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# Compatibilization mechanism of polymer blends with an *in-situ* compatibilizer

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An *in-situ* compatibilizer of poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) was used to study the effect of blend compositions on the morphology of two different blend systems, i.e. poly(ethylene-*ran*-acrylic acid) (PE-AA) and polystyrene (PS) blend, and poly(butylene terephthalate) (PBT) and PS blend. The epoxy group in PS-GMA reacted easily with the carboxylic acid group in both PE-AA and PBT, thus PS-*graft*-PE (or PS-*graft*-PBT) copolymer as a compatibilizer was formed. We have shown that when there is no PS-GMA in both blend systems, the domain size of the dispersed phase in PE-AA/PS was larger than that in PBT/PS at the same blend composition. However, by increasing PS-GMA contents the reduction in the reduced domain size, defined by the ratio of the dispersed domain size with PS-GMA to the dispersed domain size without PS-GMA, in the PE-AA/PS blend system was greater than that in the PBT/PS blend system. These are attributed to the fact that Flory interaction parameter, $\chi$, between PE-AA and PS was greater than that between PBT and PS. Based upon the experimental observation that the reduced domain size with PS-GMA contents was collapsed into one master curve regardless of blend compositions in each blend system, a compatibilization mechanism of blend with a reactive compatibilizer was proposed and discussed in terms of the interfacial area occupied by one compatibilizer chain at the interface. © 1997 Elsevier Science Ltd.

**(Keywords: compatibilization mechanism; morphology; domain size)**

## INTRODUCTION

Polymer blends often exhibit poor mechanical properties due to incompatibility resulting from the lower entropy of mixing of high molecular weight polymers and the unfavourable enthalpic interaction between the constituent components[1,2]. Enhancement in the degree of compatibility between the constituent components can be made by an addition of a compatibilizer to incompatible polymer blends. A block or a graft copolymer has been known to be very effective in reducing the interfacial tension and in improving the interfacial adhesion by making entanglements or bridging different polymer chains near the interface[3–8]. However, there are some limits to use a block or a graft copolymer as a compatibilizer in polymer blends. Since most block copolymers are in the microphase separated state at mixing temperatures, they have high viscosities, making it difficult to disperse them near the interface between two phases. Also, an added block copolymer may stay in a homopolymer phase as a micelle, rather than move to the interface[9–11]. In order to avoid these shortcomings, reactive blending techniques that *in-situ* graft or block copolymers as compatibilizers are produced due to the reaction between functional units existing in polymer blends during melt blending, have been proposed and developed[12–15]. The morphology of incompatible polymer blends in the presence of the copolymers formed by the reaction becomes very fine structure due to the reduction of the interfacial tension between the dispersed phase and the matrix[16,17] and this finer morphology can be persisted even at higher shear stresses. The ability (or efficiency) of a compatibilizer to decrease the domain size of the dispersed phase in blends depends on processing parameters, e.g. processing temperature, shear rate, the difference in viscosity or elasticity of the constituent components, the interaction parameter (or interfacial tension) between constituent components, the molecular weight, and the amount of compatibilizer formed.

Taylor[18,19] first studied the deformation and disintegration of a single Newtonian drop under the simple shear field, and considering the interfacial force and the shear force he calculated the maximum drop size ($D$), above which a drop is unstable at given shear stress, can be given by

$$D = \frac{\Gamma}{\eta_m \dot{\gamma}} F(\eta_r) \qquad (1)$$

where $\Gamma$ is the interfacial tension between two components, $\dot{\gamma}$ is the shear rate, $\eta_m$ is the matrix viscosity, and $\eta_r$ is the viscosity ratio of drop component to matrix component. According to Taylor, function $F$ in equation (1) is given by $(\eta_r + 1)/(19\eta_r/16 + 1)$.

Wu[20] found that for nylon and poly(ethylene-*ran*-propylene) rubber blend, function $F$ in equation (1) could be simply expressed by $4\eta_r^{\pm 0.84}$ where the plus sign was used for $\eta_r$ greater than 1 and minus sign for $\eta_r$ less than 1. However, since only one composition, i.e. 85/15

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wt/wt nylon/a rubber, was employed in his study, the effect of blend composition and the coalescence effect on the domain size or final morphology was not investigated.

Later, Tokita[21] reported that the droplet size of the minor phase in polymer blends with higher viscosity can be determined by the dynamic equilibrium between the breakup and coalescence of particles in the flow field under the assumption that no chemical reactions between constituent components occur. Based on this theory the equilibrium particle size ($D$) of the dispersed phase in incompatible polymer blends can be given by[21]

$$D \propto C_1\Gamma(\phi + C_2\phi^2) \qquad (2)$$

where $\Gamma$ is the interfacial tension between two components, $\phi$ is the volume fraction of the dispersed phase, positive constants of $C_1$ and $C_2$ do not depend upon $\Gamma$ and $\phi$, but depend upon shear stress and viscosity ratio between constituent components. From equation (2), the smaller volume fraction of the minor phase gives the smaller domain size of the disperse phase and near $\phi = 0.5$ the domain size of the minor phase becomes the largest, even co-continuous morphology is obtained.

Favis and Willis[22] have examined the effect of blend composition on domain size of the dispersed phase without and with a compatibilizer. Applying equation (2) to their experimental data, they could obtain a master curve of domain size vs logarithm of relative blend composition by shifting the volume fraction of one blend to the reference value in order to match domain size of the dispersed phase of one blend to that of reference blend. Note that a shifting factor of specific blend was correlated with the interfacial tension and viscosity ratio of the constituent components. Also, Favis[23] reported that for blend in the presence of a compatibilizer, the critical micelle concentration of the compatibilizer, above which there is no effect of the compatibilizer to reduce the domain size of the dispersed phase with increasing amount of the compatibilizer, is directly related to the interfacial area of the compatibilizer located between the dispersed phase and matrix phase.

Using a phenomenological approach that interfacial tension of blend with a compatibilizer decreases exponentially with the concentration of the compatibilizer, Tang and Huang[24] explained qualitatively experimental results investigated by Favis and coworkers[22,23] that with increasing amount of compatibilizer the domain size of the dispersed phase decreases very rapidly at smaller amount of compatibilizer but decreases little at a larger amount. But, they did not investigate the effect of blend composition consisting of the dispersed phase on domain size for a reactive blend system.

In this paper, we have studied the compatibilizing behaviour in two reactive blending systems, i.e. polystyrene (PS) and poly(ethylene-*ran*-acrylic acid) (PE-AA), and PS and poly(butylene terephthalate) (PBT), in the presence of the reactive compatibilizer of poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA). The reaction between carboxylic acid existing in either PE-AA or PBT and epoxy group in PS-GMA occurs very easily during melt mixing at higher temperature and the *in-situ* graft copolymer of either PE-*g*-PS or PBT-*g*-PS is formed to act as a compatibilizer between two immiscible polymer blends of PE-AA and PS, or of PBT and PS[25,26].

Emphasis was placed upon the effect of volume fraction of the dispersed phase in blend and the amount of compatibilizer on the morphology of blend. In order to find some correlations between the two effects, plots of the reduced domain size of the dispersed phase, which is defined by the ratio of the domain size of a blend with a compatibilizer to the domain size of respective blend without a compatibilizer, vs the amount of a reactive compatibilizer are considered. Finally, based on these plots we propose a compatibilization mechanism of reactive polymer blends.

