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Effect of acrylic acid content in poly(ethylene-*ran*-acrylic acid) on the morphology and mechanical properties of poly(ethylene-*ran*-acrylic acid)/polystyrene blends compatibilized by poly(styrene-*ran*-glycidyl methacrylate)

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Three poly(ethylene-*ran*-acrylic acid)s (PE-AAs) with different amounts of acrylic acid but exhibiting similar rheological properties were studied to investigate the effect of acrylic acid content in PE-AAs on the morphology and mechanical properties of PE-AA/polystyrene (PS) blend compatibilized by poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA). From morphological observations, there appears to be an optimum amount of acrylic acid in PE-AA that effectively reduces the dispersed domain size in PE-AA/PS blend systems. The existence of an optimum value is due to the combined effects of a sufficient reaction near the interface giving enough amounts of graft copolymers as a compatibilizer between PE-AA and PS, and fast diffusion of reactive species toward the interface. However, the tensile strength (σ_b) and the elongation at break (ϵ_b) for these blend systems steadily increased with an increase in the amount of acrylic acid in PE-AA. By increasing the amount of PS-GMA, σ_b and ϵ_b for all blend systems increased rapidly, and then levelled off. Impact strength of these blend systems was investigated by varying them amount of acrylic acid in PE-AA. © 1997 Elsevier Science Ltd.

(Keywords: reactive compatibilization; functional group content; poly(ethylene-*ran*-acrylic acid))

INTRODUCTION

Recently, high performance polymer blends and alloys with unique physical properties that cannot be obtained from the constituent components along have been developed by using special compatibilization methods either by adding a third component (physical compatibilization) or by inducing *in-situ* chemical reaction between blend components (chemical or reactive compatibilization)[1–4]. Since most polymer blends and alloys are immiscible, enhanced mechanical properties could not be expected without improving the degree of compatibility between the constituents and the interfacial adhesion between the two phases. Although physical compatibilization methods have been suggested to improve interfacial adhesion, chemical compatibilization methods are widely used for commercial production of polymer alloys with fine morphology and thick interface to enhance impact and/or tensile strength[4–6]. Moreover, the fine morphology cannot be changed under the high shear stresses found in the injection moulding process.

It is well established that in reactive compatibilization the amount of the functional group is very important to determine the morphology and mechanical properties[7–9]. When the total amount of the functional group is too great, this reaction results in the formation of graft copolymers of very high molecular weight or even the cross-linked structure[10]. Therefore, these copolymers are not well-distributed near interfaces due to high viscosity. On the other hand, when the amount of the functional group is insufficient, few graft copolymers are formed. Therefore, they cannot operate as an efficient compatibilizer and the final physical properties of the polymer blend can be poor. Char *et al.*[11] reported that an enhancement in interfacial adhesion between amorphous polyamide and polystyrene by the addition of a reactive compatibilizer was explained by the combined effects of the reaction near the interface and the diffusion of the reactive species toward the interface.

Very recently, we[12] have shown that the interfacial activity represented through domain size reduction increased by increasing the amount of poly(stryene-*ran*-glycidyl methacrylate) (PS-GMA) as a reactive compatibilizer for poly(butylene terephthalate) (PBT)/polystyrene (PS) blend and poly(ethylene-*ran*-acrylic acid) (PE-AA)/PS blend. The reaction between these two functional groups, i.e. the carboxylic acid groups in PBT or PE-AA and the epoxy group in PS-GMA, is known to occur very easily during melt mixing at higher temperatures[13,14].

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In this study, in order to investigate the effect of the functional group content on the domain size reduction in PE-AA/PS blend compatibilized by PS-GMA, three PE-AAs with different amounts of acrylic acid (AA) were used. Also, mechanical properties of these blends are discussed in terms of morphology which depends on the functional group contents.

EXPERIMENTAL

Materials

Table 1 summarizes the molecular characteristics of materials employed in this study. The polystyrene (PS) used in this study was a commercial grade (GPPS-G116) from Dongbu Petrochemical Co., Korea. Its number average molecular weight (M_n) of 140 000 and polydispersity index (M_w/M_n) of 2.3 were determined by gel-permeation chromatography (g.p.c.) using calibration curves for standard polystyrene.

The three poly(ethylene-*ran*-acrylic acid)s (PE-AAs), namely PE-AA(3), PE-AA(6) and PE-AA(9), employed in this study were Primacor 3150, 3340 and 3440 commercial grades from Dow Chemical Co., USA. The M_n and the polydispersity index determined by high temperature g.p.c. (Waters 150C) using calibration curves for standard PE were 20 000 and 8.7 for PE-AA(3), 14 500 and 8.8 for PE-AA(6) and 8500 and 9.0 for PE-AA(9), respectively. The amount of acrylic acid in the three PE-AAs were 3.0, 6.2 and 9.3 wt%, respectively, determined by the titration method in ASTM D 4094, and thus giving the AA units of about 8.3, 12.5 and 11.0, respectively, per chain based on M_n.

