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The Effect of the Amount of in Situ Formed Copolymers on the Final Morphology of Reactive Polymer Blends with an In Situ Compatibilizer

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ABSTRACT: The effect of the amount of in situ formed graft copolymers on the blend morphology was investigated for immiscible polymer blends of poly(butylene terephthalate) (PBT) and polystyrene (PS) having various amounts of poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) as an in situ compatibilizer. Two different blending methods were used to prepare the blends: a melt blending (MB) and a solution blending followed by an oscillatory shearing at a molten state (SOM). The molecular weight of in situ PS-*g*-PBT copolymers formed from the reaction between PS-GMA and PBT in the blend was determined by using high-temperature gel permeation chromatography (GPC). The concentration of in situ formed graft copolymers of PS-*g*-PBT in the blends [$C_{\text{copolymer}}$ (blend)] prepared by either MB or SOM was determined by solvent extraction followed by Fourier transform infrared spectroscopy (FTIR) analysis. On the basis of the GPC and FTIR results, we concluded that the PS-*g*-PBT in the blends has 1.3−2 PBT chains grafted onto a PS-GMA chain. From FTIR analysis and the morphology of the blends investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), we found that the interfacial areal density (Σ) of in situ formed PS-*g*-PBT is ∼0.1 chains/nm^2 for the blends prepared by SOM regardless of the amounts of PS-GMA added initially in the blend. However, although $C_{\text{copolymer}}$ (blend) in the blend prepared by MB was similar to that prepared by SOM, the dispersed domain size of the former was larger than that of the latter, especially for blends with a large amount of PS-GMA (20 wt %). This suggests that at least some parts of in situ graft copolymers in the blend prepared by MB are located in the matrix phase as micelles with sizes of 20−50 μm.

Introduction

The morphology of incompatible polymer blends with an in situ compatibilizer becomes a very fine structure, because copolymers formed by the reaction between functional groups existing in constituent components in the blend can reduce the interfacial tension between the dispersed phase and the matrix. Moreover, this finer morphology can persist even at higher shear stresses.

The final morphology of a polymer blend with an in situ reactive compatibilizer depends on various parameters: blend composition, interfacial tension between the dispersed phase and the matrix, processing temperature, flow type and rate, viscosity or elasticity of blend components, and the molecular weight and the amount of the in situ formed copolymer. Among these parameters, the last two affecting the interfacial properties of a blend are very important for determining the final morphology.

Much research has focused on investigating the effect of the initially added amount of an in situ compatibilizer in a reactive blend, not the *exact* amount of the in situ formed copolymers at the interface, on the final morphology owing to the experimental difficulties.[1,2] It has been reported that even if the amount of the in situ formed copolymers in the total blend becomes as much as 10 wt %, the dispersed domain size merely decreases from 4 to 2 μm.[3] However, a few studies on the interfacial reaction kinetics have shown that only ∼2 wt % in situ formed copolymers are enough to stabilize the blend morphology.[4,5] This suggests that when a blend with an in situ compatiblizer is prepared by a commonly used melt blending method, all the in situ formed copolymers are not guaranteed to be located at the interface. In this method the blend constituents and an in situ compatibilizer are put into a mixer at the same time and then are melt-mixed together.

Solution blending and precipitation methods allow one to prepare an immiscible polymer blend with a finer morphology, because phase separation is frozen kinetically during the precipitation. Using this method, one can prepare a polymer blend with an in situ compatibilizer having the same initial morphology regardless of initially added amounts of an in situ compatibilizer when there is no reaction during solution blending and precipitation.[6] Therefore, one can control the morphology of a solution-blended sample by changing the annealing time or shearing time and rate at higher temperatures, because morphological development and interfacial reaction occur at the same time.[6] Furthermore, in contrast to the above-mentioned commonly used melt blending method, for a blend prepared by this method, most in situ formed copolymers may be located at the interface between two immiscible phases when the reaction occurs, because an in situ compatibilizer is originally located in one phase miscible with it.

In this article, we have focused on the investigation of the effect of the actual amount of in situ formed graft copolymers, not the initially added amount of an in situ compatibilizer, on the blend morphology for an immiscible polymer blend. The blend system investigated in this study consisted of poly(butylene terephthalate (PBT) and polystyrene (PS) having various amounts of poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) as an in situ compatibilizer,[7−9] and the blend was prepared by two different blending methods: melt blending and solution blending followed by an oscillatory shearing at

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Table 1. Molecular Characteristics of Materials Used in This Study

symbol	trade name, supplier	M_n	M_w/M_n	numbers of reactant group
PS	GP-125, Miwon Petrochemical, Korea	55 000	3.6	
PBT	HV 1010, LG Chem. Co., Korea	25 000[a]	2.2	1.6
PS-GMA	made by suspension polymerization	46 000	2.5	6.4

[a] Determined from the measurement of intrinsic viscosity (I. V.) using the Mark−Houwink relationship (I. V. = $7.39 \times 10^{-5} M_v^{0.871}$ in which M_v is the viscosity-average molecular weight) and polydispersity index of 2.2 measured from GPC.[6]

a molten state. The molecular weight and the composition of in situ formed PS-*g*-PBT copolymers were determined to study how many chains are grafted onto a backbone chain.

Experimental Section

Sample Preparation. The molecular characteristics of polymers used in this study are given in Table 1.[6] The 75/25 wt/wt PBT/PS blends were prepared by using various amounts of PS-GMA (0, 5, and 20 wt % based on total PS phase consisting of neat PS and PS-GMA) by solution blending, and followed by precipitating the polymer into powders by using methanol. Phenol and *o*-dichlorobenzene (OCB) were used as the solvents of PBT and (PS + PS-GMA), respectively, and methanol as a nonsolvent of all polymers. To prevent any reaction between PBT and PS-GMA during preparation of polymer solution, 4.5 wt % of PBT solution in phenol was prepared in one beaker, and 1.5 wt % of a PS and PS-GMA solution in OCB was prepared in the other. PBT was dissolved completely into phenol at 60 °C, and neat PS and PS-GMA into OCB at room temperature. The two solutions were mixed at ~40 °C for 5 min, and precipitated immediately into powder form by using excess methanol.