## EXPERIMENTAL

### *Materials*

The polystyrene (PS) used in this study was a commercial grade (GPPS-G116) of Dongbu Petrochemical Co., Korea. Its number average molecular weight ($M_n$) and the polydispersity index ($M_w/M_n$) are 140 000 and 2.3, respectively, which are determined by Gel-Permeation Chromatography (g.p.c.) using calibration curves for standard polystyrenes.

The poly(ethylene-*ran*-acrylic acid) (PE-AA) was a commercial grade supplied by Dow Chemical Co. under the trade mark Primacor 3150 with $M_n$ of 20 000 and the polydispersity index of 8.7 determined by high temperature g.p.c. (Waters 150C) using calibration curves for standard polyethylenes. The amount of acrylic acid in PE-AA was 3.0 wt% determined by $^{13}$C n.m.r., thus about 8.3 AA units per chain based on $M_n$ are present.

The poly(butylene terephthalate) (PBT) was a commercial grade (HV 1010) from LG Chemical Co., Korea. The intrinsic viscosity (I.V.) was 1.0 dl g$^{-1}$ in mixed solvent of phenol and tetrachloroethane (60/40 volume ratio) at 25°C. With Mark–Houwink relationship (I.V. = $7.39 \times 10^{-5} M_v^{0.871}$) and polydispersity index of 2.2 measured from g.p.c., $M_n$ of PBT was calculated to be 25 000. The amount of carboxylic acid in PBT was determined to be 63 eq/10$^6$ g using the end-group titration method. Thus, there are approximately 1.6 carboxylic acid units per chain based on $M_n$.

The poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) prepared by a suspension polymerization was donated by LG Chemical Co., Korea. The $M_n$ and polydispersity index of PS-GMA are 46 000 and 2.5, respectively. The amount of GMA in PS-GMA is 2.0 wt% determined from $^{13}$C n.m.r.[26]. Thus, about 6.4 epoxy groups are present at each PS-GMA chain. Summary of molecular characteristics of materials employed in this study is given in *Table 1*.

### *Melt blending*

The materials as received were dried in a vacuum oven at 100°C for 1 day. The PE-AA/PS blend system with four different blend compositions of 10/90, 30/70, 50/50, and 70/30 wt/wt, and the PBT/PS blend system with five different blend compositions of 10/90, 20/80, 40/60, 70/30, and 90/10 wt/wt were prepared using various amounts of

**Table 1** Molecular characteristics of materials employed in this study

| Sample code | Number average molecular weight ($M_n$) | $M_w/M_n$ | Functional units in each chain |
|---|---|---|---|
| PS | 140 000 | 2.3 | |
| PS-GMA | 46 000 | 2.5 | 6.4 |
| PE-AA | 20 000 | 8.7 | 8.3 |
| PBT | 25 000 | 2.2 | 1.6 |

PS-GMA (0 to 10 wt% based on total PS phase consisting of neat PS and PS-GMA) using an internal mixer (Brabender Plasticorder) at speed of 50 rpm. The setting temperature of internal mixer was 200°C for PE-AA/PS blend system, and 230°C for PBT/PS blend system, respectively. However, the actual temperature inside the internal mixer was higher than the specific setting temperatures due to viscous heating[26], and thus the final temperature after mixing in the mixer was 210°C for the PE-AA/PS blend system, and 240°C for the PBT/PS blend system.

### *Morphology*

A scanning electron microscope (SEM), Jeol JSM-840A, was used to observe the morphology of specimens fractured at the cryogenic temperature after precracking with a fresh knife at room temperature, and then coated with a thin layer of gold. To determine the average particle size, Quantimet 570 image analysis (Cambridge Instruments) was used. About 200–400 particles were used to obtain the number average particle size ($M_n$) and particle size distribution of each blend.

## RESULTS AND DISCUSSION

### *PE-AA/PS blend system*

*Figure 1* shows scanning electron micrographs (SEM) of fractured surfaces for 10/90 (wt/wt) PE-AA/PS blends with various amounts of PS-GMA (wt% based on the total PS phase). Note that all blend compositions of PS/PS-GMA blend were miscible due to transparency of all blends and to the fact that any distinct phase separated domain was not seen even at a high magnification (×15 000).

It can be seen in *Figure 1* that when there is no PS-GMA, the number-average domain size ($D_n$) of dispersed phase is about 1.2 $\mu$m and the distribution of domain size (standard deviation (SD) = 0.7 $\mu$m) is very broad. Also, a discrete interface between two phases, which suggests poor interfacial adhesion, can be seen (*Figure 1a*). However, when only 1.0 wt% of PS-GMA based on the total PS phase (thus 0.9 wt% in entire blend) was added to this blend, $D_n$ of the dispersed phase decreased to 0.7 $\mu$m ± 0.3 $\mu$m, and an obscure interface region between two phases can be seen (*Figure 1b*). By increasing the amount of PS-GMA, $D_n$ of dispersed phase decreased and reached 0.3 $\mu$m ± 0.1 $\mu$m when the amount of PS-GMA is greater than 7 wt%. It can be concluded from *Figure 1* that PS-GMA plays as an effective compatibilizer between two immiscible components of PE-AA and PS.

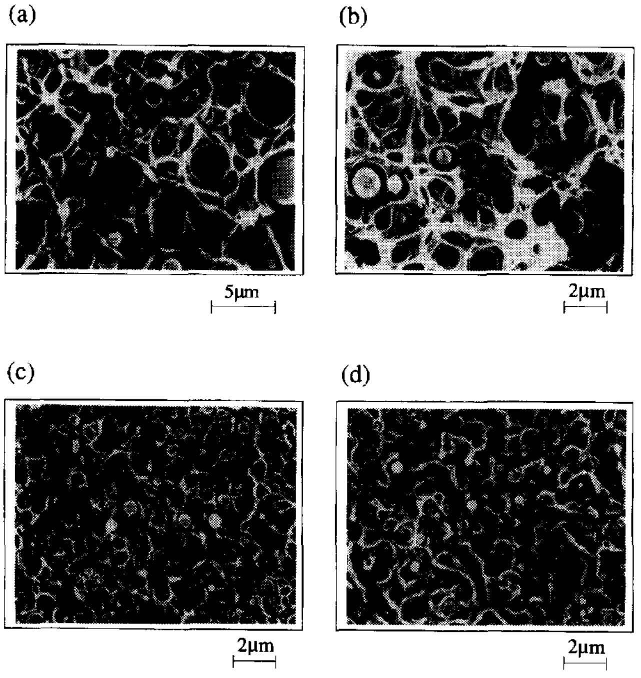

**Figure 1** Morphologies of fractured surfaces for the 10/90 (wt/wt) PE-AA/PS blends with various PS-GMA contents (wt% based on total PS phase, i.e. amount of PS-GMA divided by amounts of sum of PS-GMA and neat PS), (a) 0, (b) 1, (c) 5, (d) 7. The dispersed phase in all cases is PE-AA

*Figure 2* shows SEM morphologies of fractured surfaces for the 70/30 PE-AA/PS blends with various amounts of PS-GMA. In these blends, PS formed the dispersed phase while in the 10/90 PE-AA/PS blend PS formed the continuous phase. The decrease in both domain size and domain size distribution for the 70/30 PE-AA/PS blend by increasing the amount of PS-GMA is very similar to that given in *Figure 1*.