The poly(styrene-*ran*-glycidyl methacrylate) (PS-GMA) prepared by a suspension polymerization were donated from 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 was 2.0 wt% determined from ^{13}C n.m.r. Thus, about 6.4 epoxy groups were present at each PS-GMA chain.

Melt blending

The materials as received were dried in a vacuum oven at 100°C for 1 day. The 30/70 (wt/wt) PE-AA/PS blends were prepared using various amounts of PS-GMA (0–7 wt% based on total PS phase consisting of neat PS and PS-GMA) by an internal mixer (Brabender Plasticorder) at the speed of 50 rpm. Although the wall temperature inside internal mixer was set to 200°C, the actual temperature inside the internal mixer was higher than the specific setting temperature due to viscous heating and reaction: thus the final temperature after mixing in the mixer increased to 210°C.

Morphology

A scanning electron microscope (SEM), Jeol JSM-840A, was used to observe the morphology of specimen fractured at the cryogenic temperature using liquid nitrogen, which were then coated with a thin layer of gold. To determine the average particle size, Quantimet 570 image analysis (Cambridge Instruments) was used. About 200 to 300 particles were used to obtain the number average particle size of each blend.

Rheological properties

In order to compare viscosity and elasticity ratio of PE-AA to PS, the complex viscosities ($\eta^*(\omega)$), storage modulus ($G'(\omega)$) and loss modulus ($G''(\omega)$) of PS and the three PE-AAs as a function of angular frequency (ω) were measured by a Rheometrics Dynamic Spectrometer (Rheometrics Co., USA: RDS-II) using 25 mm parallel plates under oscillatory shear mode at 200°C and 210°C.

Mechanical properties

Melt blending samples taken from the Brabender internal mixer were compression moulded into the sheet at 200°C and quenched to room temperature. Dog-bone shape tensile test specimens were prepared. Tensile strength and strain were measured at room temperature using ASTM D 1708 method with a Universal Test Machine (Instron Co.: Model 4206). At least seven specimens per blend sample were tested using a cross-head rate of 5 mm min^{-1}. A notched Izod impact test was also performed at room temperature according to ASTM D 265.

RESULTS AND DISCUSSION

Morphology of PE-AAs/PS blends

In order to confirm the reaction between the epoxy group in PS-GMA and the carboxylic group in PE-AA, 70/30 (wt/wt) PE-AA(3)/PS-GMA blend was prepared by melt blending at 200°C[15]. About 90 wt% of PS-GMA reacted with PE-AA(3), which was determined by the ratio of the absorption peak height of 698 cm^{-1} from PS-GMA to that of 1468 cm^{-1} from PE-AA(3) measured by Fourier transform i.r. spectroscopy for the blend before and after extraction. The unreacted PS-GMA can be extracted by acetone at 50°C.

Figure 1 shows scanning electron micrographs of fractured surfaces for 30/70 (wt/wt) PE-AA(3)/PS blend with three different amounts of PS-GMA (wt% based on the total PS phase). When there is not PS-GMA in this blend, the number-average domain size (D_n) of the dispersed phase is about 6.3 μm and the distribution of domain size is very broad (standard deviation

Table 1 Molecular characteristics of materials employed in this study

Sample code	Number average molecular weight (M_n)	M_w/M_n	Functional group content (wt%)	Concentration of functional group (%)
PS	40 000	2.3	—	—
PS-GMA	46 000	2.5	2[a]	0.014
PE-AA(3)	20 000	8.7	3.0[b]	0.042
PE-AA(6)	14 500	8.8	6.2[b]	0.086
PE-AA(9)	8 500	9.0	9.3[b]	0.129

[a] Determined by ^{13}C n.m.r.

[b] Determined by titration method according to ASTM D 4094

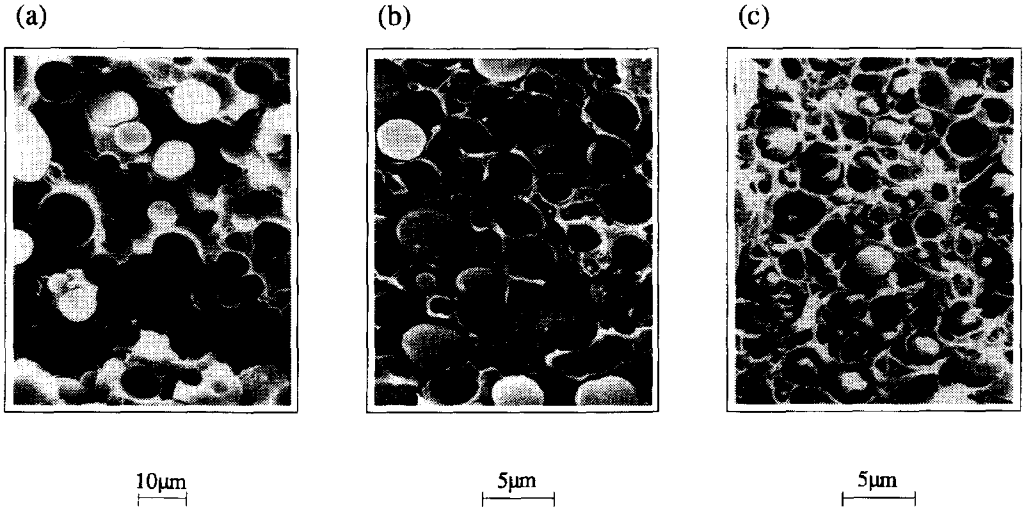

Figure 1 Morphologies of fractured srufaces for 30/70 (wt/wt) PE-AA(3)/PS blends with three different amounts of PS-GMA (wt% in total PS phase): (a) 0; (b) 3; (c) 7

