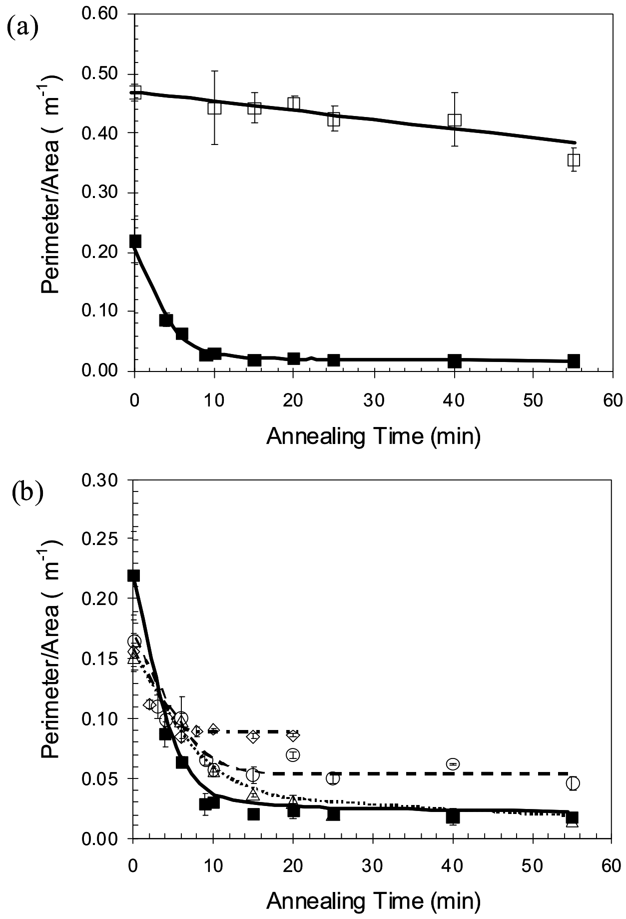

Fig. 4. Perimeter per unit area, Q, as a function of annealing time for 50/50 PS/PE blends with 1% PS–PE of various molecular weights. The ■ represents blends with no block copolymer, □ represents blends with 40k, △ represents 6k, ◇ represents 100k and ○ represents 200k. The lines represent a fit of Eq. (1) to the experimental data before the morphology stabilizes. In (b), the thick solid line—no block copolymer, dotted line—6k, dash dotted line—100k and dashed line—200k. The error bars represent the standard deviations of the results obtained for 5–15 images.

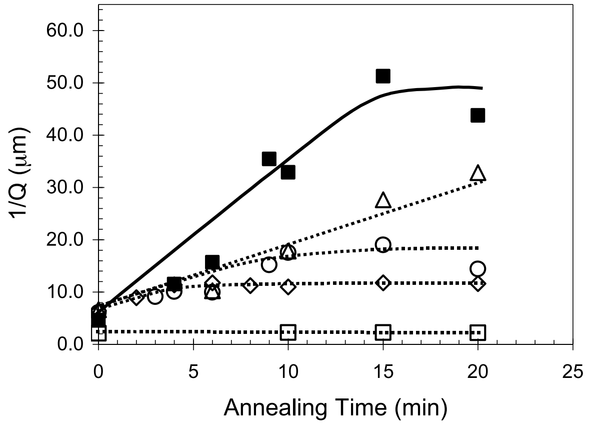

Fig. 5. The reciprocal of the specific interfacial area, $1/Q$, in 50/50 PS/PE blends as a function of annealing time. The ■ represents blends with no block copolymer. Open symbols represent blends with 1% PS–PE of various molecular weights: □—6k, △—40k, ◇—100k and ○—200k. The lines are to guide the eye.

