Compatibilizing Effects of Poly(styrene-*graft*-ethylene oxide) in Blends of Polystyrene and Butyl Acrylate Polymers

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SYNOPSIS

The compatibilizing effect of poly(styrene-*graft*-ethylene oxide) in polystyrene (PS) blends with poly(*n*-butyl acrylate) (PBA) and poly(*n*-butyl acrylate-*co*-acrylic acid) (PBAAA) was investigated. No significant effects of the graft copolymer on the domain size were found in the PBA blends. By functionalizing PBA with acrylic acid, the average size of the poly-acrylate domains was reduced considerably by the graft copolymer. Thermal and dynamic mechanical analysis of the PS/PBAAA blends revealed that the PBAAA glass transition temperature (T_g) decreased with increasing graft copolymer content. The effect of the graft copolymer in the PS/PBAAA blends can be explained by interactions across the interface due to the formation of hydrogen bonds between the poly(ethylene oxide) (PEO) side chains in the graft copolymer and the acrylic acid segments in the PBAAA phase. Hydrogen bonding was confirmed by IR analysis of binary blends of PEO and PBAAA. Partial mis-cibility in the PEO/PBAAA blends was indicated by a PEO melting point depression and by a T_g reduction of the PBAAA phase. The thermal properties of the PEO/PBA blends indicated only very limited miscibility. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The individual phases in immiscible polymer blends often retain their physical properties. Multiphase polymer blends therefore offer unique possibilities to incorporate different properties in a single material.[1] Unfortunately, immiscibility usually also leads to low degrees of phase dispersion and poor mechanical properties. The use of polymeric emul-sifiers, in the form of block and graft copolymers, represents an attractive way to control the mor-phology of immiscible polymer blends. Modification of blends by adding properly selected polymeric emulsifiers, often referred to as compatibilizers, generally provides better dispersion and increased interfacial adhesion; consequently the mechanical properties are improved. The success of this concept has been reviewed in a number of articles.[2–5]

The present article deals with the performance of poly(styrene-*graft*-ethylene oxide) (PS-PEO) as a compatibilizer in ternary immiscible blends of PS and polymers based on poly(*n*-butyl acrylate) (PBA). Previously we investigated the compatibil-izing effect of PS–PEO graft copolymers in PS blends with polyamide-6 (PA-6) and polyamide-12 (PA-12).[6] The graft copolymer was found to sta-bilize the blend morphologies. When 3 wt % of the graft copolymer was added, the weight average di-ameters of the PA-6 domains were reduced fivefold as compared to uncompatibilized samples. Similarly, the weight average diameters of the PA-12 domains were reduced threefold. The existence of hydrogen bonding between PEO ether oxygens and PA-6 amide groups in binary PEO/PA-6 blends was con-firmed by IR spectroscopy.

Polymers containing ether oxygens may interact favorably, not only with polymers containing amide groups, but also with polymers containing carboxylic acid groups. The miscibility of poly(vinyl methyl ether) and poly(ethylene-*co*-methacrylic acid) has been shown to increase with the amount of meth-acrylic acid monomer in the copolymer.[7] Similarly, the miscibility of PEO and poly(styrene-*co*-acrylic acid) (PSAA) increases with the amount of AA in

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the copolymer.[8] These results imply that by introducing a few carboxylic acid groups into the PBA chains, an increased interaction with PEO would occur, and an increase in the interfacial activity and the compatibilizing effect of the PS–PEO graft copolymer would be expected.

EXPERIMENTAL

A PS–PEO graft copolymer, designated SEO18, was prepared by anionic polymerization of EO onto a styrene copolymer containing 1 mol % acrylamide. Details on the synthesis and characterization of the graft copolymer were reported previously.[9] The characteristics of graft copolymer SEO18 are given in Table I.

A commercial general purpose PS, VESTYRON® 1202 from Hüls AG, and PEO provided by Schuchardt was used. PBA was prepared by charging 100 g toluene and 100 g BA in a glass flask. After degassing, 0.38 g 2,2′-azobisisobutyronitrile (AIBN) was added. The flask was sealed and the polymerization was allowed to proceed for 24 h at 60°C in N_2 atmosphere. The polymer was then precipitated in methanol. Poly(n-butyl acrylate-co-acrylic acid) (PBAAA) was prepared by charging 300 g toluene, 5 g AA, and 95 g BA in a glass flask. AIBN (0.38 g) was charged after degassing, and the copolymerization was allowed to proceed for 24 h at 40°C in N_2 atmosphere. The copolymer was subsequently precipitated in hexane. All polymers were dried in a desiccator for 24 h, and then vacuum dried at 50°C for a week before analysis. Molecular weight data of PS, PBA, PBAAA, and PEO are given in Table II.