Powders were washed repeatedly with fresh methanol to remove the residual solvents from the blend, dried at room temperature for 1 day, and further dried at 60 °C for 2 weeks in a vacuum. Completely dried powders were molded into a plaque of 1-mm thickness using a compression molder for 2 min at 230 °C. The reason for choosing these conditions for the compression molding is as follows. The solution-blended sample with very fine powder forms was easily molded at 230 °C into a plaque of 1-mm thickness under high pressure even though the melting temperature of the PBT used in our study was ~230 °C. Also, during this molding process, the reaction between PBT and PS-GMA did not occur due to lower temperatures and short time.[6] This was confirmed by Fourier transform infrared spectroscopy (FTIR) that is described later. We found that smaller dispersed domains with a size smaller than 0.2 μm were observed in the blends, and these domain sizes were not varied by the initially added amount of PS-GMA in the blends.[6] This indicates that the reaction between PS-GMA and PBT did not occur during the compression molding and solution blending. Because this fine morphology is at a kinetically frozen state not at a steady state, it develops into the steady morphology under shearing at higher temperatures.[6]

A shear frequency of 1 rad/s was applied to each solution-blended sample for 1 h at 245 °C by use of a Rheometrics Dynamic Spectrometer (RDS−II) with 25-mm cone and plate fixture under the strain of 0.15. The 1 rad/s frequency was chosen because the phase-separated morphology or the domain size of the dispersed phase of the solution-blended sample without PS-GMA after an oscillatory shearing at this frequency becomes similar to that of the melt blended sample without PS-GMA.

Also, we found that after the oscillatory shearing of 1 rad/s for 1 h, the morphology and the rheological properties of the solution-blended samples reached steady state. We noticed that the dispersed domain size of the solution-blended sample without PS-GMA increased with increasing frequency because of enhanced coalescence.[6] After 1 h oscillatory shearing, each blend was quenched very rapidly to room temperature (less than 1 min) by liquid nitrogen.

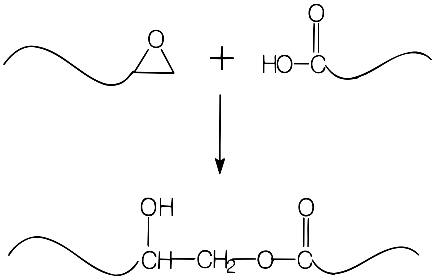

Figure 1. Schematic of the reaction between PS-GMA and PBT.

The 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA were also prepared by using a MiniMax molder at a speed of 70 rpm at 245 °C for 15 min. The morphology and the rheological properties of the melt blended sample did not change even if a further oscillatory shearing at 1 rad/s was done for 1 h. This implies that the morphology in the blend prepared by a melt blending represents a steady state. Hereafter, solution blending followed by oscillatory shearing at 1 rad/s for 1 h at 245 °C is referred to as "SOM" and the melt blending as "MB". Figure 1 is a schematic of the reaction between PS-GMA and PBT.

The morphology of each blend was investigated by scanning electron microscopy (SEM; Hitachi S 570) and by transmission electron microscopy (TEM; JEOL 1200EX). For SEM, a fractured sample surface at liquid nitrogen atmosphere was observed. To improve the phase contrast between two phases, the PS phase in the fractured specimen was further etched out by tetrahydrofuran for 5 min and then coated with a thin layer of gold. The number-average dispersed domain size (D_n) of domains greater than 200 was obtained by using a Quantimet 570 image analyzer (Cambridge Instruments). The cross-sectional area (A_i) of each particle on the micrograph was measured and then converted into the diameter (D_i) of a circle having the same cross-sectional area.

$$D_i = 2\,(A_i/\pi)^{1/2} \tag{1}$$

The specimen for TEM was sliced into a very thin film with ~50 nm thickness by a microtoming machine (MT-7000, Research and Manufacturing Company) with a diamond knife at room temperature, and then it was stained for 1 h by using ruthenium tetroxide (RuO_4) vapor. The PS phase appears dark because of staining.

FTIR Spectroscopy Analysis. A solvent extraction method was used to separate PS-*g*-PBT copolymers from blend constituents of PBT and PS. The specimen prepared by either SOM or MB was dissolved into a mixed solvent of phenol and OCB (50/50 v/v) at 50 °C for 2 h. Madec and Marechal[10] reported that the noncatalyzed reaction rate constant, *k*, of octadecanoic acid and 1-dodecyloxy-2,3-epoxy propane in OCB at 121 °C is 4.2×10^{-6} kg mol^{-1} s^{-1}. Therefore, very little, if any, reaction occurred between the unreacted PBT and PS-GMA in phenol/OCB at 50 °C. The solvent extraction procedure was as follows. First, PBT homopolymer and most PS-*g*-PBT copolymers in the blend were precipitated using toluene and separated from the above-mentioned solution. Then, PS homopolymer, unreacted PS-GMA, and a very small amount of PS-*g*-PBT copolymers were precipitated by pouring the remaining solution into excess methanol. This procedure was repeated twice on each blend for the complete separation.

A mixture of KBr powder and a few milligrams of polymer sample was pelletized for FTIR analysis. To prepare a calibration curve for quantitative FTIR analysis, PBT/PS-GMA and PBT/PS blends with the predetermined blend compositions were made by using a solution-blending method. For the determination of PS concentration in extracted PBT phase, the standard samples of PBT/PS-GMA blend with the known amount (0−25 wt %) of PS-GMA were prepared by solution blending of PBT and PS-GMA. Also, for the determination of PBT concentration in extracted PS phase, the standard samples of PBT/PS blend with the known amount (0−5 wt %) of PBT were prepared.

