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Polymer 46 (2005) 12422–12429
polymer
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Premade vs. reactively formed compatibilizers for PMMA/PS melt blends

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Received 20 July 2005; received in revised form 22 October 2005; accepted 25 October 2005
Available online 14 November 2005

Abstract

The efficiency of two compatibilization methods, adding premade copolymers versus in situ formation of copolymers, were compared by evaluating the minor phase size and size distribution. Premade diblock copolymers were formed by coupling amine terminal polystyrene (PS-NH_2) with anhydride terminal poly(methyl methacrylate) (PMMA-An) in solution. Mid-functional PMMA was coupled with the PS-NH_2 to form graft copolymers. The same block and graft copolymers were formed in situ during melt blending. After mixing, the particle size and distribution were analyzed by transmission electron microscope (TEM). While both methods compatibilized blends, in situ formation reduced the minor phase size further. For the reactive case, graft copolymers are slight better than the block ones. This is attributed to a greater capacity for reducing interfacial tension. For the premade case, block copolymers compatibilize better at low copolymer concentration while graft copolymers work better at high concentration. As the amount of block copolymers added into the blends increases, the number of micelles increases significantly. This is believed to be the reason why premade copolymers are less capable of compatibilizing blends than the reactively formed ones.

Keywords: Compatibilization; Premade copolymer; Reactively formed copolymer

1. Introduction

Block copolymers are often used to compatibilize immiscible polymer blends, functioning as macromolecular surfactants to modify interfacial properties [1–3]. Generally, there are two ways to incorporate block copolymers, adding premade copolymers or in situ formation [1,3]. In the first method, the block copolymers are synthesized in a separate step and then dispersed into the blend components. Theoretically, block copolymers should seek the interfaces during melt mixing to decrease unfavorable interactions [4,5]. In reactive compatibilization, functional polymers are added to (or just a natural part of) each blend component. During processing, complementary functional groups in each polymer react at the interfaces and form copolymers, which act as surfactants and compatibilize the blend. Both methods of compatibilization have been studied extensively [6–12]. Jerome and coworkers in their review found no evidence of commercial blends compatibilized with premade block copolymers and indicated that the in situ method is superior in compatibilization [3].

However, direct comparison of the compatibilization efficiency between premade and in situ formed copolymers has not been fully investigated yet due to the difficulty of controlling variables [3]. Sundararaj and Macosko compared the effects of premade and reactively formed copolymers on suppression of coalescence in polystyrene/poly(ethylene–propylene) (PS/EP) blends and concluded that reactive compatibilization is superior to adding premade copolymers [13]. However, the EP block in their premade copolymers was immiscible with the EP component in the blend. Moreover, the functional polymers used in their study had multiple functional groups which resulted in a branched or even cross-linked structure formed at the interfaces during processing.

Nakayama et al. studied the compatibilization efficiency of the premade and the reactively formed block copolymers with a well-defined PS/PMMA model system [14,15]. The premade block copolymer used was poly(styrene-*b*-methyl methacrylate) and the reactive system was PS-COOH/PMMA-epoxy. The particle size reduction occurred rapidly with or without compatibilizers. But the final particle diameter, *D*, did depend on the type of compatibilizer used, with the reactively formed one giving the smallest size. Only 1.4 wt% block copolymers was found in the reactive system after 20 min mixing, whereas 5 wt% block copolymer was added into the premade system. These results seemed to support the conclusion that reactively formed block copolymers are better compatibilizers than premade ones. However, it should be noted that every polymer

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doi:10.1016/j.polymer.2005.10.125

chain was functional in their reactive system. It is desirable to know whether fractions of functional polymers similar to the concentration of premade block copolymer would be as efficient.

Also, many of the functional polymers used for reactive compatibilization have multiple functional groups [16]. These functional groups are randomly distributed resulting in graft copolymers formed. Therefore, it is desirable to know how the architecture of a copolymer chain will affect its compatibilization of blends.

The purpose of this study is to compare the compatibilization efficiency of premade versus reactively formed graft and block copolymers with a PMMA/PS model system. For compatibilizers, the same precursors were used to obtain the premade and the in situ formed copolymers such that they have the same molecular weight and architecture. The complementary functional group pair used for reactive compatibilization is amine/anhydride, which is much faster than the acid/epoxy used by Nakayama. A more important difference is that the premade copolymers added to the blend are controlled to match the possible maximum amount of copolymers formed in the corresponding reactive system.