It should be noted that SEM morphologies of fractured surfaces given in *Figures 1* and *2* may not necessarily represent sample morphologies obtained by a transmission electron micrograph (TEM). The TEM morphologies of the 70/30 PE-AA/PS blends without PS-GMA and with 7 wt% PS-GMA are given in *Figures 3a* and *b*, respectively. The ultra thin section of *ca.* 50 nm thickness was prepared by microtoming with a diamond knife at room temperature and was stained by exposure to ruthenium tetroxide ($RuO_4$) vapour for one day. PS phase was stained by $RuO_4$ and thus appears dark. It can be concluded from *Figure 2a* and *Figure 3a*, and *Figure 2d* and *Figure 3b* that the domain size observed by SEM was essentially the same as that observed by TEM.

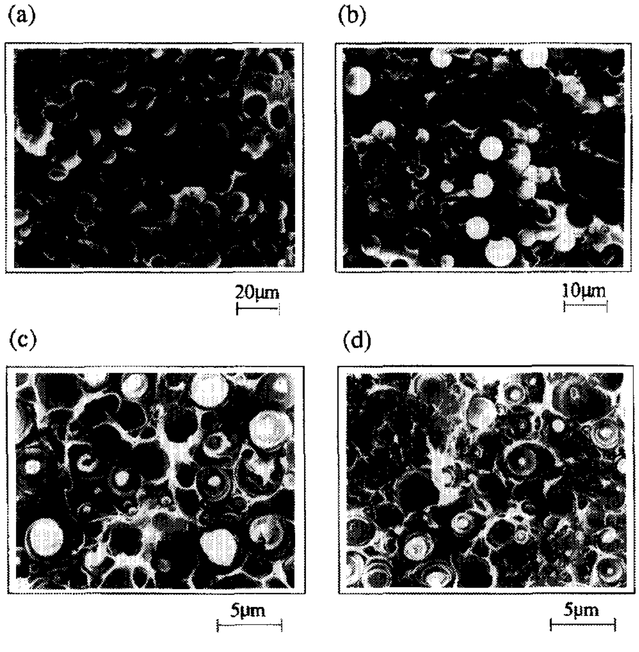

**Figure 2** Morphologies of fractured surfaces for the 70/30 (wt/wt) PE-AA/PS blends with various PS-GMA contents (wt% based on total PS phase), (a) 0, (b) 1, (c) 5, (d) 7. The dispersed phase in all cases is PS

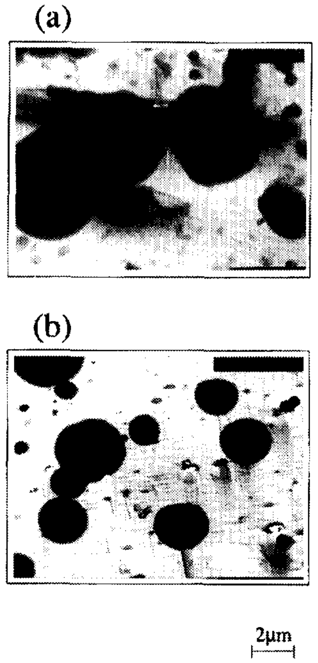

**Figure 3** Transmission electron micrographs of the 70/30 (wt/wt) PE-AA/PS blend without (a) and with 7 wt% PS-GMA (b)

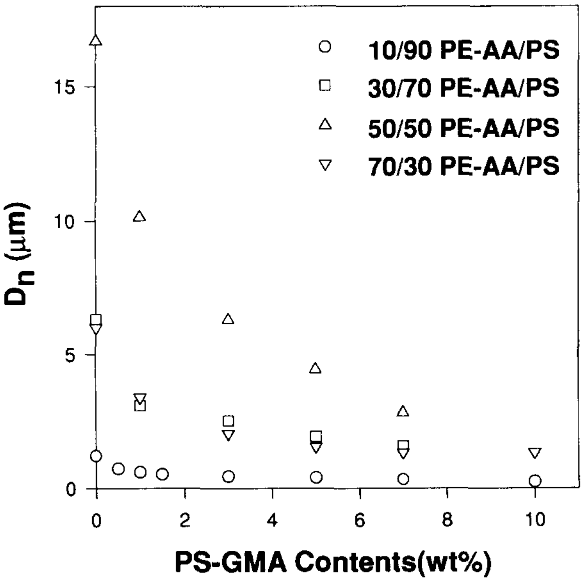

**Figure 4** Plots of the number average domain size ($D_n$) of the disperse phase vs PS-GMA contents for four different blend compositions of PE-AA/PS (wt/wt), (○) 10/90, (□) 30/70, (△) 50/50, and (▽) 70/30. Here, PE-AA formed the dispersed phase in 10/90, 30/70, and 50/50 PE-AA/PS blends, but PE-AA formed the continuous phase in 70/30 PE-AA/PS blend

The summary of the number-average domain size ($D_n$) of the dispersed phase for four different blend compositions of PE-AA/PS system with the amount of PS-GMA is given in *Figure 4*. These curves are often referred to as emulsification curves[23]. It can be seen in *Figure 4* that: (i) by increasing the amount of PS-GMA, $D_n$ for all blends decreases rapidly at lower amounts of PS-GMA but decreases rather slowly at higher amounts of PS-GMA. This is well consistent with the experimental results investigated by Favis[23] that by increasing the amount of compatibilizer a rapid decrease in domain size of the dispersed phase was found at smaller amounts of compatibilizer, followed by a levelling out to a near constant value of the diameter when a critical concentration of the compatibilizer was reached; (ii) $D_n$ for the 50/50 PE-AA/PS blend is the largest and that for the 10/90 PE-AA/PS blend is the smallest among PE-AA/PS blends employed in this study. A blend with symmetric composition often shows the poorest compatibility and the largest domain size can be expected, which is also predicted by equation (2); (iii) $D_n$ (~10 µm) of the 50/50 PE-AA/PS blend with only 0.5 wt% PS-GMA (thus, 1 wt% of PS-GMA in total PS phase) is about half of that without PS-GMA (~17 µm); (iv) $D_n$ for the 30/70 PE-AA/PS blend is almost the same as that for the 70/30 PE-AA/PS blend in spite of the fact that PE-AA becomes the dispersed domain structure in the former blend, while PS becomes the dispersed domain structure in the latter blend.

The dispersed domain size in a blend increases as the elasticity of dispersed phase increases, but it decreases as matrix viscosity increases due to equation (1)[27]. Among two components of PE-AA and PS, PE-AA has more elasticity than PS, while complex viscosity ($\eta^*$) ratio, measured at the frequency ($\omega$) of 17.5 rad $s^{-1}$ and 210°C, of PE-AA to PS was 0.14 as shown in *Figures 5* and *6*. The average shear rate inside the internal mixer employed in this study was calculated to be 17.5 rad $s^{-1}$[26]. The 30/70 PE-AA/PS blend consists of the dispersed phase of PE-AA with higher elasticity and the matrix phase of PS with higher viscosity, while the 70/30 PE-AA/PS blend consists of the dispersed phase of PS with lower elasticity but the matrix phase of PE-AA with lower viscosity. Therefore, it can be expected that the domain size for the 30/70 PE-AA/PS blend would be similar to that for the 70/30 PE-AA/PS blend.