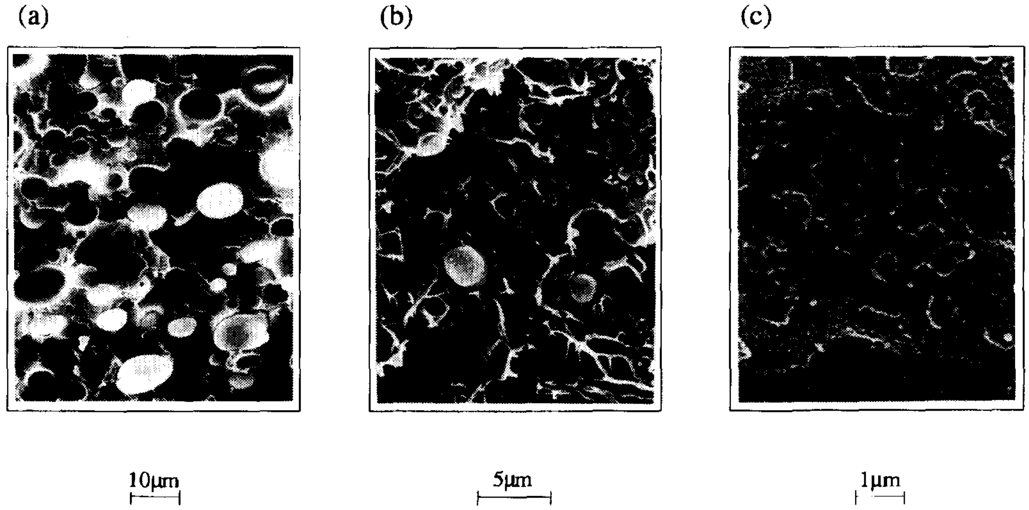

Figure 2 Morphologies of fractured surfaces for 30/70 (wt/wt) PE-AA(6)/PS blends with three different amounts of PS-GMA (wt% in total PS phase): (a) 0; (b) 3; (c) 7

(SD) = 2.8 μm). Also, a discrete interface between the two phases, which suggests poor interfacial adhesion, can be seen (*Figure 1a*). When only 3.0 wt% of PS-GMA was added to this blend, D_n of dispersed phase decreased to 2.5 μm ± 1.2 μm (*Figure 1b*). By increasing the amount of PS-GMA, D_n of dispersed phase decreased and reached 1.6 μm ± 0.8 μm when the amount of PS-GMA was 7 wt% (*Figure 1c*). It can be concluded from *Figure 1* that PS-GMA served as an effective compatibilizer between two immiscible components of PE-AA and PS as expected[13-15].

Figures 2 and *3* show morphologies of fractured surfaces for 30/70 (wt/wt) PE-AA(6)/PS blend and 30/70 (wt/wt) PE-AA(9)/PS blend with three different amounts of PS-GMA. The decrease in both domain size and domain size distribution with increase in the amount of PS-GMA is very similar to that given in *Figure 1*. Although AA contents in PE-AA(9) is 9.3 wt%, PE-AA(9) does not have any phase-separated domain consisting of homo-poly(acrylic acid) itself since all PE-AAs used in this study are known to be made by random copolymerization of ethylene and acrylic acid.

The summary of D_n of the dispersed phase for three different PE-AAs/PS blend systems with various amounts of PS/GMA is given in *Figure 4*. These curves are often referred to as an emulsification curve[16]. It can be seen in *Figure 4* that: (i) with increase in the amounts of PS-GMA, rapid decrease in domain size of the dispersed phase was found with smaller amounts of compatibilizer, followed by a levelling off to a near constant value of the diameter when a critical concentration of the compatibilizer was reached. This is consistent with the experimental results reported by Favis *et al.*[16,17] and by the present authors[12]; (ii) with increase in the amount of PS-GMA, the extent of reduction in the domain size for PE-AA(6)/PS blend system is the largest; (iii) when PS-GMA is not present in the blends, D_n for PE-AA(3)/PS blend is the largest and D_n for the PE-AA(9)/PS blend is the smallest among the three PE-AAs/PS blends.