2. Experimental

2.1. Materials

Characteristics of the nonfunctional and functional polymers used in this study are listed in Table 1. The nonfunctional polymers, PS and PMMA were synthesized by anionic polymerization. Anhydride-terminal PMMA (PMMA-eAn) and middle-anhydride PMMA (PMMA-mAn) were synthesized by atom transfer radical polymerization (ATRP) with functional initiators. They were fluorescently labeled by copolymerization of methyl methacrylate with fluorescently labeled monomers [17]. Amine-terminal PS (PS-NH_2) was also synthesized by ATRP. The molecular weights of these polymers were determined by size exclusion chromatography (SEC). The functionalities of PMMA-An were measured by coupling with two molar equivalents of PS-NH_2 in dry tetrahydrofuran (THF) for 2 days at room temperature followed by SEC analysis with a fluorescence detector. The functionality of PS-NH_2 was determined by measuring the extent of coupling reaction with PMMA-eAn (without fluorescence label) with a UV detector on SEC.

Table 1
Nonfunctional and functional polymers used in this work

Polymer	M_n (kg/mol)	M_w/M_n	Functionality	Viscosity at 100 s^{-1}, 180 °C (Pa s)
PS	18	1.05	–	40
PMMA	13	1.17	–	2100
PS-NH_2	26	1.14	0.85	90
PMMA-eAn	15	1.21	~1	–
PMMA-mAN	18	1.27	0.90	–
PMMA-*b*-PS	41		–	–
PMMA-*g*-PS	44		–	–

2.2. Preparation of premade copolymers

Premade copolymers, PMMA-*b*-PS and PMMA-*g*-PS, were prepared by coupling of PMMA-eAn/PMMA-mAn and PS-NH_2 in THF at room temperature for 1 day followed by precipitation into methanol. After drying for 2 days in a vacuum oven, conversions were measured by using SEC with a fluorescence detector. The coupling reaction conditions and product properties are listed in Table 2. To prepare PMMA-*b*-PS, PS-NH_2 was added in 30 mol% excess (10% excess based on functionality). PMMA-eAn was found to be completely consumed to form PMMA-*b*-PS. In the products, besides the 84 wt% block copolymer, there was 11 wt% non-functional PS and 5 wt% PS-NH_2 left from the coupling reaction. For PMMA-*g*-PS, the actual PS-NH_2 excess was 16 mol% and the PMMA-mAn conversion was measured to be 95 wt%. In the product, besides the graft copolymer, there was 25 wt% homopolymer left, which included 5 wt% PMMA/PMMA-mAn and 20 wt% PS/PS-NH_2.

2.3. Blend preparation and characterization

Blends were prepared using a preheated cup-rotor mixer (MiniMax CS-183MMX, Custom Scientific Instrument, Inc.) with three stainless steel balls at 180 °C [18]. The composition of the blends is summarized in Table 3. For all the blends, the overall PMMA/PS composition is 70/30. The amount of premade copolymers in the blends is based on the possible maximum amount of copolymers in the corresponding reactive blends. For example, 2.7 wt% of PMMA-*b*-PS is the maximum amount of copolymer that could possibly be formed in RB1, thus 3.3 wt% (2.7 wt% PMMA-*b*-PS) premade block copolymer mixture (BCP) was added to PB1.

All the blends in this study were prepared by one-step mixing in which all the polymers were dry-blended at room temperature and fed to the mixer. For the blends with premade copolymers, blend samples were taken after 20 min mixing followed by quenching in liquid N_2. For the reactive blends, about 10 mg of blend samples were taken at several time intervals during mixing to monitor conversion that was measured by SEC with the fluorescence detector.

The morphology of the blends was characterized using TEM (Jeol 1210). A specimen was first annealed at 180 °C under vacuum for 10 min and then was microtomed into 50 nm thick slices at room temperature using a diamond knife. The PS

Table 2
Preparation of premade copolymers

Copolymer	Molar ratio of reaction solution PMMA-An: PS-NH_2	Composition of product mixture (wt%)		
		Copolymer	PMMA/ PMMA-An	PS/PS-NH2
PMMA-*b*-PS	1:1.10	84%	0	11%/5%
PMMA-*g*-PS	1:1.16	75%	2%/3%	10%/10%

Table 3
Composition and morphology properties of the blends prepared

Blend	PS	PS-NH$_2$	PMMA	PMMA-An	CP[a]	D_{VS} (μm)	D_{vs}/D_n	Σ (chain/nm^2)	Σ/Σ*
NB	30	–	70	–	–	6.62	15.6	–	–
RB1	15	15	69	1	1.6	1.61	9.5	0.21	1.0
RB2	15	15	66.5	3.5	6.5	1.05	4.8	0.54	2.7
RB3	15	15	63	7	12.1	0.34	1.9	0.32	1.7
PB1	28.3	–	69	–	2.7	1.30	5.7	0.27	1.4
PB2	23.9	–	66.5	–	9.6	0.76	4.5	0.58	2.9
PB3	17.9	–	63	–	19.1	1.07	6.3	1.61	8.1
RG1	15	15	68.7	1.3	1.1	1.03	4.3	0.09	0.8
RG2	15	15	65.3	4.7	4.6	1.09	5.5	0.37	3.4
RG3	15	15	60.7	9.3	9.0	0.32	1.8	0.22	3.0
PG1	28.3	–	68.6	–	2.9	2.66	12.7	0.57	5.2
PG2	23.9	–	65.0	–	10.4	1.09	5.5	0.83	7.5
PG3	18.0	–	60.1	–	20.5	0.44	2.2	0.67	6.1

All compositions are weight percentages.