High-Temperature Gel Permeation Chromatography (GPC). To determine the molecular weight of in situ PS-*g*-PBT copolymers formed during the reaction between PS-GMA and PBT in the blend, we extracted the graft copolymers from the blend by a solvent/nonsolvent method. First, the graft copolymers were ground into fine powders and the unreacted PBT was removed from the blend by using trifluoroacetic acid (TFA) for 2 days. TFA is a good solvent for PBT but a nonsolvent for PS and PS-*g*-PBT. The fine powders could be obtained when the solution was passed through a packing column (∼1 cm) made of a Celite-545 (Aldrich Chemical) with a size of ∼5 μm. Filter paper was not good for the separation of PS and PS-*g*-PBT from TFA solution, because the strong acid of TFA could tear the filter paper. When the TFA-soluble solution was precipitated with methanol, any characteristic peak corresponding to PS could not be detected in the FTIR spectra. Fine powders of PS, unreacted PS-GMA, and PS-*g*-PBT copolymers placed above the Celite layer were dissolved in the mixed solvent of phenol/OCB (50/50 v/v) at 50 °C for 2 days. Then, PS and unreacted PS-GMA were removed by using toluene, which is a good solvent for both PS and unreacted PS-GMA, but a nonsolvent for PS-*g*-PBT copolymers. Thus, only PS-*g*-PBT copolymers were obtained as the precipitates. When the toluene-soluble solution was precipitated using methanol, any characteristic peak corresponding to PBT was not detected in the FTIR spectra. These extraction procedures were repeated twice. The molecular weight and molecular weight distribution of PS-*g*-PBT copolymers were determined by high-temperature GPC (PL-GPC210; Polymer Laboratory Co.) at 150 °C using trichlorobenzene (TCB) as the solvent of PBT, PS, and PS-*g*-PBT copolymers. Only the reflective index difference between the solvent and polymers could be monitored because the device for measuring the UV difference between the solvent and polymers was not available on this GPC. For the purpose of comparison, GPC chromatograms of unreacted PS-GMA and unreacted PBT were also obtained. A calibration curve based on monodisperse PS was used to determine the molecular weight.

Results and Discussion

We found that no reaction occurred between PS-GMA and PBT in the blend during the solution blending and subsequent compression molding. This was confirmed by the fact that the PS (or PBT) concentration in the extracted PBT (or PS) was negligibly small (less than 0.1 wt %) when the above-mentioned FTIR analysis was performed. This lead us to consider that, for the solution-blended sample with PS-GMA, the reaction between carboxylic acid in PBT and epoxy group in PS-GMA started to occur during the oscillatory shearing at 245 °C.

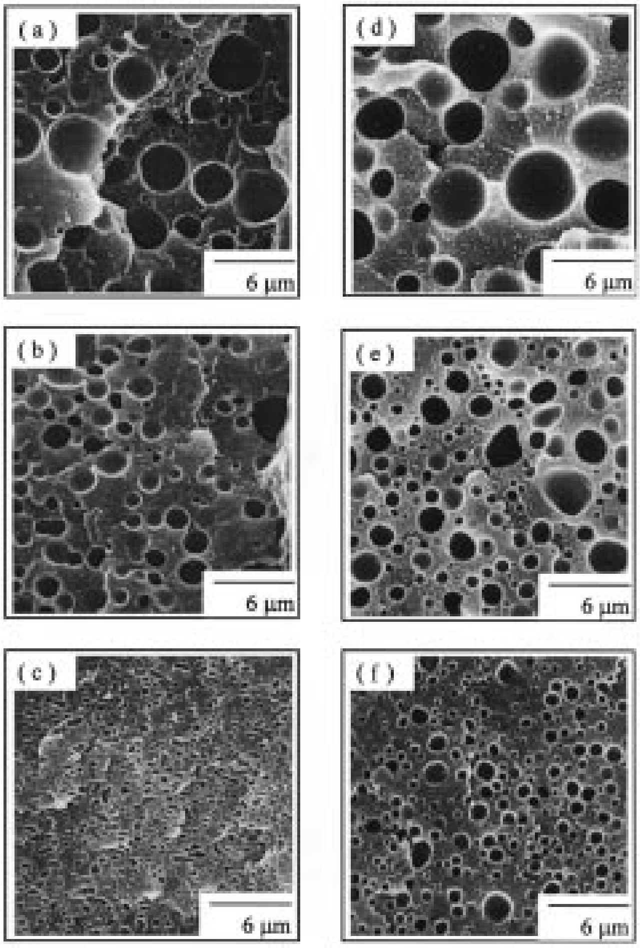

Figure 2. Scanning electron micrographs of 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA based on total PS phase prepared by SOM (a−c) and by MB (d−f). The amount of PS-GMA: a, d, 0 wt %; b, e, 5 wt %; and c, f, 20 wt %.

Figure 2 shows scanning electron micrographs of 75/25 wt/wt PBT/PS with various amounts of PS-GMA prepared by SOM (a−c) and by MB (d−f). When there is no PS-GMA, the dispersed domain size, $D_{0,\mathrm{m}}$, in the sample prepared by MB is similar to that, $D_{0,\mathrm{s}}$, in the sample prepared by SOM. Whereas the domain sizes of the MB samples with 5 and 20 wt % PS-GMA are 1.25 μm and 0.79 μm, respectively, those of the SOM samples with 5 and 20 wt % PS-GMA are 1.00 μm and 0.3 μm, respectively. For the MB and SOM with 5 wt % PS-GMA, the difference in domain size is not great (less than 25%). However, for the blends with 20 wt %, the domain size of MB is about the twice that of SOM. Even if a different sequence for melt blending is used—for instance, pellets of PS and PS-GMA are mixed at 245 °C for 3 min, then PBT is added to this mixture—we found that the dispersed domain size of the blend is similar to that of a blend prepared by melt mixing three components at the same time. Therefore, we conclude that the morphological development in SOM is different from that in MB regardless of the sequences for melt blending. During melt blending, the blend of PBT/PS/PS-GMA has two kinds of interface, one between PS and PBT and the other between PS-GMA and PBT. The reaction at the interface between PS-GMA and PBT to form in situ PS-*g*-PBT copolymers occurs simultaneously with a morphological change from very large dispersed domain size on the order of millimeters (namely pellet size) to the final small domain size**.** Some portions of in situ formed PS-*g*-PBT copolymers near the interface between PBT and PS can move toward the interface between PS and PBT phases because of decreasing unfavorable interaction. However, the rest aggregate into micelles in the matrix; thus, they are hard to diffuse into the interface between PS and PBT. Therefore, these portions cannot play a role in effective compatibilizers.