1% 40k PS–PE, the addition of 1% PS–PE reduces the $c_1\Gamma$ to about half of that of the neat blend, with no evident dependence on molecular weight of PS–PE. However, 1% 40k PS–PE decreases the normalized $c_1\Gamma$ by factor of over 300. This implies that the morphology of the blend with 1% 40k PS–PE has already been stabilized during mixing. It should be noted that the $c_1\Gamma$ values shown in Table 2 do not directly indicate the interfacial tension change by addition of the block copolymer, since it is uncertain how block copolymer at the interface affects c_1 and Γ individually.

Fig. 6 shows the SEM images of the blends with varying concentrations of 40k PS–PE. The phase size of the quenched samples shown in the left column decreases as the PS–PE concentration increases from 0 to 1%. Annealing the blends with 0.1% block copolymer for 15 min results in coarsening of the morphology, but the phase size is much smaller than the neat blend as shown in Fig. 6(f) and (d). Increasing the concentration to 0.3% yields better suppression of coarsening. However, the morphology after 15 min of annealing is coarser than the blend with 1% 40k PS–PE (Fig. 6(f) and (h)). The $1/Q$ versus annealing time is plotted in Fig. 7. The blend with 0.1% 40k PS–PE shows similar morphology change during initial annealing to that of the blend with no PS–PE, resulting in the same $c_1\Gamma$ as that of the neat blend (Table 2). However, the change in morphology stops after 4 min of annealing. The blend with 0.3% shows slower coarsening, with the normalized $c_1\Gamma=0.4$, and smaller $1/Q$ after stabilization. At this concentration, the 40k PS–PE is comparable to 1% 100k or 200k PS–PE in compatibilization efficiency.

4. Discussion

The interfacial coverage, Σ, of block copolymer is a useful parameter for understanding the compatibilization efficiency of block copolymers in immiscible polymer blends. We estimated Σ for the cocontinuous blends by:

$$\Sigma=\frac{w_{\mathrm{bcp}}\rho_{\mathrm{bcp}}N_{\mathrm{av}}}{QM_{\mathrm{n}}} \tag{2}$$

where w_{bcp} is the weight fraction of block copolymer in the blend, ρ_{bcp} is the density of block copolymer (0.855 g/cm^3 for the PS–PE [13]), N_{av} is Avogadro's number, and M_{n} is the number average molecular weight of the block copolymer. We assumed that all the block copolymers added to the blends reside at the interface, thus Σ in Eq. (2) is an apparent interfacial coverage. The maximum interfacial coverage, $\Sigma_{\max}$, is calculated based on a lamellar structure of the pure PS–PE. For the 6k, 100k and 200k PS–PE, $\Sigma_{\max}$ is estimated to be 0.47, 0.18 and 0.15 chains/nm^2, respectively, using $\Sigma_{\max}=0.25$ chains/nm^2 for the 40k PS–PE [13] and the scaling relation, $\Sigma_{\max}\sim M_{\mathrm{n}}^{-1/3}$ [32].

Table 2 shows $\Sigma/\Sigma_{\max}$ for the blends after mixing and after coarsening is suppressed during annealing. Excess