[a] Samples designated PB and RB are diblock copolymers, PG and RG are graft copolymers.

phase was selectively stained with RuO$_4$ (0.5% aqueous solution) for 20 min to increase contrast.

2.4. Particle size analysis

The minor phase particle size was extracted from the TEM images with software (AnalySIS Image Processing, Soft Imaging System Corp.). The area of each dispersed domain in the TEM images, A_i, was measured and the equivalent diameter, D_i, was calculated by Eq. (1). The volume-to-surface-area-average and number-average particle sizes, D_{VS} and D_n, were calculated for each blend using Eqs. (2) and (3) respectively. The particle size distribution is evaluated by the ratio of D_{VS}/D_n. A total of 1000–4000 particles (about 200 for NB1) from 2 to 3 images were analyzed for each sample.

$$D_i = 2\left(\frac{A_i}{\pi}\right)^{1/2} \quad (1)$$

$$D_{VS} = \frac{\sum_i D_i^3}{\sum_i D_i^2} \quad (2)$$

$$D_n = \frac{\sum_i D_i}{n} \quad (3)$$

3. Results and discussion

3.1. Reaction conversion in reactive blending

With fluorescent labels on PMMA-eAN and PMMA-mAn, their conversions in the coupling reactions could be measured with a fluorescence detector coupled to SEC even at low functional polymer concentration. Fig. 1 shows the PMMA-An conversion changes with mixing time. As shown, the aliphatic amine/anhydride coupling reaction is very fast and final conversions are reached in 10 min for all the blends. The times to reach these final conversions seem to be independent of functional polymer concentration or on the location of functional groups along a polymer chain. Similar trends were found in our previous competitive reaction study [19]. It is likely that the time is determined by the blend morphology development under mixing. As described by Macosko and coworkers, during blending, the minor phase is stretched out into sheets, which then breaks into droplets [12,20]. These droplets can be stretched further and broken into smaller size under flow. But they can also coalesce to form bigger droplets. The final morphology is the result of equilibrium between breakup and coalescence. With reactive compatibilization, when new interfaces are created, they are rapidly filled with copolymers generated by the coupling reaction. The copolymers formed reduce interfacial tension which aids drop breakup and also prevent coalescence, both of which result in smaller drops. When drops become too small to be broken up by the flow, interfaces become saturated with copolymers and reactive generation stops.

The PMMA-An conversions at 20 min of mixing are summarized in Table 4. As shown, the conversions are around 60% for PMMA-eAn and 40% for PMMA-mAn. None of the reactions are complete even under excess PS-NH$_2$.

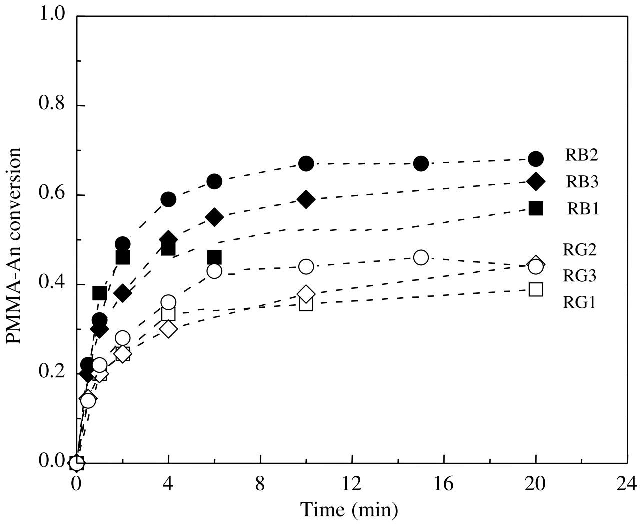

Fig. 1. PMMA-An conversions vs. mixing time for the reactive blends.

Table 4
Characteristics of the coupling reactions between PMMA-An and PS-NH_2

Blends	PMMA-An conversion at 20 min mixing (%)	Rate constant (kg/(mol min))	Ratio of rate constant (end/middle)
RB1	57	74.5	2.7
RB2	68	81.5	2.5
RB3	63	74.5	2.9
RG1	39	27.7	
RG2	44	32.9	
RG3	44	26.0	

The incomplete reaction is attributed to saturation of copolymers at the interfaces. This is common for reactive compatibilization with dilute functional polymers in the blends and has been observed by others [17,19,21].