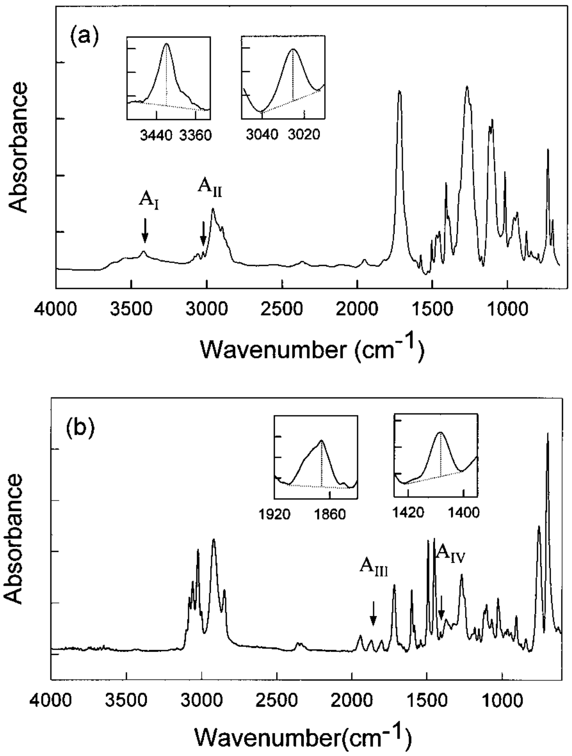

Figure 3. FTIR spectra of (a) 90/10 wt/wt PBT/PS-GMA and (b) 4/96 wt/wt PBT/PS. The absorbance of each characteristic peak indicated by the arrow was calculated by the height from the baseline as shown in the insets.

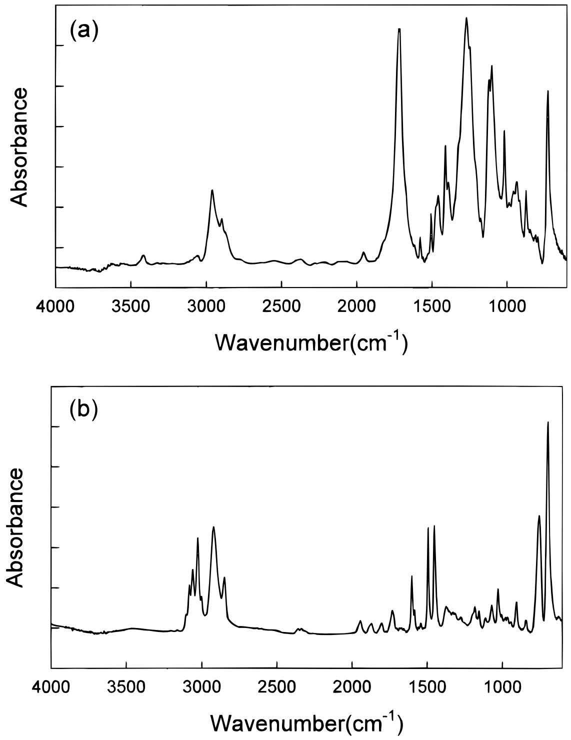

Figure 4. FTIR spectra of (a) neat PBT and (b) neat PS.

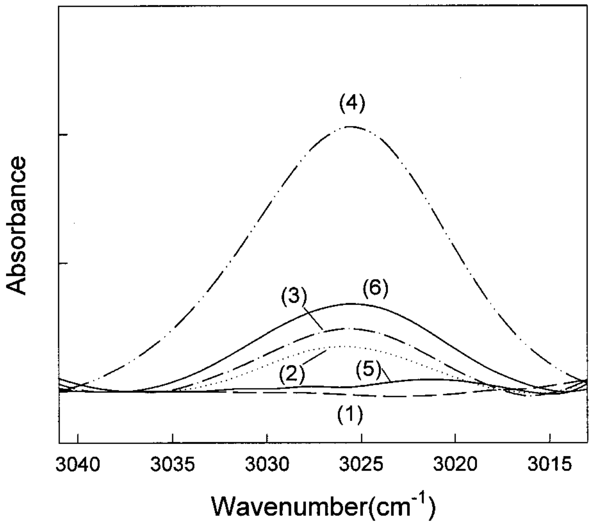

Figure 5. FTIR spectra at $\nu = 3025$ cm^{-1} normalized by the absorbance of the peak of A_I for the PBT/PS-GMA blend at various predetermined amounts of PS-GMA (1−4), and for in situ formed PBT-*g*-PS copolymers extracted from 75/25 PBT/PS blends with 5 and 20 wt % PS-GMA prepared by SOM (5, 6): (1) PS-GMA 1 wt %; (2) 3 wt %; (3) 4 wt %; (4) 10 wt %; (5) PS-GMA 5 wt %, extracted; (6) 20 wt %, extracted.

On the other hand, because the finer initial morphology found in the solution-blended sample is frozen kinetically owing to precipitation, the dispersed domain can be easily increased by phase separation at higher temperatures resulting from high incompatibility of the constituent components and large mobility of the chains with increasing time. However, because almost all of PS-GMA can exist in the PS phase, in situ formed copolymers are located at the interface between PBT and PS phases. In other words, during shearing of the solution-blended sample at 245 °C, there is little, if any, possibility that in situ formed copolymers are located in the PBT matrix as micelles. Therefore, the growth of the dispersed domain in the solution-blended sample during the shearing at 245 °C is more efficiently suppressed than in a melt-blended sample.