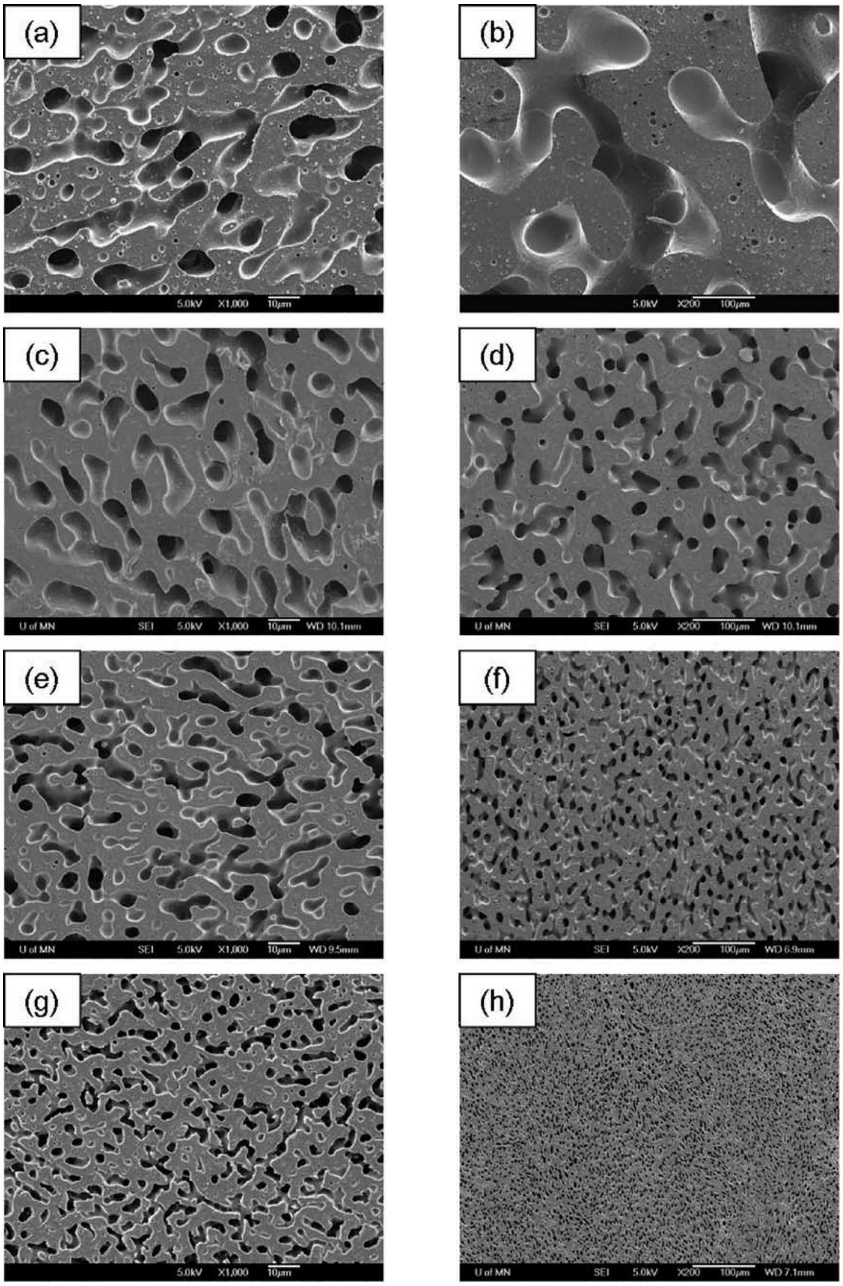

Fig. 6. SEM micrographs of 50/50 PS/PE polymer blends with various amounts of 40k PS–PE, prepared by mixing at 50 rpm for 10 min at 170 °C. All micrographs on the left represent blends quenched immediately after mixing, while all micrographs on the right represent blends annealed for 15 min at 170 °C. (a) and (b) have no block copolymer, (c) and (d) have 0.1%, (e) and (f) have 0.3% and (g) and (h) have 1%. (Scale bar = 10 μm on left and 100 μm on right).

amount of block copolymer can be estimated by $(\Sigma/\Sigma_{\max}-1)/(\Sigma/\Sigma_{\max})$. It is evident that more than 90% of 6k PS–PE is not at the interface for the quenched sample. In addition, the 6k PS–PE at the interface cannot stop coarsening and results in $\Sigma/\Sigma_{\max}=91.6$ after 30 min of annealing. Lyu et al., have used the same block copolymers to investigate the mechanism for suppressing coalescence of PE droplets in a PS matrix [13]. They also found that the 6k PS–PE was least effective in suppressing coalescence. This was attributed to solubility of the 6k PS–PE in the homopolymers, which reduces the amount of block copolymer at the interface. The authors estimated that >90% of this low molecular weight block copolymer will dissolve in the homopolymers.