Independent of functional polymer concentration, the coupling reaction between PMMA-eAn and PS-NH_2 has a higher reaction rate than that between PMMA-mAn and PS-NH_2. To quantitatively compare this difference, the early stage conversions (α) at $t<2$ min are fit with a second-order reaction kinetics model [19] and $\alpha/(1-\alpha)$ is plotted vs. t as shown in Fig. 2. The rate constants for the coupling reaction of end and middle functional PMMA-An with PS-NH_2 are obtained from the slope and are summarized in Table 4. The rate constant ratio between PMMA-eAn and PMMA-mAn is around 2.7, which is consistent with our previous results for the competitive reaction between end and middle PMMA-An with PS-NH_2 [19].

3.2. Blend morphology

Before observation with TEM, all the blends were annealed at 180 °C. This helps to reduce the effect of processing history on the particle shape. The viscosity of the minor phase PS is about 50 times less than the PMMA matrix. As shown in Fig. 3(a) for RG3, the minor phase PS is highly stretched after mixing. During annealing, the stretched sheet breaks into drops by Rayleigh-type instability. The interfacial areas before and after annealing were analyzed by the standard procedure developed by Galloway et al. [22] and a slightly increase was found after annealing, which also supports the idea of sheet breakup [13]. No further change in diameter was observed between 10, 20 and 60 min of annealing. The theoretical breakup time for this system is less than 1 min [23]. No significant differences were detected by SEC in the reaction conversions before and after annealing. Thus TEM's of 10 min annealed samples were used for all the blends.

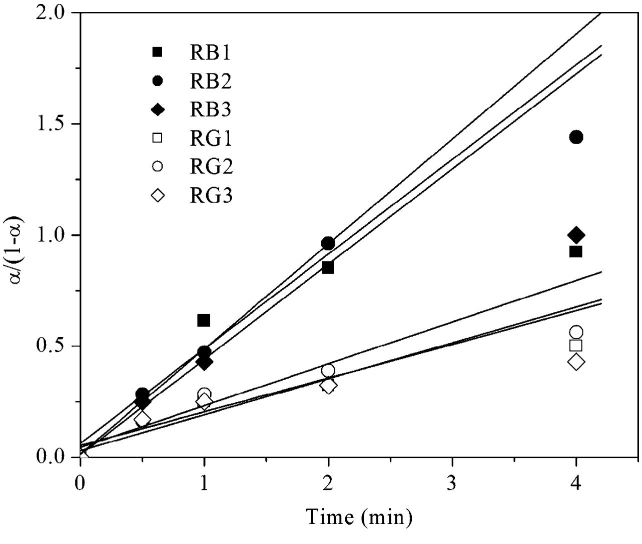

Fig. 2. Short time conversion data fit to second-order reaction kinetics.

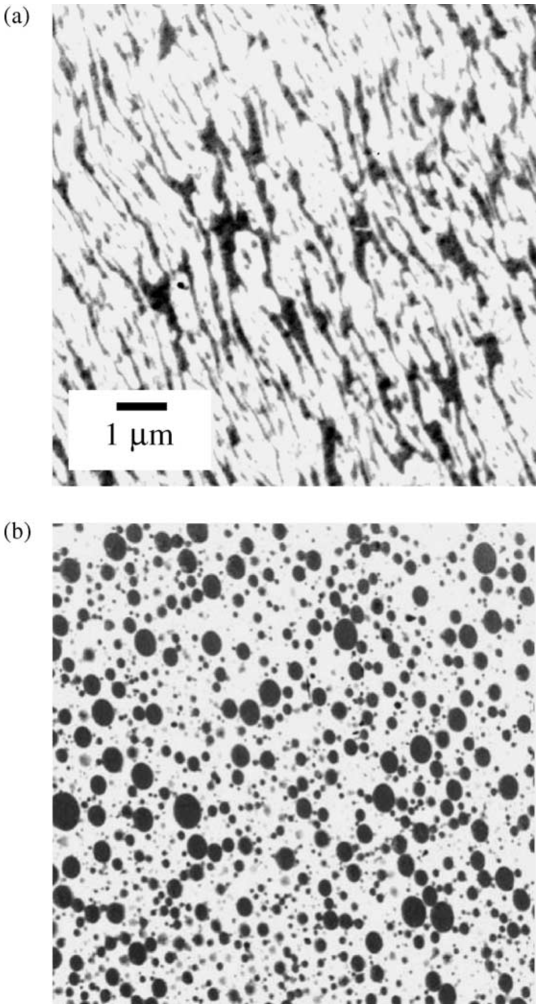

Fig. 3. Annealing of reactive compatibilized PS/PMMA blend RG3 at 180 °C. (a) 0 min; (b) 10 min.

Fig. 4 shows the morphology of the 70/30 PMMA/PS blend without any compatibilizers. Clearly, the PS particle size is large ($D_{VS}=6.62$ μm) and the distribution is broad ($D_{VS}/D_n=15.6$). By adding either premade or reactively formed compatibilizers, the particle size and distribution are greatly decreased, as shown in Fig. 5 and Table 3.