The FTIR spectra of 90/10 wt/wt PBT/PS-GMA blend and 4/96 wt/wt PBT/PS blend which were prepared for a calibration curve are given in Figures 3a and 3b, respectively. Figure 3a shows that (i) the peak indicated by the arrow at $\nu = 3400$ cm^{-1} (A_I for its absorbance) corresponds to −OH in PBT, which does not appear in the neat PS (Figure 4b); and (ii) the peak indicated by the arrow at $\nu = 3025$ cm^{-1} (A_{II}) corresponds to the aromatic C−H stretch in PS, which does not appear in the neat PBT (Figure 4a). Figure 3b lso shows that (i) the peak indicated by the arrow at $\nu = 1870$ cm^{-1} (A_{III}) corresponds to the characteristic peak of the aromatic ring in the PS, which does not appear in the neat PBT (Figure 4a), and (ii) the peak indicated by the arrow at $\nu = 1408$ cm^{-1} (A_{IV}) corresponds to the aliphatic CH_2 of PBT, which does not appear in the neat PS (Figure 4b).

The absorbance of each characteristic peak was calculated by the height from the baseline as shown in the inner boxes in Figures 3a and 3b. By this method, we could obtain the expression given in eq 2 for the determination of the amount of PS in a blend, which was obtained by using PBT/PS-GMA blends with predetermined amounts of 0−25 wt % PS-GMA.

$$A_{II}/A_I = 12.43696\, C_{PS}\ (\text{extract}) \qquad (2)$$

Similarly, an expression for the determination of the amount of PBT in the blend was given by eq 3, which was obtained by using PBT/PS blends with predetermined amounts of 0−5 wt % PBT.

$$A_{IV}/A_{III} = 17.45777\, C_{PBT}\ (\text{extract}) \qquad (3)$$

Table 2. The Concentration and the Interfacial Areal Density of In Situ Formed Copolymers for 75/25 PBT/PS Blends

	blending method			
	SOM		MB	
	PS-GMA5	PS-GMA20	PS-GMA5	PS-GMA20
D_n (μm)	1.00	0.30	1.25	0.79
C_{PS} (extract) (wt %)	1.6	5.6	1.5	6.0
$C_{copolymer}$ (blend) (wt %)	1.5	5.4	1.4	5.7
Σ (chains/nm^2)	0.10	0.10	0.12[a]	0.30[a]

[a] Calculated assuming that all the in situ formed PBT-*g*-PS during MB is located at the interface.

The correlation coefficients for the linear regression given in eqs 2 and 3 are 0.997 and 0.991. Here, C_{PS} (extract) and C_{PBT} (extract) in eqs 2 and 3 are the concentration of PS in the extracted PBT-rich phase and the concentration of PBT in the extracted PS-rich phase, respectively. The above-mentioned linear regression was done on the basis of all data including the condition that the value of A_{II}/A_I (or A_{IV}/A_{III}) should be zero when C_{PS} (PBT) [or C_{PBT} (PS)] equals zero. Almost all the PS-*g*-PBT copolymers were found to exist in the PBT-rich phase, and the PBT concentrations in the extracted PS phase [C_{PBT} (extract)] were less than 0.1 wt % and 0.3 wt % for the blends with 5 wt % and 20 wt % PS-GMA, respectively. Therefore, we could neglect C_{PBT} (extract), that is, eq 2 used to determine the amount of in situ formed PS-*g*-PBT.

The FTIR spectra near $\nu = 3025$ cm^{-1} for PS-*g*-PBT extracted from 75/25 PBT/PS blends with 5 and 20 wt % PS-GMA prepared by SOM are given in Figure 5. Also, these FTIR spectra for the PBT/PS-GMA blends with known content of PS-GMA are added for comparison. From Figure 5 and eq 2, the values of C_{PS} (extract) for the SOM and the MB samples are calculated and given in Table 2.

The interfacial areal density of an in situ formed copolymer (Σ) is given by:

$$\Sigma = \frac{C_{\text{copolymer}}\,(\text{blend})N_{\text{av}}\rho_{\text{blend}}D}{6M_{\text{copolymer}}\phi_{\text{d}}} \tag{4}$$

where $C_{copolymer}$ (blend) is the copolymer concentration in the total blend, which is obtained by:

$$C_{\text{copolymer}}\,(\text{blend}) = \frac{C_{\text{PS}}\,(\text{extract})w_{\text{PBT}}M_{\text{copolymer}}}{M_{\text{PS-GMA}}} \tag{5}$$

Here, N_{av} is Avogadro's number, ρ_{blend} is the density of the blend, D is the diameter of the dispersed domain, and ϕ_d is the volume fraction of the dispersed phase. ρ_{blend} is calculated by using a mixing rule, $\rho_{blend} = w_{PBT}\rho_{PBT} + w_{PS}\rho_{PS}$, where w_i is the weight fraction of blend component i, and ρ_{PBT} and ρ_{PS} at 245 °C are 1.24[11] and 0.94 g/cm^3,[13] respectively. By substituting eq 5 into $C_{copolymer}$ (blend) of eq 4, we could calculate the Σ given in Table 2 using only the value of C_{PS} (extract) obtained from the FTIR analysis, even if the values of $C_{copolymer}$ (blend) and $M_{copolymer}$ were not determined.

However, $C_{copolymer}$ (blend) and $M_{copolymer}$ are very important for characterizing the in situ formed PS-*g*-PBT copolymers. To determine $M_{copolymer}$, the number of grafted chains on the backbone chain should be estimated. Guegan et al.[4] showed that poly(methyl methacrylate-*ran*-glycidyl methacrylate) (PMMA-*r*-GMA) reacts with carboxylic acid terminal polystyrene (PS−COOH) at only one reactive site investigated by size exclusion chromatography (SEC) analysis. Also, Sha et al.[14] reported that randomly carboxylated deuterated PS (dPS-*r*-COOH) may couple with epoxy at one reactive site per dPS-*r*-COOH chain judged by the fracture toughness experiment of epoxy/high-impact polystyrene interfaces reinforced by grafted chains. This suggests that only a single PBT chain might be grafted onto a backbone chain of PS-GMA.