For the blends with 40k PS–PE, $\Sigma/\Sigma_{\max}$ after mixing increases from 0.3 to 1.1 as the block copolymer concentration increases from 0.1 to 1%. Since the solubility of 40k PS–PE in the bulk phases is low [13], a part of the block copolymer chains will be trapped into micelles above its critical micelle concentration (CMC). Using transmission electron microscopy, Lyu et al. found that micelles of 40k PS–PE started to appear at 0.25% [13]. Thus, we can

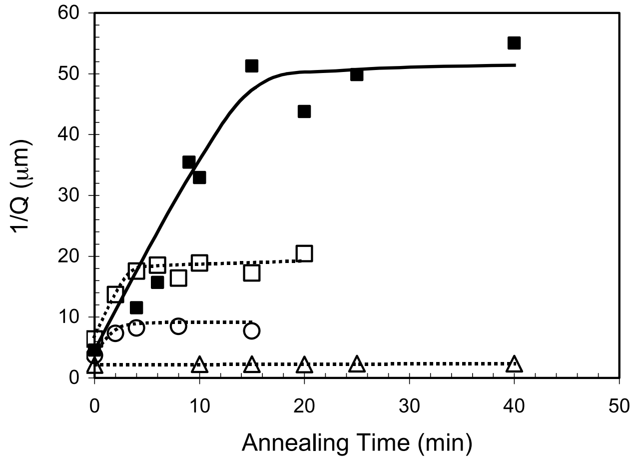

Fig. 7. The reciprocal of the specific interfacial area, $1/Q$, in 50/50 PS/PE blends as a function of annealing time. The ■ represents blends with no block copolymer, □ represents blends with 0.1% 40k PS–PE, ○ represents blends with 0.3% 40k PS–PE and △ represents blends with 1% 40k PS–PE. The lines are to guide the eye.

neglect micelle formation in the blends with 0.1% 40k PS–PE. The normalized $c_1\Gamma=0.8$ for the blend with 0.1% 40k PS–PE suggests that $\Sigma/\Sigma_{\max}=0.3$ after mixing slightly slowed down the initial coarsening during annealing. Further coarsening stops when $\Sigma/\Sigma_{\max}\sim 1$. This implies that for the blends with 40k PS–PE the morphology change during annealing stops due to saturation of the interface with the block copolymer.

At 0.3%, the 40k PS–PE concentration is approximately equal to the CMC reported by Lyu et al. Thus, most of the block copolymer will be at the interface with very few micelles in the bulk phases. A $\Sigma/\Sigma_{\max}>1$ after stabilizing the morphology indicates that some (∼20%) of the block copolymer in the blend is trapped in micelles. The finer morphology after mixing (Fig. 2(c)) and negligible coarsening during annealing of the blend with 1% 40k PS–PE implies that the interface has been saturated during mixing. This is supported by $\Sigma/\Sigma_{\max}>1$ after mixing. Again, we estimate about 20% of the block copolymer forms micelles in the bulk phases.

For higher molecular weight block copolymers, the apparent $\Sigma/\Sigma_{\max}\geq 1$ for the quenched sample. However, further coarsening (normalized $c_1\Gamma\sim 0.4$) is observed until $\Sigma/\Sigma_{\max}$ reaches ∼3. This implies that the actual interfacial coverage is insufficient to completely suppress morphology change. A $\Sigma/\Sigma_{\max}\sim 3$ when coarsening is suppressed suggests that more than 70% of 100k or 200k PS–PE added to the blend is not in the interface during mixing and annealing, due to micelle formation.