For the blends with 2.7 wt% premade block copolymers, PS particle size decreases down to ~1 μm. Increasing the block copolymer amount to 9.6 wt% and 19.1%, the phase structure does not change much as shown in Fig. 5. However, the number of micelles increases significantly. For premade graft copolymers, the PS particles at low copolymer concentration are larger than those in the blends with premade block copolymers.

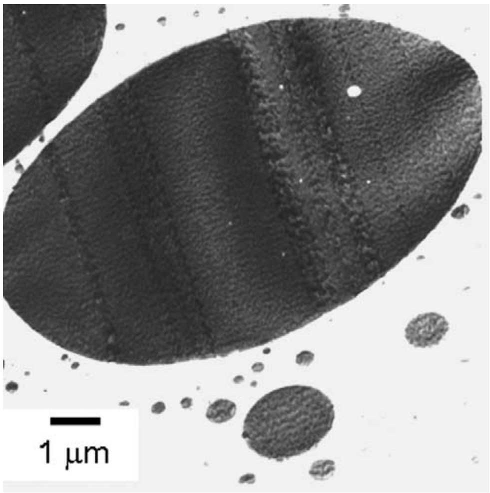

Fig. 4. PS/PMMA blend without any compatibilizer. The sample was annealed at 180 °C for 10 min before imaging.

However, as the amount of graft copolymers increases, the minor phase becomes finer. It is surprising to find that at high copolymer concentration the blend morphology with premade graft copolymers is finer than that with premade block ones.

Fig. 5 also shows the morphology of the blends compatibilized with reactively formed copolymers. Particle size decreases as functional polymer concentration increases. This is reasonable since the amount of copolymer in the blends increases with functional polymer concentration (as shown in Table 3). At similar copolymer concentration, the phase structures are comparable for both block and graft copolymers. As the concentration reaches about 10 wt%, the minor phase size is reduced down to less than 1 μm.

3.3. Interfacial coverage and phase stability

To better understand the role of copolymer on compatibilization, the copolymer interfacial coverage Σ, which is defined as the number of copolymer chains per unit area, is calculated.