### *PBT/PS blend system*

*Figure 7* gives SEM morphologies of fractured surfaces for the 10/90 (wt/wt) PBT/PS blends with various amounts of PS-GMA (wt% based on the total PS

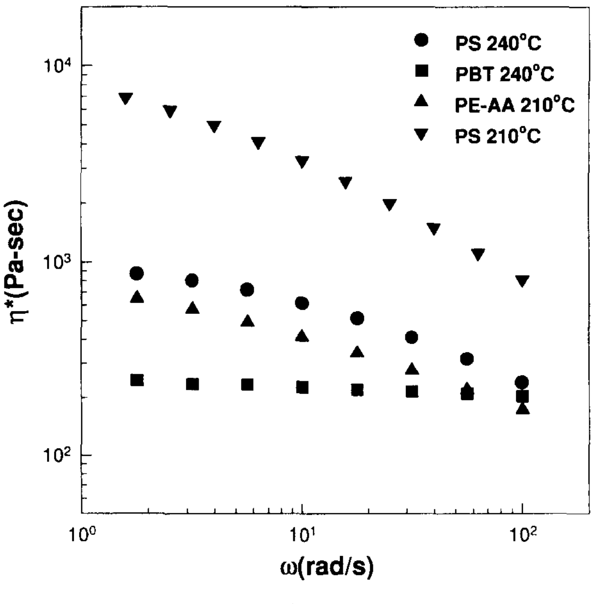

**Figure 5** Complex viscosity ($\eta^*(\omega)$) vs frequency ($\omega$) for neat polymers; (●) PS at 240°C; (■) PBT at 240°C; (▲) PE-AA at 210°C; (▼) PS at 210°C

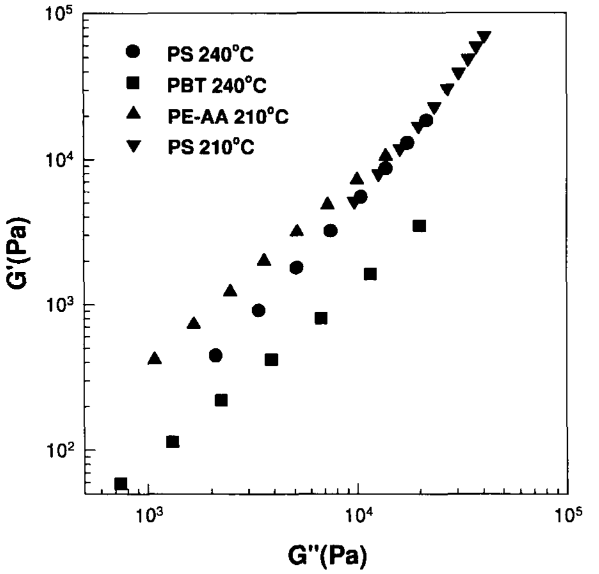

**Figure 6** Log $G'(\omega)$ vs $\log G''(\omega)$ plots for neat polymers; (●) PS at 240°C; (■) PBT at 240°C; (▲) PE-AA at 210°C; (▼) PS at 210°C

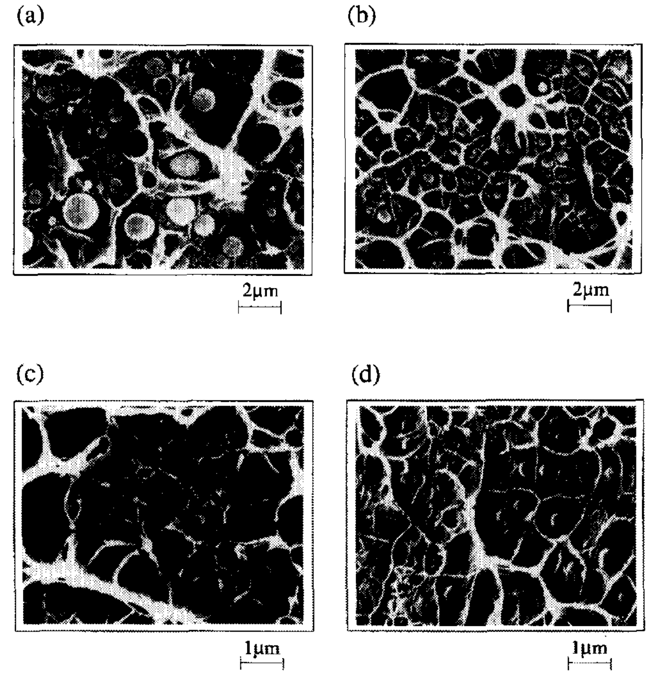

**Figure 7** Morphologies of fractured surfaces for 10/90 (wt/wt) PBT/PS blends with various PS-GMA contents (wt% based on total PS phase, i.e. the amount of PS-GMA divided by the amounts of sum of PS-GMA and neat PS), (a) 0, (b) 1, (c) 5, (d) 7. The dispersed phase in all cases is PBT

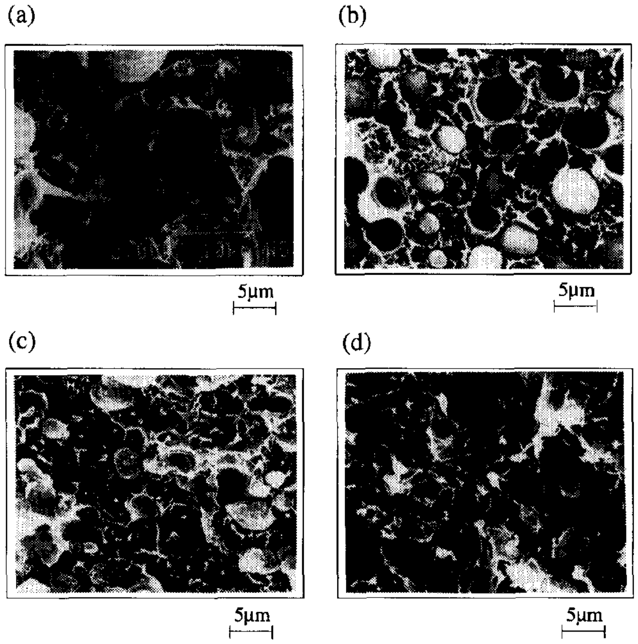

**Figure 8** Morphologies of fractured surfaces for the 70/30 (wt/wt) PBT/PS blends with various PS-GMA contents (wt% based on total PS phase), (a) 0, (b) 1, (c) 5, (d) 7. The dispersed phase in all cases is PS