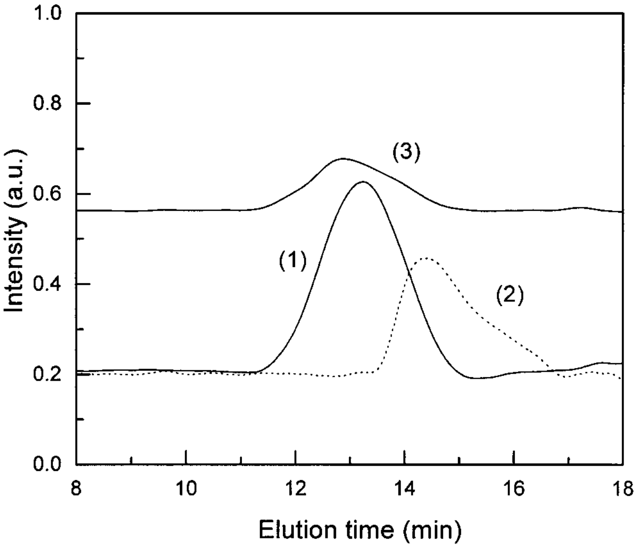

Figure 6. GPC chromatograms of (1) neat PS-GMA, (2) neat PBT, and (3) PS-*g*-PBT copolymer extracted from the blend.

But, in the blend used in this study, it is unlikely that only one chain was grafted because the number of reactant groups of GMA in one PS-GMA chain is as many as 6.4. Therefore, in this study, $M_{copolymer}$ was directly measured by high-temperature GPC analysis as described previously. Figure 6 shows GPC chromatograms of neat PBT and PS-GMA, and PS-*g*-PBT copolymers extracted from the blend. We found that GPC chromatograms of neat PBT and PS-GMA were the same as those experienced at the same condition for the blend preparation. This implies that the degradation of the PBT or PS-GMA during the sample preparation is negligible. Based on PS standard curves, the weight-average molecular weights (M_w) of neat PBT and PS-GMA, and PS-*g*-PBT copolymers are determined to be 15 000, 137 000, and 156 000, respectively. This implies that the molecular weight of the PS-*g*-PBT graft copolymers formed in the blend is about the sum of one PS-GMA and 1.3 PBT chains, that is, the graft copolymer has 1.3 PBT chains grafted onto a PS-GMA chain if the values of M_w are used. The M_w of neat PS-GMA obtained here is very near that given in Table 1. But, the M_w of the neat PBT obtained here is less than that of PBT given in Table 1. This is not caused by the degradation of PBT during the blend preparation, but by the difference between the hydrodynamic volumes of PBT and PS. On the other hand, the number-average molecular weights (M_n) of neat PBT and PS-GMA, and PS-*g*-PBT copolymers are determined to be 6 300, 47 000, and 60 000, respectively. This suggests that in the graft copolymer two PBT chains are grafted onto a PS-GMA chain if the values of M_n are used. Therefore, on the basis of M_w and M_n obtained from Figure 6, we conclude that the molecular weight of the PS-*g*-PBT graft copolymers formed in the blend is about the sum of a PS-GMA and 1.3−2 PBT chains. Furthermore, we found that when FTIR analysis was used for the extracted PS-*g*-PBT copolymers, the weight fraction of PBT in the graft copolymers was determined to be 46%, which implies that the graft copolymer has 1.8 PBT chains grafted onto a PS-GMA chain. For the determination of the composition of the PS-*g*-PBT copolymer by using FTIR analysis, PBT/PS-GMA blends with the known amount (30−70 wt %) of PS-GMA were used as the standard samples. The GPC chromatograms of PS-*g*-PBT copolymers extracted for all blends used in this study are almost the same. This implies that even though the amount of PS-GMA is 20 wt % in the dispersed phase (namely, 5 wt % in the total blend), the number of grafted chains is similar regardless of preparation method (SOM vs MB) and the amount of PS-GMA added. Therefore, we have concluded from the GPC and FTIR results that the PS-*g*-PBT copolymer in the blend has 1.3−2 PBT chains grafted onto a PS-GMA.

Once the $M_{\mathrm{copolymer}}$ is obtained, $C_{\mathrm{copolymer}}$ (blend) is calculated by eq 5. The calculated values of $C_{\mathrm{copolymer}}$ (blend) for SOM and MB samples are given in Table 2. The values of $C_{\mathrm{copolymer}}$ (blend) given in eq 5 are similar to those obtained by the double-extraction method described in the Experimental Section. In Table 2 the dispersed domain size of the SOM sample with 20 wt % PS-GMA is smaller than that of the MB sample with the same amount of PS-GMA, although both blends have almost the same amount of in situ formed graft copolymers. This leads us to conclude that at least some parts of in situ graft copolymers formed during melt blending are not located at the interface, especially when the amount of PS-GMA in the blend is large (20 wt %). Thus, the interfacial activity of MB is less efficient than that of SOM.

In the SOM sample, the value of Σ of ~0.1 chains/nm^2 does not vary with initially added amounts of the in situ compatibilizer (see Table 2). This value seems to be reasonable when compared with other experiments conducted by Macosko and co-workers,[4,15] who showed that Σ of 0.1 chains/nm^2 is sufficient to inhibit the coalescence of the dispersed domain, and by Dai et al.,[16] who reported that the maximum value of Σ for poly(styrene-*b*-2-vinylpyridine) (PS-*b*-PVP) in the PS/PVP system is ~0.15 chains/nm^2.