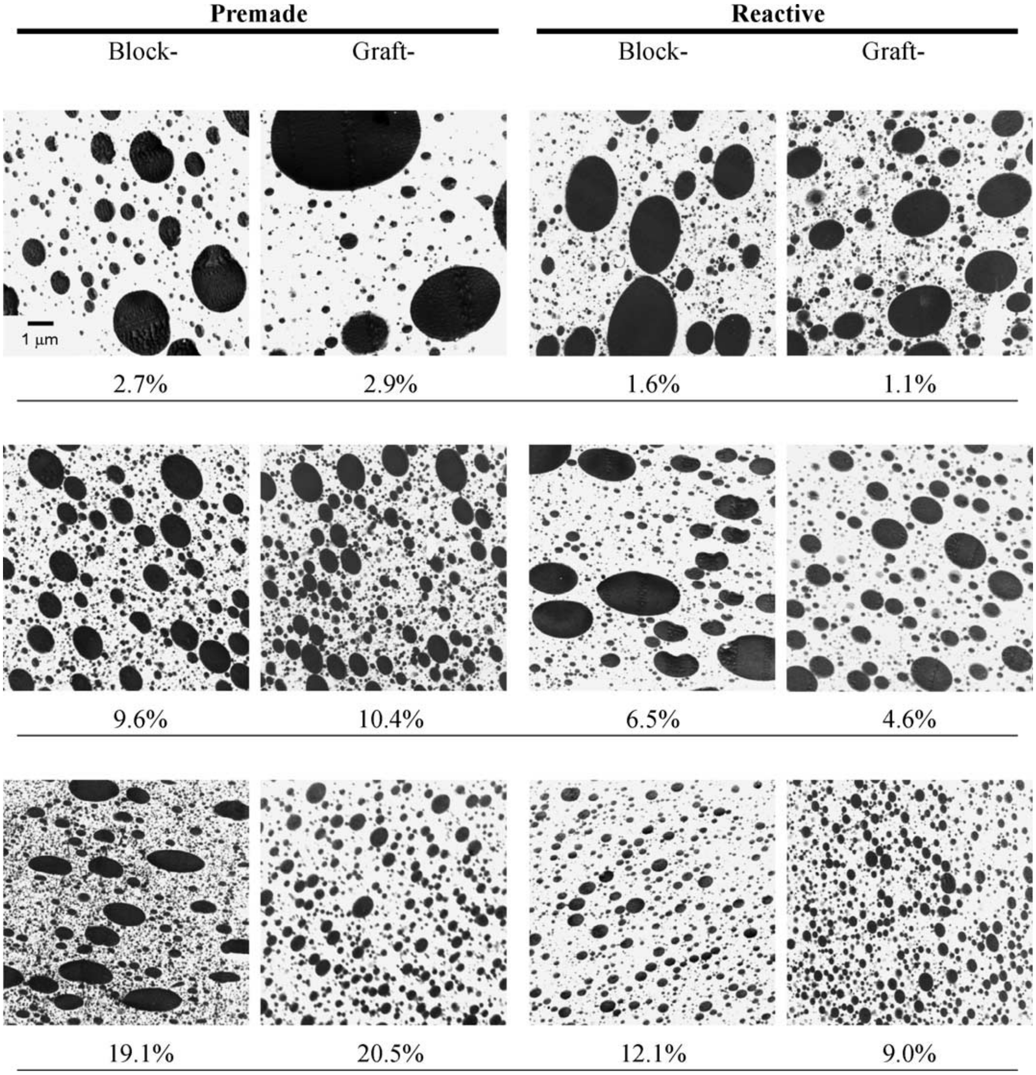

Fig. 5. Morphology of the PMMA/PS blends compatibilized by different concentration of premade and reactively formed, block versus graft copolymers.

Using the measured particle size and assuming all the copolymers stay at the interfaces, Σ is estimated by Eq. (4).

$$\Sigma = \frac{\rho_{\mathrm{PS}} D_{\mathrm{VS}} N_{\mathrm{a}} X}{6\phi_{\mathrm{PS}} M_{n,\mathrm{co}}} \tag{4}$$

where, ϕ_{PS} is the weight fraction of the minor phase, $M_{n,\mathrm{co}}$ is the number average molecular weight of the copolymer, ρ_{PS} is the density of PS, X is the weight fraction of copolymer in the blend, and N_{a} is the Avogadro constant. The interfacial coverage for all the compatibilized blends is summarized in Table 3.

The maximum interfacial coverage Σ^* can be estimated by assuming a dense monolayer of copolymers at the interface. Considering a symmetric diblock copolymer at flat interfaces, the thickness of the monolayer is half of the lamellar spacing in the ordered block copolymer phase. Thus the block copolymer interfacial coverage can be estimated by Eq. (5).

$$\Sigma^* = \frac{\text{thickness of copolymer monolayer}}{\text{volume of one chain}} \tag{5}$$

Russell et al. studied the lamellar spacing for a series of symmetric PMMA-*b*-PS copolymers with small angle neutron scattering [24]. They built a relationship between the interfacial area occupied by a copolymer chain and the degree of polymerization of the copolymer. Thus, the maximum interfacial coverage for the copolymer can be estimated from the empirical equation shown by Eq. (6).

$$\Sigma^* = 2.06N^{-0.39} \tag{6}$$

With this equation, the maximum interfacial coverage of PMMA-*b*-PS for the blends here is calculated to be 0.20 chain/nm^2. There has been no report of the interfacial area occupied by a Y-shaped PMMA-*g*-PS graft copolymer chain. However, the data for Y-shaped PS-*g*-polyisoprene (PI) [25] and PS-*g*-poly(2-vinylpyridine) (PVP) [26,27] are available in literature and they were found to be larger than that of the corresponding diblock copolymers with similar molecular weight and composition. Kim et al. quantitatively compared the interfacial area occupied by a graft and block PS–PI copolymer and found that the graft copolymer has about 1.7 times larger interfacial area than the block one [28]. We used the same value for PMMA-*g*-PS/PMMA-*b*-PS. From Eq. (6), the maximum interfacial coverage for a diblock copolymer with the molecular weight and composition of PMMA-*g*-PS is ~0.19 chain/nm^2. Therefore, the maximum interfacial coverage for PMMA-*g*-PS is estimated to be ~0.11 chain/nm^2.

Table 3 shows the values of Σ/Σ^*, the fraction of droplet interfaces covered by copolymers. Except for RB1 and RG1, Σ/Σ^* is larger than 1 for all the blends. This means that all the interfaces should be saturated with copolymers assuming all the copolymers prefer interfaces. Lyu predicted the minimum interfacial coverage ($\Sigma_{\min}$) to prevent particle coalescence with a film rupture theory [29] and he proposed $\Sigma_{\min} = h_{\mathrm{c}}/Nb^3$, where h_{c} is the critical film thickness that will damp film fluctuation, N is the degree of polymerization of copolymer, and b is the mean-average segment length. With his theory, h_{c} is calculated to be about 4 nm for PMMA/PS at 180 °C. Thus $\Sigma_{\min}/\Sigma^*$ are 0.035 and 0.055 for the block and graft copolymer respectively. For all the compatibilized blends studied here, the fraction of coverage is much higher than $\Sigma_{\min}/\Sigma^*$. Therefore, the final morphology should be stable. We monitored the morphology stability by annealing the blend at 180 °C for 10, 20 and 60 min. There was no significant increase on particle size, in agreement with the prediction.