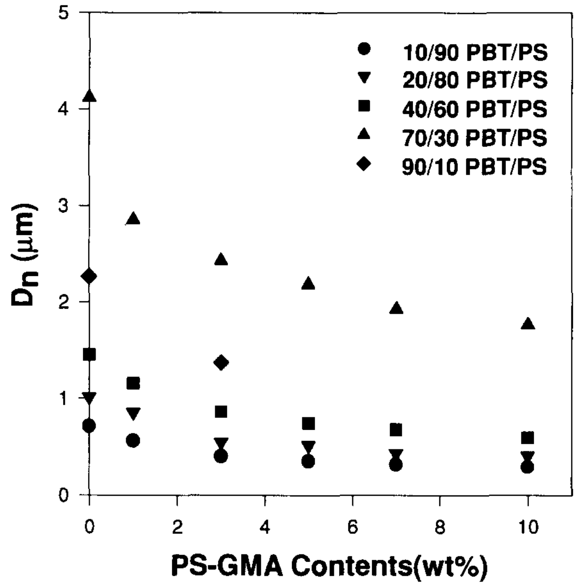

**Figure 9** Plots of the number average domain size ($D_n$) of the disperse phase vs PS-GMA contents for five different blend compositions of PBT/PS (wt/wt), (●) 10/90, (▼) 20/80, (■) 40/60, (▲) 70/30, and (◆) 90/10. Here, PBT formed the dispersed phase in 10/90, 20/80, and 40/60 PBT/PS blends, but PBT formed the continuous phase in 70/30 and 90/10 PBT/PS blends

phase). When there is no PS-GMA, the number-average domain size ($D_n$) of the dispersed phase is about 0.8 $\mu$m and the discrete interface between two phases can be seen (*Figure 7a*). With increasing the amount of PS-GMA, $D_n$ of dispersed phase decreases.

SEM micrographs for the 70/30 PBT/PS blends by increasing amount of PS-GMA are given in *Figure 8*. It was found that in the 70/30 PBT/PS blend PS became the dispersed phase, while in the 10/90 PBT/PS blend PS formed the continuous phase. The trend of decrease in both domain size and domain size distribution for PBT/PS blend system by increasing the amount of PS-GMA is very similar to that for the PE-AA/PS blend system given in *Figures 1* and *2*.

Changes in $D_n$ by the amount of PS-GMA for five different blend compositions of the PS/PBT system are given in *Figure 9*. It is rather unusual to find that: (i) the domain size of the 70/30 PBT/PS is larger than the 40/60 PBT/PS blend; (ii) the domain size of the 90/10 PBT/PS is much larger than that of the 10/90 PBT/PS blend although in the 70/30 and 90/10 PBT/PS blends the dispersed phase is PS. This is quite different compared with PE-AA/PS blend system (see *Figure 4*). It can be attributed to the fact that the 70/30 PBT/PS blend consists of the dispersed phase of PS with higher elasticity and the matrix phase of PBT with lower viscosity, while the 40/60 PBT/PS blend consists of the dispersed phase of PBT with lower elasticity and the matrix phase of PS with higher viscosity as shown in *Figures 5* and *6*.

It can be concluded from *Figures 4* and *9* that either PE-*g*-PS or PBT-*g*-PS copolymer formed by the reaction of two functional groups between epoxy group in PS-GMA and either acrylic acid in PE-AA or carboxylic acid in PBT, becomes an effective compatibilizer between two immiscible polymer blends of PS and either PE-AA or PBT. It is very interesting to find in *Figures 4* and *9* that by increasing the amount of PS-GMA, $D_n$ for all PE-AA/PS and PBT/PS blend compositions decreases very rapidly at lower amounts of PS-GMA, but the reduction in domain size with PS-GMA is rather gradual at higher amounts of PS-GMA.

Thus, one attempts to consider whether or not the change in domain size of the dispersed phase with increasing amount of PS-GMA for all blend compositions can be collapsed into one master curve when the reduced domain size ($D_r$) is considered. Here, $D_r$ is defined by the ratio of the domain size ($D$) of each blend composition with PS-GMA to that ($D_o$) of respective blend composition without PS-GMA. The rationale behind considering this master curve is that the domain size of the dispersed phase of a blend with PS-GMA can be postulated by

$$D \sim g[D_o(\chi, \dot{\gamma}, \eta_m, \eta_r, \phi, \text{etc.}), \Gamma_r(\chi, \phi_c)] \qquad (3)$$

where $D_o$ depends on Flory's interaction parameter ($\chi$), shear rate ($\dot{\gamma}$), matrix viscosity ($\eta_m$), viscosity ratio ($\eta_r$) of disperse component to matrix component, and volume fraction ($\phi$) of component forming domain structure in blend, etc. The expression of $D_o$ in equation (3) can be obtained from equations (1) and (2) since $\chi$ is related to the interfacial tension $\Gamma_o$[28,29]. Here, all parameters in $D_o$ *do* change very little, *if any*, when melt processing conditions are fixed at each $\phi$. But, the relative interfacial tension ($\Gamma_r$) in equation (3), the ratio of the interfacial tension ($\Gamma$) of a blend with a compatibilizer to that ($\Gamma_o$) of respective blend without a compatibilizer, is certainly a function of the amount of compatibilizer, $\phi_c$[4,30,31]. However, if $\Gamma_r$ is assumed to change *very little* with blend compositions, the reduced diameter ($D_r$) is independent of blend compositions, thus a master curve can be obtained.

Plots of the reduced diameter vs the amount of PS-GMA for four different blend compositions of PE-AA/PS system, and five different blend compositions of PBT/PS system are given in *Figure 10*, from which one notes that a master curve for each blend system was obtained regardless of blend compositions in two different blend systems.

*Reduction in the reduced domain size*

One raises three fundamental questions found in *Figures 4*, *9*, and *10*: (i) when there is no compatibilizer, why $D_n$ of the disperse phase for the PE-AA/PS system is greater than that for the PBT/PS system at the same volume fraction of the dispersed phase; (ii) by increasing the amount of PS-GMA why the reduction in the reduced domain size for the PE-AA/PS blend system is greater than that for the PBT/PS blend at given amount of PS-GMA; (iii) why plots of the reduced domain size of the dispersed phase vs the amount of PS-GMA fall into one master curve for all blend compositions.

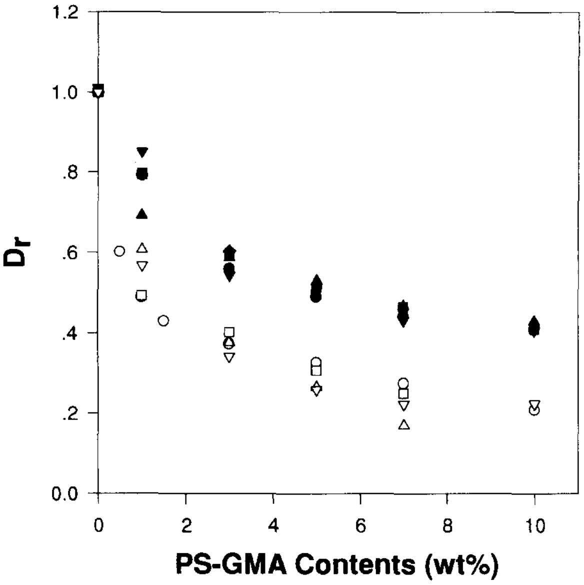

**Figure 10** Plots of the reduced domain size ($D_r$) of the disperse phase vs PS-GMA contents (wt% based on total PS phase) for two different blend systems. Blank symbols are for PE-AA/PS blend system with different blend compositions of PE-AA/PS (wt/wt), (○) 10/90, (□) 30/70, (△) 50/50, and (▽) 70/30. Filled symbols for PBT/PS blend system with different blend compositions of PBT/PS (wt/wt), (●) 10/90, (▼) 20/80, (■) 40/60, (▲) 70/30, and (◆) 90/10