We have proposed reduced domain size (D_r) instead of actual domain size to investigate the interfacial activities for reactive blend systems, where D_r was defined by the ratio of the domain size of each blend system with the

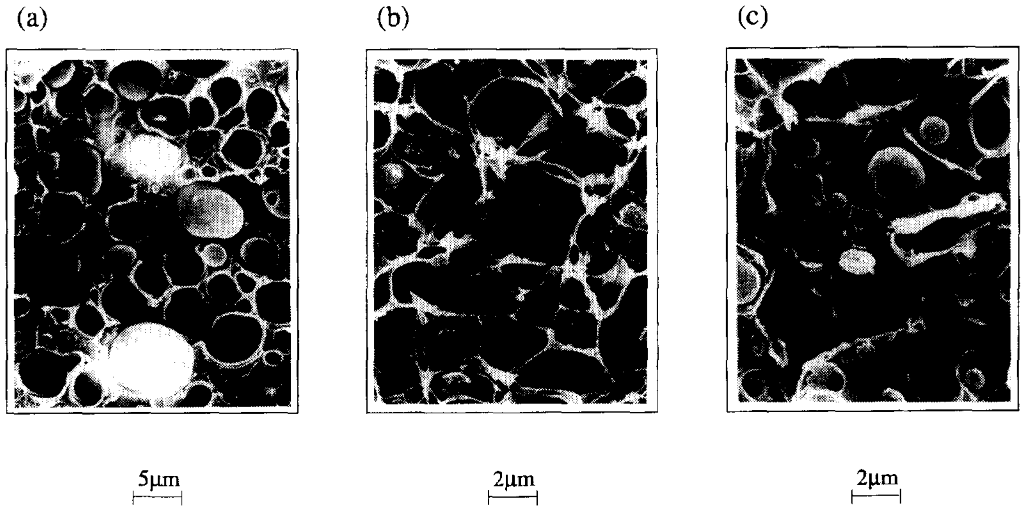

Figure 3 Morphologies of fractured surfaces for 30/70 (wt/wt) PE-AA(9)/PS blends with three different amounts of PS-GMA (wt% in total PS phase): (a) 0; (b) 3; (c) 7

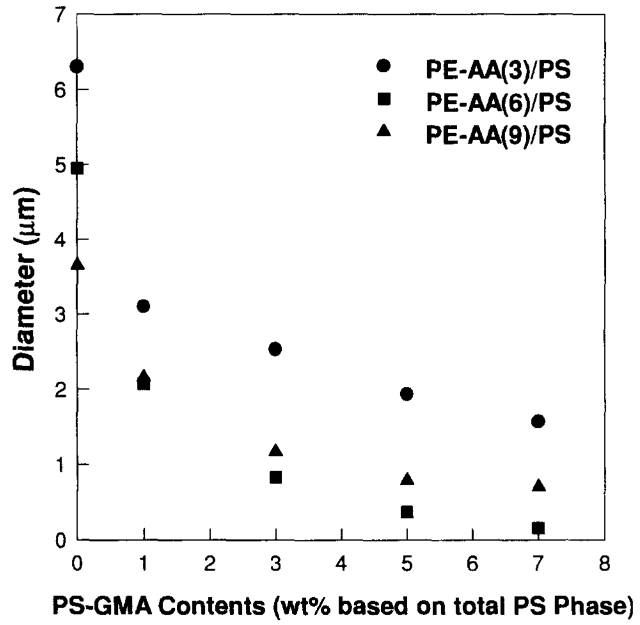

Figure 4 Plots of the number average domain size (D_n) vs the amount of PS-GMA for three different PE-AAs/PS blends: (●) PE-AA(3)/PS; (■) PE-AA(6)/PS; (▲) PE-AA(9)/PS. All blend compositions are 30/70 (wt/wt) PE-AA/PS

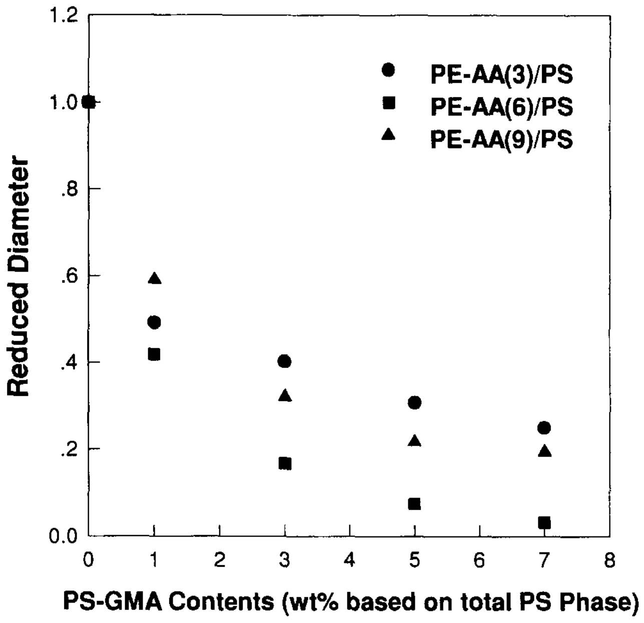

Figure 5 Plots of the reduced domain size (D_r) vs the amount of PS-GMA for three different PE-AAs/PS blends: (●) PE-AA(3)/PS; (■) PE-AA(6)/PS; (▲) PE-AA(9)/PS. All blend compositions are 30/70 (wt/wt) PE-AA/PS