3.4. Compatibilization efficiency

To quantitatively compare the efficiency of these compatibilization methods, the particle sizes of the blends were extracted out from the TEM images and are summarized in Fig. 6. As shown, for the reactive case, graft copolymers can reduce particle sizes more than block ones at the same copolymer concentration, even though both of them compatibilize blends well. For the premade case, at low concentration, block copolymers work as well as the reactively formed ones. As the amount of block copolymer put into the blends increases, the particle size begins to level off above a certain concentration. Premade graft copolymers are poorer compatibilizers compared with block ones at low concentration. But as the concentration increases, the particle size decreases gradually. At the highest concentration studied here, graft copolymers work much better than the premade block ones and even as well as the reactively formed ones except that it needs more copolymers.

According to Retsos et al. for the (PS + PI-*g*-PS)/PI system with PS block as the graft chain and PI homopolymer as the matrix, at copolymer composition of ~40% PI, the graft copolymer reduces interfacial tension much more than the corresponding PS-*b*-PI with similar molecular weight and composition [30]. Although there is no interfacial tension comparison between PMMA-*g*-PS vs. PMMA-*b*-PS available yet, the PMMA/PS system studied here is similar to the PS/PI system in terms of copolymer architecture and composition.

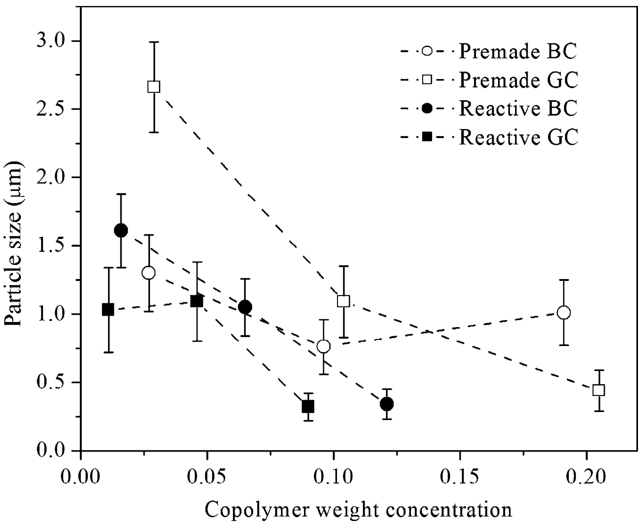

Fig. 6. Particle size, D_{VS}, changes with copolymer concentration for all the compatibilized blends. The 'error bars' are one standard deviations of D_i.