To answer question (i), we consider from equation (3) that $D_o$ is a function of $\Gamma_o$ or $\chi$ and then we estimate the value of $\chi$ between PE-AA and PS, and that between PBT and PS. As the interaction parameter between constituent components becomes smaller, and better the miscibility, and thus the smaller the domain sizes of the disperse phase of a blend without a compatibilizer. This is because the domain size will be proportional to the interfacial tension[20] and interfacial tension is proportional to $\chi^{1/2}$[32]. In the context of mean-field theory, the effective interaction energy, $\Lambda_{eff}$ of random copolymer and homopolymer is given by[33,34]

$$\Lambda_{eff} = \phi_{PE}\Lambda_{PE-S} + (1 - \phi_{PE})\Lambda_{AA-S} - \phi_{PE}(1 - \phi_{PE})\Lambda_{PE-AA} \qquad (4)$$

where $\phi_{PE}$ is the volume fraction of PE in PE-AA and $\Lambda_{ij}$ is the interaction energy between two monomers $i$ and $j$ which equals $(\chi_{ij}/V_{ref})RT$, where $V_{ref}$ is the reference volume, $R$ is the gas constant, and $T$ is the absolute temperature.

Since $\Lambda_{ij}$ is not available in the literature at the present time, we estimate these values from solubility parameters due to Hildebrand[35].

$$\Lambda_{ij} = (\delta_i - \delta_j)^2 \qquad (5)$$

where $\delta_i$ and $\delta_j$ are the solubility parameters of components $i$ and $j$, respectively. Although the values of $\delta$ vary widely from one reference to another, in this study we estimate that the values of $\delta$ of PS, PE, PAA, and PBT are 18.7, 15.1, 24.9, and 20.9 $(\mathrm{J\,cm^{-3}})^{0.5}$, respectively, which were calculated by group contributions method[36]. Using these values, $\Lambda_{\mathrm{eff}}$ is calculated to be $10.7\,\mathrm{J\,cm^{-3}}$ for PE-AA/PS blend by equations (4) and (5). Also, $\Lambda_{\mathrm{PS-PBT}}$ is calculated to be $4.8\,\mathrm{J\,cm^{-3}}$.

Therefore, the fact that when there is no compatibilizer the domain size of the dispersed phase for PE-AA/PS blend system is greater than that for PBT/PS blend system shown in *Figures 4* and *9*, may be attributed to the difference in $\Lambda$ (or $\chi$) between two blend systems, namely $\Lambda$ for the former blend is greater than that for the latter blend although many possible uncertainties are incurred in estimating solubility parameters.

Next, we consider the second question, which is also related to the values of $\chi$ for each blend system with various amounts of PS-GMA compatibilizer since $\Gamma_r$ is a function of $\chi$[32]. This can be done when the statistical thermodynamic theory developed by Leibler[30,37] was applied to this blend system. In Leibler theory, a block copolymer was used as a compatibilizer, and thus it seems unreasonable to directly compare the predictions with our experimental data since in this study a graft copolymer instead of a block copolymer is formed due to the reaction between two functional groups. Nevertheless, we use predictions made by Leibler[30,37] since an appropriate theory for the reactive compatibilizer system is not available in the present time.

Among two brush limits in Leibler theory[30,37], we use the predictions based on the dry brush limit, in which the homopolymer does not penetrate the brush formed by the copolymers, under an assumption that the reaction between reactive compatibilizer and other polymer having different functional group occurs near the interface and a graft copolymer stays near the interface. In the dry brush limit, total number of chain segments of homopolymer $P$ is greater than $N^{2/3}$ where $N$ is the total number of chain segments in an *in-situ* formed copolymer. Because the molecular weight of PS-GMA is less than that of PS homopolymer and average chain lengths of $P$ are also greater than $N$ in each case, the dry brush limit is reasonable.

The interfacial reduction ($\Delta\Gamma$) obtained by the dry brush limit is independent of the homopolymer molecular weights and is given by[30,37]

$$\frac{\Delta\Gamma}{\Gamma_0} = \left(\frac{\sqrt{48}}{9}\right)\mu^{3/2}(\chi N)^{-(1/2)} \qquad (6)$$

where $\Gamma_0$ is the interfacial tension of polymer blend without a compatibilizer, and the chemical potential $\mu$ is given by[30,37]

$$\mu = \ln\phi^{+} + f\chi N \qquad (7)$$

where $f$ is the volume fraction of the component in copolymer which is miscible to homopolymer forming the dispersed phase, thus the value of $f$ was 0.3 for PE-AA/PS and 0.35 for PBT/PS, respectively. Note that $\phi^{+}$ is the volume fraction of a copolymer in the matrix phase and given by

$$\phi^{+} = \frac{\phi_0}{[\phi_{\mathrm{M}} + \phi_{\mathrm{D}}\exp\{\chi(N_{\mathrm{A}} - N_{\mathrm{B}})\}]} \qquad (8)$$

where $\phi_0$, $\phi_{\mathrm{M}}$, and $\phi_{\mathrm{D}}$ are the volume fraction of a copolymer, of matrix component, and of disperse component. $N_{\mathrm{A}}$ and $N_{\mathrm{B}}$ are the number of segments of the component in the copolymer miscible to homopolymer forming the dispersed phase and that miscible to homopolymer forming the matrix phase. Since, in this study, $\exp[\chi(N_{\mathrm{A}} - N_{\mathrm{B}})]$ is negligible compared to $\phi_{\mathrm{M}}$, $\phi^{+}$ is simply expressed by $\phi_0/\phi_{\mathrm{M}}$. This means that $\phi^{+}$ is equal to the volume fraction of PS-GMA in total PS phase.

The surface coverage $\sum/b^2$ of one copolymer is related to $\mu$ and $\chi$[30,37]

$$\sum/b^2 = \left(3/\sqrt{2}\right)(N/\mu)^{1/2} \qquad (9)$$

where $b$ is the Kuhn length.

In the calculation process, the reference segment size is equal to $100\,\mathrm{g\,mol^{-1}}$, so that the average chain lengths of $P$ are 800 for the PE-AA/PS blend, and 825 for the PBT/PS blend, respectively. The total number of chain segments $N$ of *in-situ* formed copolymers is calculated to be 660 for the PE-*g*-PS copolymer, and 710 for the PBT-*g*-PS copolymer. These values are obtained by the assumption that the total number of chain segments of PE-*g*-PS copolymer is just the summation of two number-averaged molecular weights of PE-AA and PS-GMA divided by the reference segment size, and that of PBT-*g*-PS copolymer is also the summation of two number-average molecular weights of PBT and PS-GMA divided by the reference segment size.

In order to obtain $\chi$ for a blend system having different amounts of PS-GMA, the decrease in interfacial tension ($\Delta\Gamma$) with the amount of PS-GMA for two blend systems must be obtained. However, to measure interfacial tension experimentally by the breaking thread method[38] or the pendant drop method[39] is not an easy task. For instance, for blends with reactive compatibilizer, the breaking thread method is not useful since the reaction may occur during measurement. The pendant drop method is not good for polymer blends having high molecular weights due to higher viscosities.