compatibilizer (PS-GMA) to that of respective blend without PS-GMA[12]. By using D_r process parameters such as shear rate, viscosity, elasticity and temperature can be eliminated. Plots of the D_r vs the amount of PS-GMA for three different PE-AAs/PS blend systems are given in *Figure 5*. The reduced domain size reduction of the PE-AA(6)/PS blend is the greatest among the three PE-AAs/PS blend systems. For the PE-AA(3)/PS blend system, the amount of acrylic acid in PE-AA is not large enough to provide sufficient amounts of graft copolymers. On the other hand, for the PE-AA(9)/PS blend system, owing to too much graft reaction between functional groups, graft copolymers with very large molecular weight or even cross-linked copolymers can be formed. The excessively grafted copolymer can shield the PS sections of the grafted copolymer chains into the PS phase and retard the diffusion of reactive species toward the interface. In this situation, graft copolymer does not act as an effective compatibilizer[10]. For the PE-AA(9)/PS blend system, a significant reduction in interfacial tension and domain size cannot be expected. Therefore, there appears to be an optimum amount of acrylic acid in PE-AA. The existence of an optimum value is due to the combined effects of a sufficient reaction near the interface giving enough amounts of graft copolymers as a compatibilizer between PE-AA and PS, and fast diffusion of reactive species toward the interface.

We consider a reason that the domain size of the dispersed phase in the PE-AA(9)/PS blend without PS-GMA is smaller than that in PE-AA(3)/PS and PE-AA(9)/PS blends, which is shown in *Figure 4*. It is known that the domain size of the dispersed phase in an immiscible polymer blends, i.e. without compatibilizer, prepared by melt blending depends mainly on three factors: (a) viscosity and elasticity ratio of disperse phase to continuous phase; (b) the magnitude of applied shear stress or shear rate; (c) interaction parameter between constituent components[18].

First, the rheological properties of PS and three PE-AAs are considered in order to explain the behaviour of (iii). Plots of complex viscosity ($\eta^*(\omega)$) vs frequency (ω) and plots of logarithmic storage modulus ($G'(\omega)$) vs logarithmic loss modulus ($G''(\omega)$) for three PE-AA copolymers and neat PS at 210°C are given in *Figures 6* and *7*. It can be seen in *Figures 6* and *7* that; (i) zero shear viscosity (η_0) of PE-AA(3) is slightly larger than that of PE-AA(6) or PE-AA(9). It is rather interesting to note that although M_n of PE-AA(3) was 2.35 times greater than that of PE-AA(9), the difference in η_0 between PE-AA(3) and PE-AA(9) is less than 30wt%. This suggests that as AA content increases at constant molecular weight, η_0 increases. Thus, in order to have similar value of η_0 or melt flow index (MFI) for two PE-AAs with different amounts of AA, the molecular weight of the PE-AA with a higher amount of AA should be less than that of the PE-AA with a smaller amount of AA; (ii) $\eta^*(\omega)$ at $\omega = 17.5\,\text{rad s}^{-1}$ for three PE-AAs is almost the same, where $\omega = 17.5\,\text{rad s}^{-1}$ represents the average shear rate in internal mixer employed in this study[13]; (iii) the elasticity difference among three PE-AAs determined by plots of log $G'(\omega)$ vs log $G''(\omega)$ was very small. Plots of log $G'(\omega)$ vs log $G''(\omega)$ are very useful to determine elasticity or morphological change in polymer blend, block copolymer and liquid crystal polymer[19]. From *Figures 6* and *7*, the differences in viscosity and elastic ratio of disperse phase to continuous phase among three PE-AAs/PS blends without PS-GMA are too small to explain large difference in D_n given in *Figure 4*. It is also expected that shear stress applied to three blend systems is almost the same due to the same rotating speed of the internal mixer and the similar viscosity of the three blend systems.

Thus, we considered the effect of the interaction parameters between PE-AAs and PS on the domain size in three PE-AAs/PS blends. As the interaction parameter between constituent components becomes smaller, the better miscibility and the smaller domain sizes of the dispersed phase can be obtained. In the context of mean-field theory, the effective interaction energy, Λ_{eff} of copolymer and homopolymer is given by[20,21]:

$$\Lambda_{\text{eff}} = \phi_{\text{PE}}\Lambda_{\text{PE-PS}} + (1-\phi_{\text{PE}})\Lambda_{\text{PAA-PS}} - \phi_{\text{PE}}(1-\phi_{\text{PE}})\Lambda_{\text{PE-PAA}} \qquad (1)$$

where ϕ_{PE} is the volume fraction of PE in PE-AAs and Λ_{ij} is the interaction energy between two monomer i and j which equals to $(\chi_{ij}/V_{\text{ref}})RT$, where χ_{ij} is Flory interaction parameter, V_{ref} is the reference volume, R is the gas constant and T is the absolute temperature. Since values of Λ_{ij} are not available in the literature at the present time, these values are estimated from the solubility parameter of Hildebrand[22].