An optimal molecular weight of pre-made block copolymers for compatibilization can be explained by considering three important factors: (1) block copolymer diffusion, (2) their propensity to form micelles, and (3) the relative stabilization effect at the interface of the block copolymer by reducing interfacial tension and coalescence and/or changing the stiffness of the interface. Low molecular weight copolymers such as the 6k PS–PE have the advantage that they can quickly move to the interface and have a higher CMC. However, their stabilization effect is small due to their solubility in the bulk phases, leading to less interfacial coverage. Higher molecular weight block copolymers provide a better stabilization effect, but they diffuse more slowly and are trapped in micelles at lower concentration. Therefore, it can be expected that the best performance will be achieved with intermediate molecular weight block copolymers. Braun et al., described a mechanism that supports these observations [33]. They attributed finer morphologies to interfaces being torn apart mechanically due to high entanglement densities at compatibilized interfaces. This allows stresses arising during mixing to be efficiently transmitted to the interface, causing break-up of domains. Low molecular weight block copolymers (i.e. 6k PS–PE) do not form enough entanglements for a significant effect, while high molecular weight block copolymers (i.e. 100k PS–PE and 200k PS–PE) have low mobility, leading to lower concentration at the interface and reduced break-up effects.

The existence of an optimal molecular weight for block copolymer compatibilizers has also been observed in previous studies [10,13,34,35]. Retsos et al. investigated polystyrene/polyisoprene (PS/PI) blends and found that intermediate molecular weight PS–PI diblock copolymers led to the greatest reduction of interfacial tension [10]. This result was attributed to the high molecular weight block copolymers forming micelles, which prevented a large portion of the block copolymer from reaching the interface. Lyu et al., found that intermediate molecular weight PS–PE diblock copolymers provided superior coalescence suppression in PS/PE blends [13]. Macosko et al., showed that adding intermediate molecular weight polystyrene–poly(methyl methacrylate) (PS–PMMA) diblock copolymers to PS/PMMA blends led to the smallest domain sizes and minimized annealing effects [34]. Maric and Macosko found that intermediate molecular weight polystyrene–poly(dimethyl siloxane) (PS–PDMS) diblock copolymers provided the best stabilization of PS/PDMS blends [35].

5. Conclusions

The effect of block copolymers of varying molecular weight and concentration on the morphology of 50/50 PS/PE blends was investigated using SEM with image analysis. Although, the addition of 6k block copolymer to the blends did not affect the morphology significantly, it slowed coarsening of the morphology during annealing. The presence of 1% 40k block copolymer dramatically reduced the phase size and provided excellent stabilization during annealing. Blends with varying concentration of 40k PS–PE showed that increasing concentration causes reduction of the phase size and a shorter time for coarsening suppression.

This suggests that there is an optimum concentration above which further addition of block copolymer yields no improved suppression of coarsening during annealing. It was also shown that coarsening is suppressed by interfacial saturation of the block copolymer. The addition of 100k or 200k block copolymer to the blend did not reduce the phase size as much as the 40k block copolymer, but did stabilize the morphology at the early stages of annealing. Overall, the block copolymers were ranked in order of stabilization effectiveness: $6\text{k} < 200\text{k} < 100\text{k} \ll 40\text{k}$.

The existence of an optimal molecular weight block copolymer is likely due to a balance between the ability of the block copolymer to reach the interface and its relative effectiveness as a compatibilizer. The 6k block copolymer can reach the interface quickly, but does not have a large effect due to its solubility in the bulk phases. In contrast, the 100k and 200k block copolymers affect coarsening, but diffuse more slowly and a large portion may be trapped in micelles. The 40k block copolymer has an intermediate effect and ~80% can reach the interface during mixing, leading to the best overall performance.

As shown above, post-mixing processing can dramatically affect the morphology of immiscible polymer blends. This change in morphology can have detrimental effects on the blend properties, making it imperative to stabilize the blend morphology. The results of these experiments will aid in the selection of optimal compatibilizers for cocontinuous polymer blends. Previous experiments have used high molecular weight block copolymer compatibilizers because of their relatively large stabilization effect [16,18,36]. However, as shown above, high molecular weight block copolymers can be less effective than those with intermediate molecular weights. The improved stability of cocontinuous polymer blends with optimal compatibilizers will help to expand their potential applications.