Therefore, in this study we assume that $\Delta\Gamma$ could be proportional to the decrease in domain size of the dispersed phase ($\Delta D$) in a particular blend

$$\Delta\Gamma/\Gamma_0 = (\Gamma_0 - \Gamma)/\Gamma_0 \approx \Delta D/D_0 = (D_0 - D)/D_0 \qquad (10)$$

where $\Gamma$ and $D$ are interfacial tension and domain size of blend with a compatibilizer, and $\Gamma_0$ and $D_0$ are interfacial tension and domain size of blend without compatibilizer. Many research groups[3,4,20,40,41] have used equation (10) in order to explain reduction in the domain size with the amount of compatibilizer. However, the validity of equation (10) must be carefully checked for blends having a reactive compatibilizer, which is beyond the scope of this study.

Changes in calculated values of $\chi$, and $\sum/b^2$ for PE-AA/PS and PBT/PS blend systems with the amount of PS-GMA are given in *Figure 11* and *Figure 12*, respectively. It should be mentioned that when the wet brush limit instead of the dry brush limit is used to these blend systems, the trend of decrease in $\chi$ and $\sum/b^2$ with the amounts of PS-GMA is *similar* to that found in *Figures 11* and *12*, but the absolute values are different from those in *Figures 11* and *12*. We note in *Figure 11* that $\chi$ values calculated by the Leibler theory[30,37] for the PE-AA/PS blend system are greater than those for the PBT/PS blend system at fixed amount of PS-GMA, which is qualitatively consistent with $\chi$ values obtained

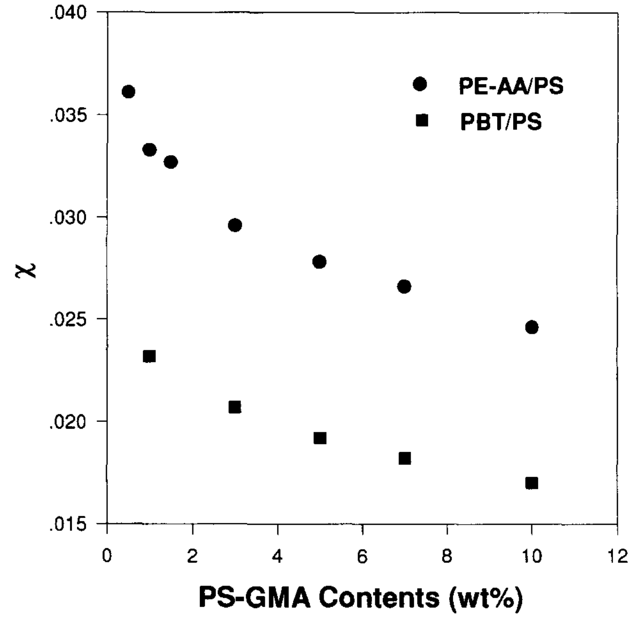

**Figure 11** Changes in the calculated values of $\chi$ with PS-GMA contents (wt% based on total PS phase) for two different blend systems by the dry brush limit of Leibler theory

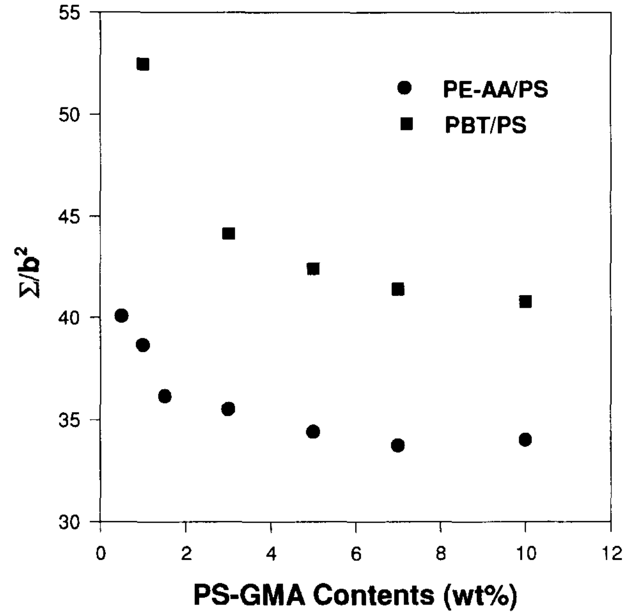

**Figure 12** Changes in the calculated values of $\Sigma/b^2$ with PS-GMA contents (wt% based on total PS phase) for two different blend systems by the dry brush limit of Leibler theory. Here, $\Sigma$ is the surface area per copolymer and $b$ is the Kuhn length

by equations (4) and (5).

It should be pointed out that according to Noolandi and co-workers[31,42], $\Delta\Gamma$ with amount of block copolymer depends upon the total number of segments of block copolymer, $N$, and $\chi$. The larger the values of $N$ and $\chi$ are, the larger $\Delta\Gamma$ at given amount of block copolymer is expected although the critical micelle concentration of compatibilizer is significantly reduced. It is rather difficult to directly compare the reduction in dispersed phase size ($\Delta D$) with the amount of PS-GMA for PE-AA/PS blend with that for PBT/PS blend due to different processing temperature and the concentration of functional group, namely, carbonyl unit of PE-AA and PBT. The difference in the reaction kinetics between two blend systems gives rise to change the concentration of the *in-situ* formed copolymer at interface. However, in this study one can consider that $N$ of a graft copolymer formed for two blend systems does not vary significantly. Therefore, $\chi$ becomes a major parameter to affect the ability of the reduction in the domain size of the dispersed phase.

It may be concluded from *Figure 11* and the above analysis that the main reason that: (i) $D_n$ of the dispersed phase for the PE-AA/PS blend system is larger than that for the PBT/PS system when there is no compatibilizer in these blends; (ii) with increasing the amount of PS-GMA the reduction in $D_n$ of the dispersed phase for the former blend system is greater than that for the latter blend, might be due to the larger $\chi$ for the former blend than that of the latter blend.

It can be seen in *Figure 12* that (i) calculated values of surface coverage for PBT/PS blend are greater than those for PE-AA/PS blend; (ii) the surface coverage decreases with increasing amount of compatibilizer. This is because the smaller $\chi$ for a blend is, the less stretching of a graft copolymer chain near the interface. When we take Kuhn length of $b$ as 0.68 nm[43], we found that interfacial area occupied by one chain of the compatibilizer for the PE-AA/PS blend system was decreased from 18 nm$^2$ to 16 nm$^2$ as the amount of PS-GMA was increased from 0.5 wt% to 10 wt%, while this value for the PBT/PS blend system was decreased from 24 nm$^2$ to 19 nm$^2$ as the amount of PS-GMA was increased from 1.0 wt% to 10 wt%.

### *Master curve*

We consider a reason(s) why all curves of $D_r$ for different blending compositions can be collapsed into one master curve shown in *Figure 10*. The efficiency of a compatibilizer in reducing domain size of the disperse phase with the concentration of the compatibilizer has been related to the interfacial area occupied by the compatibilizer molecule[23,24,44,45]. Under the assumption that all compatibilizers go to the interface, Paul and Newman[46] obtained that the interfacial area ($a$) occupied by one compatibilizer chain is given by

$$a = \frac{6\phi M}{D_n N_{AV} W} \tag{11}$$

where $\phi$ is the volume fraction of the dispersed phase, $M$ is the number-average molecular weight of the compatibilizer, $D_n$ is the number-average diameter of the dispersed phase, $N_{AV}$ is the Avogadro number, and $W$ is the mass of the compatibilizer per unit volume. Using values of $D_n$ given in *Figure 10*, we calculated that the interfacial areas per compatibilizer molecule for 10/90, 30/70, and 50/50 PE-AA/PS blend compositions with 7 wt% PS-GMA based on total PS phase were 2.6, 2.1, and 2.1 nm$^2$, respectively.