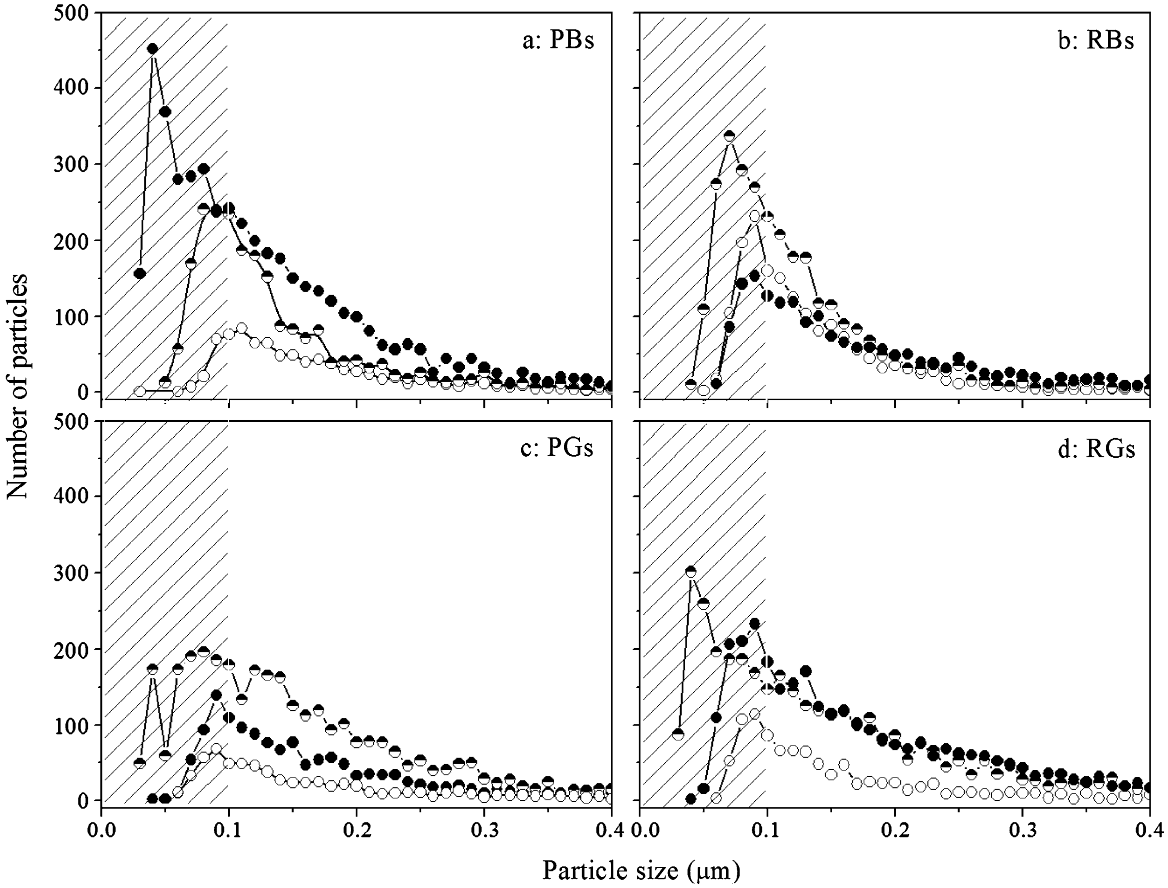

Fig. 7. Particle size distribution for different blends. Particles with size smaller than 100 nm are considered as micelles or swollen micelles. Copolymer concentration: open, the lowest concentration; half-open, middle concentration; and solid, the highest concentration (Table 3).

Thus it is reasonable to expect similar behavior: PMMA-*g*-PS is more efficient on reducing interfacial tension than PMMA-*b*-PS. This partially supports the result that reactively formed graft copolymers are better compatibilizers than the block ones.

At this point, it is still hard to understand the behavior of premade graft and block copolymers at low concentrations. To clarify this question, more work is needed. However, from Fig. 5, we do find a big difference between the numbers of micelles with premade block vs. graft copolymers. Fig. 7 summarizes the number of particles vs. particle size (here only the particle size smaller than 0.4 μm is plotted). Particles with size smaller than 100 nm are considered as micelles or swollen micelles. Comparing Fig. 7(a) and (c), the number of micelles increases greatly with copolymer concentration for the premade block case, while kept similar for the premade graft case. It seems that block copolymers prefer to stay in the bulk phase as micelles instead of at the interface, while graft ones still prefer to reach the interfaces even at high concentration.

For the reactive case, Fig. 7(b) and (d) show that the numbers of micelles do not change much with copolymer concentration, neither with copolymer architecture. They are both smaller than that of the premade block copolymers. This is reasonable to consider the compatibilization process as following. For reactive compatibilization, copolymers are formed at interfaces. As they fill the interface, interfacial tension is decreased. Thus the interfaces become rough and some of the rough interfaces or even copolymers can be pinched out to form micelles or swollen micelles [31]. This micelle formation can be considered as a secondary process. For the premade blends, copolymers are mixed together with homopolymers and they first appear as micelles in the homopolymer phases. During blending, copolymers must diffuse through the bulk phase to the interfaces. The compatibilization is controlled by this diffusion step. Thus, the efficiency of premade copolymers is reduced.

4. Summary

With either premade or in situ formed copolymers as compatibilizers, the particle size of PMMA/PS blend can be decreased down to ∼1 μm scale and the particles are stable during static annealing. For the system studied here, generally reactively formed copolymers have better compatibilization efficiency than premade ones. For the reactive blends, graft and block copolymers can both compatibilize blends well and they can reduce the particle size down to 0.3 μm with about 10 wt% copolymers in the blends. It was found that graft copolymers work slightly better than block ones at the same concentration and we speculated that this is due to a greater capacity for reducing interfacial tension. For the premade blends, at low copolymer concentration block copolymers compatibilize better than graft ones on reducing particle size and even as well as the reactively formed ones. However at high concentration, graft copolymers work better.

Acknowledgements

This research has been supported by grants from the MRSEC program of the National Science Foundation under Award Number DMR-0212302, IPRIME (the Industrial Partnership for Research in Interfacial and Materials Engineering at the University of Minnesota) and the Dow Chemical Company. The authors thank Robert Jérôme and Zhihui Yin of the University of Liêge for providing the PS-NH_2, Bongjin Moon for synthesis of the functional PMMAs, and Steve Hahn of the Dow Chemical Company for providing the PS (18 kg/mol).

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[23] The breakup time, t_b is estimated to be on the order of 10 s for our system without compatibilizers but with similar viscosity as the blend components, fiber diameter of 200 nm, and the interfacial tension 1.5 mN/m for PS/PMMA. With compatibilizers, the interfacial tension should be less thus t_b will be longer. The quenching time after blending is much less than 10 s. Therefore, further annealing is required for the minor phase to have Rayleigh-typed breakup and for the blends to reach their equilibrium morphology.
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