But, for the MB sample, if all of the in situ PS-*g*-PBT copolymers formed during melt blending were located at the interface, the values of Σ would be high as shown in Table 2. When the interfacial thickness (l) between the PBT matrix and the PS domain was assumed to be half of the lamellar spacing[15] of a PS-*g*-PBT copolymer, a value of Σ of 0.36 chains/nm^2 was obtained by substituting the interfacial volume, ϕ_{int} into $C_{\mathrm{copolymer}}$ (blend) in eq 4. Here, ϕ_{int} is expressed by $(6l/D)\phi_{\mathrm{d}}$. Also, half of the lamellar spacing was calculated to be 29.7 nm[17] by using Helfand's theory[19] with the following expression of the interaction parameter (χ) between PBT and PS:

$$\Lambda = \frac{\chi RT}{V_{\mathrm{ref}}} = (\delta_{\mathrm{PS}} - \delta_{\mathrm{PBT}})^2 \tag{6}$$

where R is the gas constant, T is the absolute temperature, and V_{ref} is the reference volume given by $V_{\mathrm{ref}} = (v_{\mathrm{PS}}[M_{\mathrm{o}}]_{\mathrm{PS}} v_{\mathrm{PBT}}[M_{\mathrm{o}}]_{\mathrm{PBT}})^{0.5}$, where v_{PS} and v_{PBT} are specific volumes of PS and PBT, and $[M_{\mathrm{o}}]_{\mathrm{i}}$ is the monomeric molecular weight of component i. Although the values of the solubility parameter, δ, vary widely from one reference to another, in this study we estimate that the δ values of PS and PBT are 18.7 and 20.9 (J/cm^3)$^{0.5}$, respectively,[8] as calculated by the group contribution method.[20] When Meier's theory[21] was used, half of the domain spacing for above the PS-*g*-PBT copolymer was calculated to be 35.6 nm, which is about 1.2 times that obtained by Helfand's theory.

In addition, when a Σ of 0.1 chains/nm^2 is required to stabilize the domain size,[4,15,16] only 1.54 and 2.44 wt % PS-*g*-PBT copolymers are enough to do so for the melt-blended samples with 5 and 20 wt % PS-GMA, respectively. This suggests that for the MB with 20 wt % PS-GMA, less than 35% of in situ formed graft copolymers are actually located at the interface, and the remaining exist in the matrix as micelles.

To find whether micelles indeed exist in the PBT matrix, we took transmission electron micrographs for the SOM and MB samples, which are given in Figure 7. The average dispersed domain sizes of SOM samples with 5 and 20 wt % PS-GMA are 0.9 and 0.3 μm, respectively. Also, those of MB samples with 5 and 20 wt % PS-GMA are 1.1 and 0.7 μm, respectively. Therefore, the dispersed domain sizes in Figure 7 are consistent with those in Figure 2 and Table 2. For SOM samples with 5 and 20 wt % PS-GMA, the number of very small particles looking like micelles in the matrix is a rather small. However, as shown in Figure 7c and 7d, the MB samples with 5 and 20 wt % have very fine dispersed domains of size 20−50 nm, and the domain size of the bigger PS phase is consistent with SEM results. These finer dispersed domains are considered as the waste (or micelles) of in situ formed graft copolymers between the PBT and PS phase.

Because the theory developed by Leibler et al.[22] and extended by Roe[23] allows us to calculate the theoretical micelle size, we could compare this with the experimental results shown in Figure 7. In this study, we assumed that the core in the micelle consists of entire PS chains in PS-*g*-PBT, whereas the corona consists of PBT chains in PS-*g*-PBT and homopolymer PBT. Using eq 4 and this theory,[22,23] we calculated the core radius and corona length to be 21.9 and 21.3 nm, respectively, whereas the unperturbed root-mean-square end-to-end distance, $\langle R^2\rangle_0^{(1/2)}$, for PS and PBT chains in PS-*g*-PBT is 13.5 and 21.0 nm, respectively. The large increase (1.62 times) in the size of PS chains in the core compared with $\langle R^2\rangle_{0,\mathrm{PS}}^{(1/2)}$ is attributed to the fact that this copolymer is in a very strong segregation limit because χN of this PBT-*g*-PS is 95.5. The predicted value of 21.9 nm for the core radius (or 43.8 nm in diameter) is in good agreement with experimental micelle sizes of 20−50 nm shown in Figure 7, even if many assumptions made in the calculation are considered.[24]

Recently, an experiment[25] demonstrated that the interface is not necessarily covered by only a single layer of in situ formed graft (or block) copolymers. Thus, even if a dense single layer of a block copolymer covers the entire interface, a fresh reactant polymer in bulk phase can diffuse and arrive at some positions of the interface because the interface can undulate because of reduced interfacial tension. Multiple layered interface or self-assembled morphology in the reactive blend could be seen for the case that the reaction rate was faster than the interfacial area generation rate by the interfacial undulation, and this behavior was accelerated by an