Also, the values of $a$ for 10/90, 20/80, and 70/30 PBT/PS blend compositions with 10 wt% of PS-GMA based on total PS phase were calculated to be 1.8, 2.8 and 2.6 nm$^2$, respectively. Through this estimation, the area per molecule of the copolymer formed by the reaction remains the same in spite of difference in the blend compositions. Notice that in this estimation of the value of $a$ we assume that the molecular weight ($M$) of

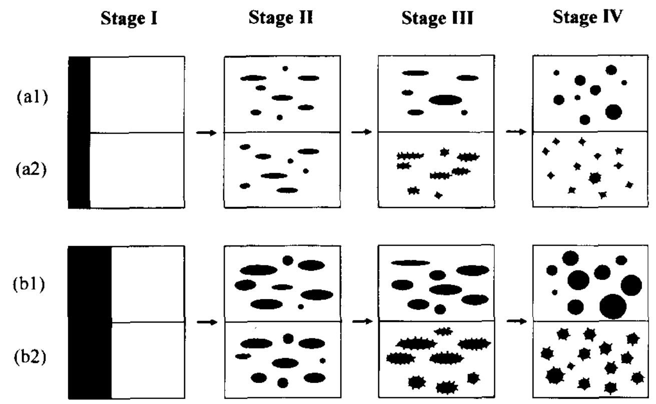

**Figure 13** Schematic of formation of domain structures with mixing times (Stages I–IV) for two blend compositions: the 10/90 blend composition without a reactive compatibilizer (a1) and with a reactive compatibilizer (a2); the 30/70 blend composition without a reactive compatibilizer (b1) and with a reactive compatibilizer (b2). Dark points at the interface represent copolymer formed by the reaction

copolymer as a compatibilizer was taken as 46 000, which is the molecular weight of PS-GMA, since it is difficult to know the exact molecular weight of the graft copolymer and the error in estimating the molecular weight can be cancelled out due to the $W$ term in equation (11). In other words, when two PBT chains are grafted to one chain of PS-GMA, $M$ of a compatibilizer formed by the reaction is equal to 96 000. However, in this case $W$ becomes 2.1 times greater than that obtained by the assumption of $M$ equal to 46 000 since $W$ is the mass of the compatibilizer and proportional to $M$.

The $a$ value of 2 nm$^2$ obtained in this study is comparable to that of 2.6 nm$^2$ for a low-density polyethylene/polystyrene blend with a block copolymer reported by Fayt *et al.*[47], but smaller than the $a$ value of 5.0 nm$^2$ for PE/Nylon with ionomer reported by Favis[23]. It should be mentioned that the value of $a$ calculated by equation (11) is much smaller than that of $\Sigma$ obtained by equation (9), since the value of $a$ was calculated using the assumption that all compatibilizers go to the interface.

Based on *Figure 10* and the above analysis of calculating $a$, we propose a compatibilization mechanism for two different blend compositions of 10/90 and 30/70 blends without and with a reactive compatibilizer as shown in *Figure 13*. At the early stage of the melt mixing, macroscopic separated morphology of original blend (Stage I) forms to be the highly elongated dispersed phase due to melting and the shearing force (Stage II)[48]. Note that in this stage the domain size of the dispersed phase of the 30/70 blend composition is larger than that of the 10/90 blend composition due to larger dispersed volume.

It should be mentioned that Sundararaj and Macosko[49] reported that the domain size of poly(styrene-*co*-maleic anhydride) (PSMA)s with 1.6 wt% and 17 wt% maleic anhydride in the matrix of Nylon 6,6 was not varied with blend composition of PSMA even when volume fraction of PSMA in this blend varied significantly from 0.05 to 0.4. This can be explained that in both blends of PSMAs/Nylon 6,6 there is so much the amount of functional group of MA which gives sufficient graft copolymers formed by the reaction. We made similar observation that for 90/10 (wt/wt) and 70/30 (wt/wt) PE-AA/PS-GMA blends the distinct phase-separated domain could not be seen even at the magnification of 15 000[50]. Also, for 75/25 (wt/wt) and 50/50 (wt/wt) PBT/PS blend the distinct phase-separated domain could not be detected when the amount of PS-GMA in total PS phase is greater than 25 wt%[26]. However, in this study, the amount of PS-GMA in total PS phase is not much, the dispersed domain size for one blend composition might differ from that for other blends.

For blend with a compatibilizer the reaction between the well distributed functional groups in each phase will take place and *in-situ* formed copolymer reduces the interfacial tension between two phases which results in smaller dispersed domain size and smaller domain size distribution [*Figure 13* (a2, b2) in stages III and IV]. However, the area per *in-situ* formed copolymer would be the same in spite of difference in overall blend composition. Once the dispersed domain is developed, the domain size would not be increased further through the coalescence process, since the *in-situ* formed copolymer suppresses the coalescence process by stabilizing the interface[49].

But, for blends without a compatibilizer the breaking mechanism can be counter-balanced by a coalescence mechanism where the disperse domain size and the size distribution both become larger [*Figure 13* (a1, b1) in Stages III and IV].

Therefore, it can be concluded that when the reactive group in the polymer chain is *well* distributed over the respective phase, thus the concentration remains the same through that phase, the efficiency of interfacial activity of the formed copolymer, for instance reduction of the dispersed domain size, remains the same in spite of different blend compositions. This is because the area occupied by an *in-situ* formed copolymer at interface might have similar value regardless of different blend compositions. As long as the area per *in-situ* formed copolymer remains the same regardless of different blend compositions, a master curve given in *Figure 10* could be expected.

## CONCLUDING REMARKS

In this study, we have shown that an *in-situ* compatibilizer of PS-GMA played a role as an effective compatibilizer between two different blend systems of PE-AA/PS and PBT/PS, in that the domain size and the domain size distribution of the dispersed phase decreased with increasing amount of PS-GMA. Also, with increasing amount of PS-GMA, the domain size of the dispersed phase for all blend compositions in two blend systems decreased rapidly at lower amounts of PS-GMA, but decreased rather slowly at higher amounts of PS-GMA.

The domain size of the dispersed phase in the PE-AA/PS blend system was larger than that in the PBT/PS blend system at the same blend composition when there is no PS-GMA in both blend systems. However, with increasing PS-GMA contents the reduction in the reduced domain size in the PE-AA/PS blend system turned out to be greater than that in the PBT/PS blend system. These are attributed to the fact that $\chi$ between PE-AA and PS was greater than that between PBT and PS, which were calculated by the solubility parameters as well as predicted by the dry brush limit of the Leibler theory[30,37].

It is quite interesting to note that the reduced domain size for all blend compositions with compatibilizer contents was collapsed into one master curve although blend compositions investigated in this study vary significantly from one blend to another. This may be explained by almost the same interfacial area occupied by one compatibilizer chain for all blend compositions.

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