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

where δ_i and δ_j are the solubility parameters of components 1 and 2, respectively. Although the solubility parameters varies widely from one reference to another, in this study we estimated that the solubility parameters for PS, PE and poly(acrylic acid) are 18.7, 15.1 and 24.9 $(\text{J cm}^{-3})^{(1/2)}$, respectively, which were calculated by the group contribution method[23]. From equations (1) and (2), Λ_{eff} were calculated to be 10.7, 8.9 and 6.7 J cm^{-3} for PE-AA(3)/PS, PE-AA(6)/PS and PE-AA(9)/PS blends, respectively. It is very gratifying to find that the effective interaction energy decreases with increase in AA content in PE-AA although many possible uncertainties are incurred in estimating solubility parameters. Based on the above analysis, the reason that the domain size of the dispersed phase in the PE-AA(9)/PS blend without PS-GMA is smaller than that in the other two blends appears to be the smaller value of effective interaction energy of the PE-AA(9)/PS blend compared to the other two.

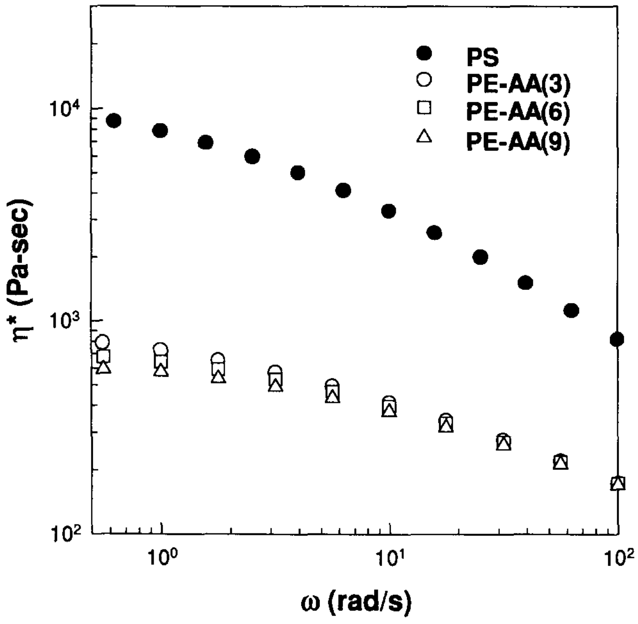

Figure 6 Complex viscosity ($\eta^*(\omega)$) vs frequency (ω) for three different PE-AA copolymers and neat PS at 210°C: (○) PE-AA(3); (□) PE-AA(6); (△) PE-AA(9); (●) PS

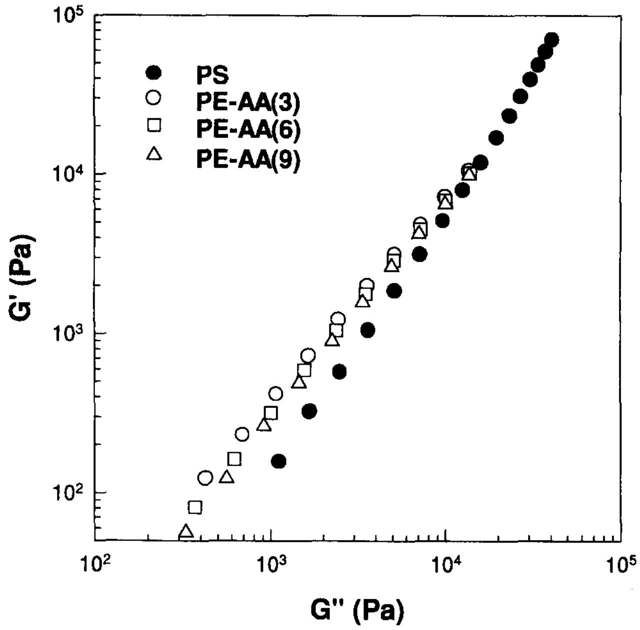

Figure 7 Log $G'(\omega)$ vs log $G''(\omega)$ plots for three different PE-AA copolymers and neat PS at 210°C: (○) PE-AA(3); (□) PE-AA(6); (△) PE-AA(9); (●) PS

Mechanical properties of PE-AAs/PS blends

Figure 8 shows the change in the elongation at break (ϵ_b) with the PS-GMA content for three different PE-AAs/PS blend systems. It is known that the elongation at break is very sensitive to the state of the interface[24,25]. ϵ_b increases considerably from 3.5 to 8% for the 30/70 PE-AA(9)/PS blend with increase in the content of PS-GMA to 7 wt%. This is near twice ϵ_b of neat PS, 4.2%. By increasing the amount of PS/GMA, ϵ_b for all blend systems increases rapidly, and then levels off. The behaviour seen in *Figure 8* is similar to the experimental results investigated by Fayt *et al.*[26]. ϵ_b increases with increase in the amount of acrylic in PE-AA at a fixed concentration of PS-GMA (*Figure 8*). This is not consistent with a change in domain size reduction with varying the amount of acrylic acid in PE-AA. Domain size reduction is related with not only sufficient amount of graft copolymer but also the diffusion of reactive species into the interface. On the other hand, ϵ_b is mainly attributed to the interfacial adhesion. When the amount of acrylic acid in PE-AA increases, the interfacial adhesion in the reactive blend[27] and then ϵ_b increase.