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References

[1] Utracki LA. Polymer alloys and blends. Munich: Hanser; 1989.
[2] Hara M, Sauer JA. J Macromol Sci RMC 1998;C38:327.
[3] Paul DR, Bucknall CB. In: Paul DR, Bucknall CB, editors. Introduction. New York: Wiley; 2000.
[4] Koning C, Van Duin M, Pagnoulle C, Jerome R. Prog Polym Sci 1998;23:707.
[5] Baker W, Scott CE, Hu GH, editors. Reactive polymer blending. Cincinnati, OH: Hanser; 2001.
[6] Anastasiadis SH, Gancarz I, Koberstein JT. Macromolecules 1989;22:1449.
[7] Hu W, Koberstein JT, Lingelser JP, Gallot Y. Macromolecules 1995;28:5209.
[8] Chapleau N, Favis BD, Carreau PJ. J Polym Sci, Polym Phys 1998;36:1947.
[9] Verdier C, Vinagre HTM, Piau M, Joseph DD. Polymer 2000;41:6683.
[10] Retsos H, Margiolaki I, Messaritaki A, Anastasiadis SH. Macromolecules 2001;34:5295.
[11] Mekhilef N, Favis BD, Carreau PJ. J Polym Sci, Polym Phys 1997;35:293.
[12] Lyu S, Bates F, Macosko C. ACS Polym Prepr 1999;40:1016.
[13] Lyu S, Jones TD, Bates FS, Macosko CW. Macromolecules 2002;35:7845.
[14] Harrats C, Fayt R, Jerome R, Blacher S. J Polym Sci, Polym Phys 2003;41:202.
[15] Bourry D, Favis BD. J Polym Sci, Polym Phys 1998;36:1889.
[16] Lyngaae-Jorgensen J. Int Polym Proc 1999;3:213.
[17] Li J, Ma PL, Favis BD. Macromolecules 2002;35:2005.
[18] Chuai CZ, Almdal K, Lyngaae-Jorgensen J. Polymer 2003;44:481.
[19] Dedecker K, Groeninckx G. Polymer 1998;39:4993.
[20] Veenstra H, van Lent BJJ, van Dam J, Posthuma de Boer A. Polymer 1999;40:6661.
[21] Willemse RC, Posthuma de Boer A, van Dam J, Gotsis AD. Polymer 1999;40:827.
[22] Harrats C, Blacher S, Fayt R, Jerome R, Teyssie P. J Polym Sci, Polym Phys 1995;33:801.
[23] Yuan Z, Favis BD. SPE ANTEC Technical Papers. San Francisco, CA; 2002.
[24] Yuan Z, Favis BD. Biomaterials 2004;25:2161.
[25] Bates FS, Rosedale JH, Bair HE, Russell TP. Macromolecules 1989;22:2557.
[26] Gehlsen M. Catalytic hydrogenation of polymers: synthesis and characterization of model polyolefins. Ph.D. University of Minnesota; 1993.
[27] Ndoni S, Papadakis C, Bates F, Almdal K. Rev Sci Instrum 1995;66:1090.
[28] Galloway JA, Macosko CW. Polym Eng Sci 2004;44:714.
[29] Galloway JA, Montminy MD, Macosko CW. Polymer 2002;43:4715.
[30] Doi M, Ohta T. J Chem Phys 1991;95:1242.
[31] Vinckier I, Laun HM. J Rheol 2001;45:1373.
[32] Bates FS, Fredrickson GH. Phys Today 1999;52:32.
[33] Braun D, Fisher M, Hellman GP. Polymer 1996;37:3871.
[34] Macosko C, Guegan P, Khandpur A, Nakayama A, Marechal P, Inoue T. Macromolecules 1996;29:5590.
[35] Maric M, Macosko CW. J Polym Sci, Polym Phys 2002;40:346.
[36] Fayt R, Jerome R, Teyssie P. J Polym Sci, Polym Phys 1989;27:775.