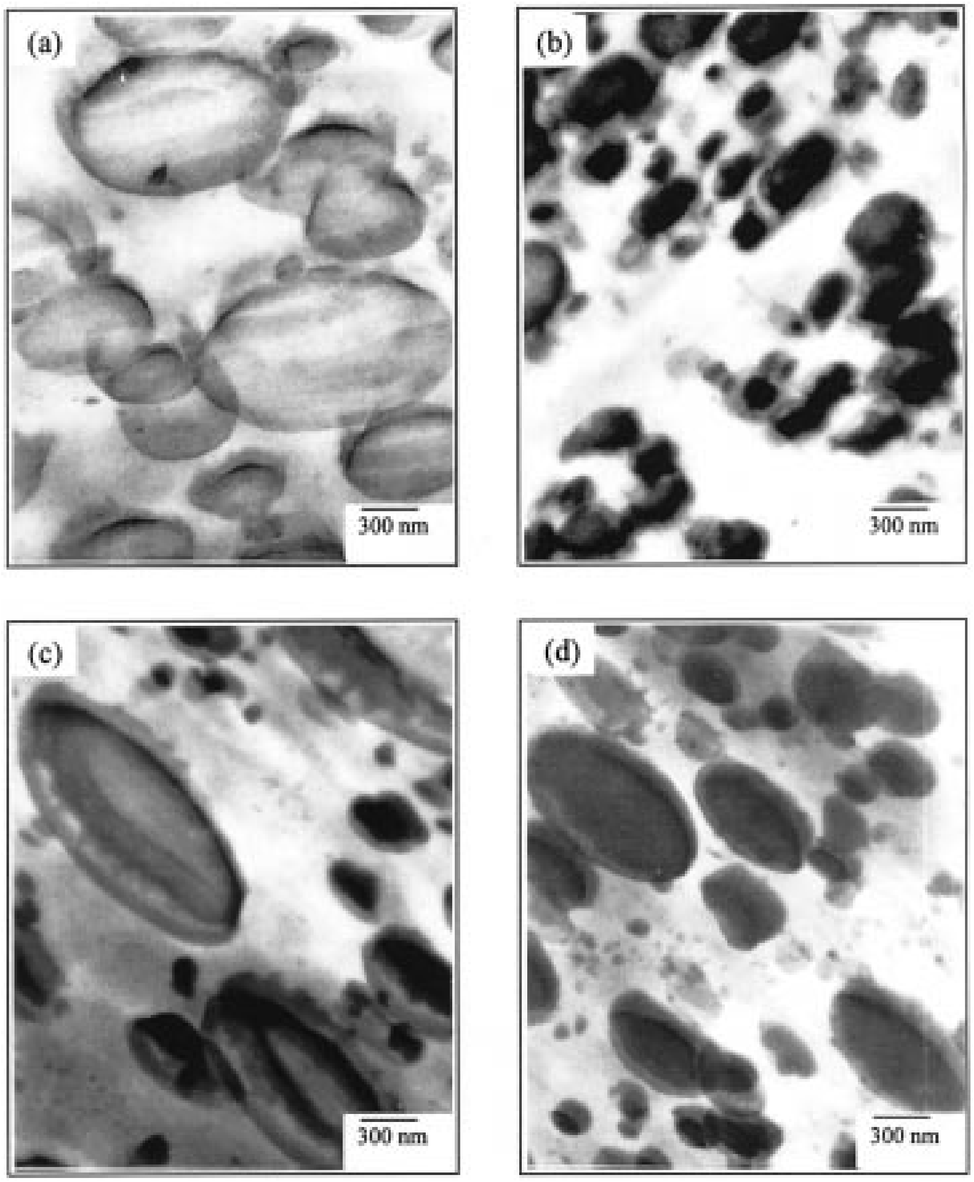

Figure 7. Transmission electron micrographs of 75/25 wt/wt PBT/PS blends with various amounts of PS-GMA based on total PS phase prepared by SOM (a, b) and by MB (c, d). The initially added amount of PS-GMA in each blend: a, c, 5 wt %; and b, d, 20 wt %.

external flow.[25] However, in this study we could not observe the multiple layered interface (or undulated interface) for the PBT/(PS + PS-GMA) blend as shown in Figure 7. Although the exact explanation of the absence of the multiple layered interface in this study compared with the results in ref 25 is not clear, we made the following speculations as the reasons for this observation: (1) the smaller amount of reactive compatiblizer (20 wt % in the minor PS phase) compared with that (100 wt % in the minor PI phase) in ref 25; (2) the different type of in situ formed copolymer, namely the graft copolymers in this study versus the block copolymers in ref 25, where the deformation of the interface covered with graft copolymers might be more difficult than that covered with block copolymers; (3) the larger molecular weight (MW) of in situ formed copolymers in this study compared with the MW of block copolymer in ref 25. Therefore, the small particles of 20−50 nm shown in Figure 7d were not formed due to the pinch-off from the interface by the undulation but were due to the micelles.

Based on Figures 2 and 7 and Table 2, we propose schematically the morphological development of a reactive blend prepared by SOM and MB as shown in Figure 8. We conclude that whenever a MB method is used, it is inevitable to have some parts of in situ graft copolymers at the matrix phase as micelles; thus the interfacial activity is not as good as that prepared by SOM.

Conclusions

In this study, on the basis of FTIR analysis and SEM and TEM, we have shown that for an immiscible blend of PBT and PS with PS-GMA prepared by SOM, the interfacial areal density (Σ) of in situ formed PS-*g*-PBT is $\sim$0.1 chains/nm^2 regardless of the initially added amounts of PS-GMA in the blend. However, it was found that although the amount of in situ formed graft copolymers in a blend prepared by a MB method is similar to that in another blend prepared by SOM, the dispersed domain size of the former is larger than that of the latter. This leads us to conclude that for MB samples at least some parts of in situ formed graft

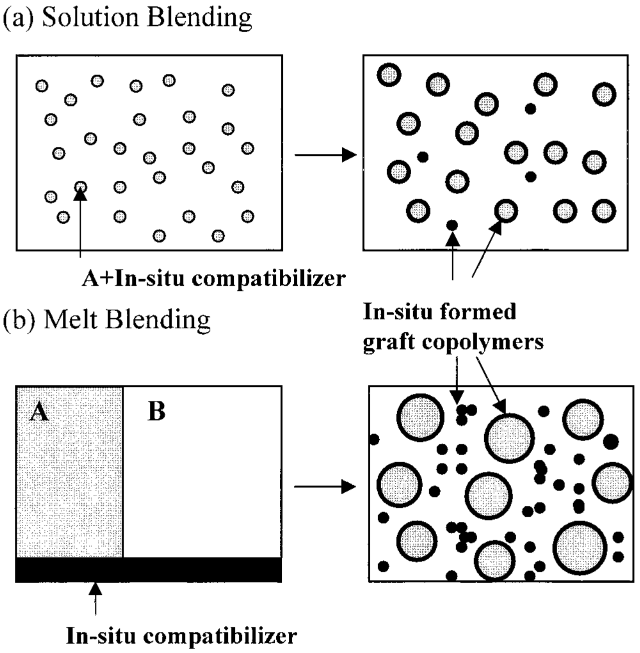

Figure 8. Schematic of morphological development for blends prepared by (a) SOM and (b) MB.

copolymers exist in the matrix as micelles with sizes of 20−50 nm. However, for SOM samples, almost all in situ formed graft copolymers are located at the interface between PBT and PS phases. Therefore, even if a larger amount of in situ graft copolymers is obtained by an extraction method for MB samples, it does not necessarily guarantee that the dispersed domain sizes in these blends should be on the order of submicrons. From the molecular weight determined by GPC and the composition by FTIR of PS-*g*-PBT copolymer, we conclude that the graft copolymer in the blend has 1.3−2 PBT chains grafted onto a PS-GMA chain.

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