The qualitative extent of the reaction between the functional groups was investigated by measuring the elasticity from the plots of log $G'(\omega)$ vs log $G''(\omega)$. As shown in *Figure 9*, graft copolymers with high molecular weight have higher elasticity than homopolymer[19]. The elasticity for PE-AA/PS blends without PS-GMA is found to be the same but the elasticity for PE-AA/PS blends with 7 wt% PS-GMA increases with increase in the amount of acrylic acid in PE-AA. Since the difference in the amount of acrylic acid for three PE-AAs used in this study is rather small (i.e., 6 wt% difference), it is of interest to study whether ϵ_b for PE-AA/PS blends increase with increase in the AA content in PE-AA up to more than 20 wt%. This is a subject for future investigation.

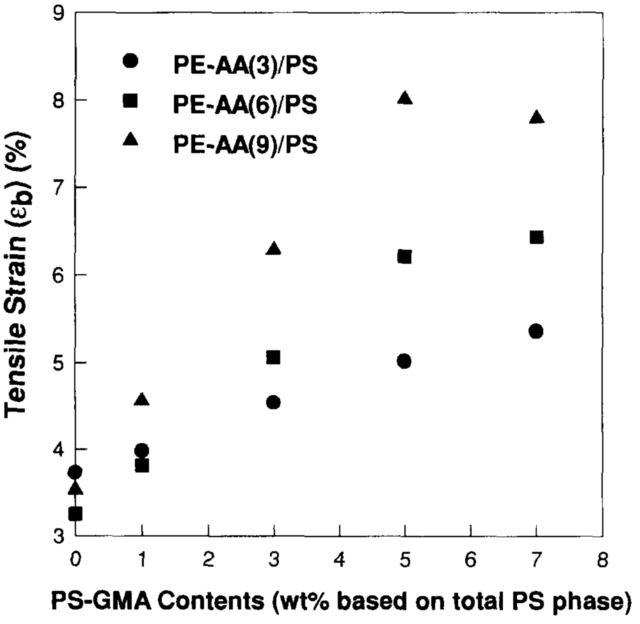

Figure 8 Change in elongation at break (ϵ_b) with PS-GMA content for three different PE-AAs/PS blends: (●) PE-AA(3)/PS; (■) PE-AA(6)/PS; (▲) PE-AA(9)/PS. All blend compositions are 30/70 (wt/wt) PE-AA/PS

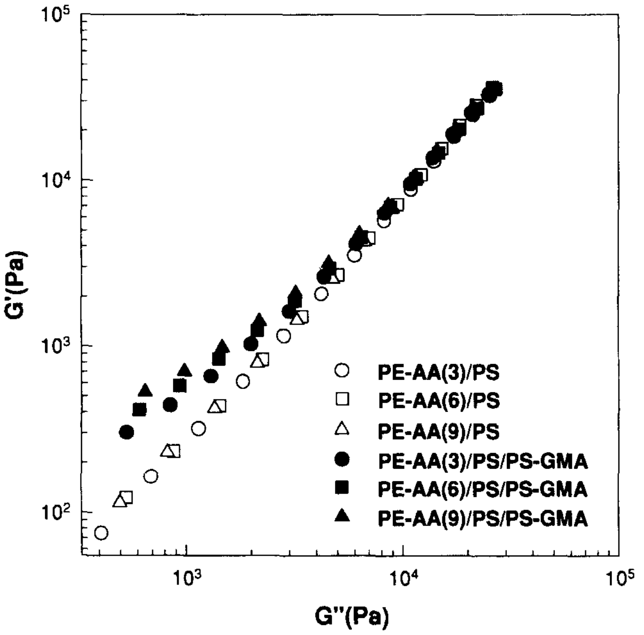

Figure 9 Log $G'(\omega)$ vs log $G''(\omega)$ plots for three PE-AAs/PS blends with and without 7 wt% PS-GMA: open symbols, without PS-GMA; filled symbols, with PS-GMA

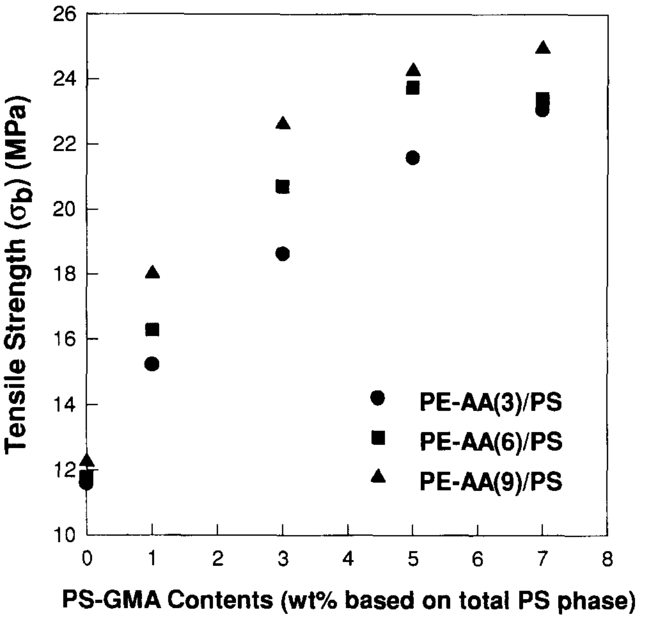

Figure 10 Change in tensile strength at break (σ_b) with PS-GMA content for three different PE-AAs/PS blends: (●) PEAA(3)/PS; (■) PEAA(6)/PS; (▲) PEAA(9)/PS. All blend compositions are 30/70 (wt/wt) PE-AA/PS

Figure 10 shows the change in the tensile strength with varying content of PS-GMA for the three different PE/AAs/PS blend systems. The behaviour of the increase in the tensile strength with increase in the amount of PS-GMA for the blends is similar to that in the elongation at break. As seen in *Figures 8* and *10*, there appears to be a critical amount of PS-GMA above which mechanical properties do not increase significantly to any extent.

Figure 11 shows that a significant improvement of the Izod impact strength with increase in the amount of PS-GMA for the three PE-AAs/PS blend systems is seen, but the change in impact strength depends little upon the amounts of acrylic acid in PE-AA. According to McKay[28] and Chang *et al.*[29], for a polymer blend prepared by reactive compatibilization, finer phase dispersion *does not* necessarily guarantee an improvement in impact properties. Rather, impact strength of polymer blends is known to depend on not only the domain size of the dispersed phase (or inter-particle distance) but also interfacial adhesion[30-33]. In order to investigate in detail the effects of the domain size and interfacial adhesion on impact and tensile properties, more work is needed.

CONCLUDING REMARKS

In this study, we have shown that the reduction in the domain size of the dispersed phase in a 30/70 (wt/wt) PE-AA/PS blend compatibilized by PS-GMA depended significantly on the amount of the functional group of acrylic acid in PE-AA when rheological properties of PE-AAs were almost the same. Specifically, the effective domain size reduction of the PE-AA(6)/PS blend system is larger than that of the other two blend systems, the PE-AA(3)/PS and PE-AA(9)/PS blends. Thus, it can be speculated that to reduce effectively the dispersed domain size in PE-AA/PS blend systems, there appears to be an optimum amount of acrylic acid in PE-AA which is due to the combined effects of the reaction to form sufficient amounts of graft copolymers as a compatibilizer between PE-AA and PS and the diffusion of reactive species toward the interface. One might explain the effect of diffusion on the morphology of the PE-AA/PS blend system in the presence of PS-GMA if one employs PE-AAs with the same amounts of functional units of AA in PE-AA but different molecular weights of PE-AA, which is a subject for future investigation.

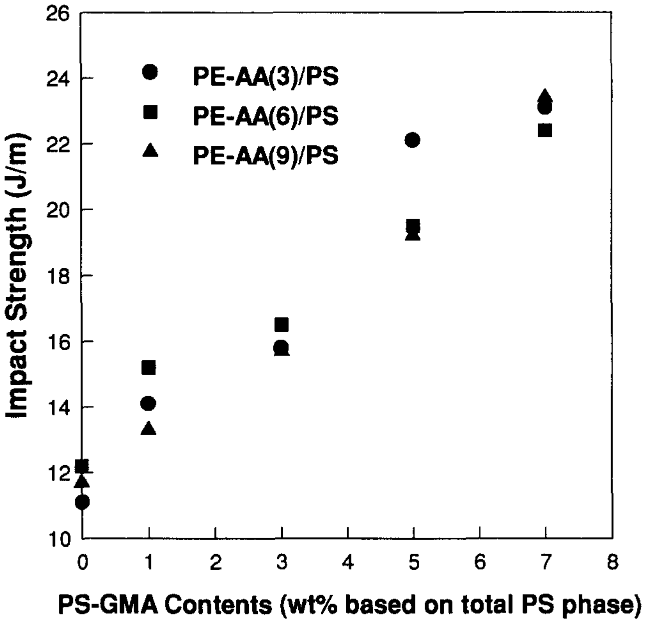

Figure 11 Change in Izod impact strength with PS-GMA content for three different PE-AAs/PS blends: (●) PE-AA(3)/PS; (■) PE-AA(6)/PS; (▲) PE-AA(9)/PS. All blend compositions are 30/70 (wt/wt) PE-AA/PS

The elongation at break (ϵ_b) for the 30/70 PE-AA(9)/PS blend system is the largest among the three PE-AAs/PS blend system employed in this study, which is different from the behaviour of domain size reduction. Also, by increasing the amounts of PS-GMA, ϵ_b for all blend systems increases rapidly, and then levels off. A significant improvement of the Izod impact strength with increase in the amount of PS-GMA for the three PE-AA/PS blend systems is observed, but the change in impact strength is little dependent upon the amounts of acrylic acid in PE-AA.

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