Molecular weight measurements were carried out by gel permeation chromatography (GPC) on two Waters μ-Styragel linear columns using tetrahydrofuran (THF) as the eluent. PS standards (Polysciences) were used for calibrating the PS, PBA, and PBAAA samples, and PEO standards were used

Table I   Data for Graft Copolymer SEO18

$\overline{M}_n$ (main chain) (g/mol)	80,000
$\overline{M}_n$ (side chain) (g/mol)	10,900
PEO content (wt %)	51
$\overline{M}_n$ between side chains (g/mol)	10,400
T_{melt} (°C)	58
ΔH_f (J/g)	64
T_c (°C)	38
ΔH_c (J/g)	63

Table II   Molecular Weight Data for Polymer Samples

Sample	$\overline{M}_n$ (g/mol)	$\overline{M}_w/\overline{M}_n$
PS	53,000	1.9
PBA	26,000	6.5
PBAAA[a]	60,000	3.8
PEO	11,000	1.2

[a] Contains 8 mol % of AA (standard deviation 0.2).

for the PEO sample. The amount of acrylic acid in PBAAA was determined by titration of a toluene/methanol solution (9/1 v/v) with a standardized $0.089 M$ potassium methoxide solution using phenolphthalein as indicator.

Transmission IR spectra were obtained with a Bruker IFS 66 FTIR equipped with a deuterated triglycine sulfate (DTGS) detector. The analyses were performed on thin films made by solution casting from dilute chloroform solutions onto KBr disks. The maximum absorption in all spectra were below 0.5. All samples were vacuum dried at ambient temperature for 48 h prior to analysis.

Blends of PS/PBA containing 0 and 5 wt % of SEO18 and of PS/PBAAA containing 0, 1, 3, and 5 wt % of SEO18 were prepared in a Brabender mixer using screw-type rollers. The weight ratio of PS and the BA polymers were in all cases 80 : 20. All homopolymers were vacuum dried for 48 h at 80°C, and the graft copolymer was dried for 1 week at ambient temperature under vacuum. Approximately 50 g of a mixture of the various polymers was fed simultaneously to the mixer head, and mixing proceeded for 10 min at 190°C with a roller rate of 30 rpm. After mixing, the blends were collected and cooled at ambient temperature before characterization.

PBAAA and PBA were extracted from their respective binary PS blends for differential scanning calorimetry (DSC) analysis. The blends were dissolved in THF, and the PS components were precipitated in butanol. After removal of PS by filtration and of THF by evaporation, the PBAAA and PBA residues were vacuum dried for 48 h at ambient temperature before analysis.

The thermal properties of the pure polymers, and of the polymer blends, were analyzed with a Mettler TA 3000 DSC system under N_2 purge. The samples (5–10 mg) were first annealed at 150°C for 10 min before cooling from 150°C down to −150°C at 20°/min. The temperature was then scanned from −150° to 150°C at 20°C/min. Evaluation of the DSC

data was performed with Mettler Graphware TA72. Glass transition temperatures (T_g) were determined from the inflection points of the heating thermograms. The heats of crystallization (ΔH_c) and of fusion (ΔH_f) were determined by integration, and peak values of the thermograms were reported as crystallization (T_c) and melt (T_{melt}) temperatures. The difference in glass transition temperature noted on two runs of the same sample was always less than 3°C.

Sample bars (10 × 55 mm, thickness approximately 0.7 mm) for studies of morphology and dynamic mechanical properties were compression molded at 180°C for 4 min. The morphologies of the samples were studied with an ISI 100A SEM. Sample bars of the PS/PBA and PS/PBAAA blends were freeze fractured in liquid nitrogen. The PBA and PBAAA phases in the fracture surfaces were extracted with butanol, after which the surfaces were coated with 25-nm layers of Au/Pd prior to SEM analysis.

A Brabender torsional pendulum was used to analyze the dynamic mechanical properties of the PS/PBA and PS/PBAAA blends. The temperature was scanned from −120°C up to 100°C at 1°C/min.

RESULTS AND DISCUSSION

PEO/PBA and PEO/PBAAA Miscibility

Tang et al.[10] reported the use of PBA–PS graft copolymers as compatibilizers for blends of PBA and PS. The domain sizes were reduced and the mechanical properties of the blends improved due to the presence of the graft copolymer. This is an example of the use of an "identical" compatibilizer, that is, the graft copolymer segments were structurally identical with the corresponding phases in the blend. A nonidentical compatibilizer has segments structurally different from the blend components. One of the most important factors that determines the success of a nonidentical compatibilizer is the miscibility of the different segments with the blend components. In the present work a PS–PEO graft copolymer was used as a compatibilizer for PS/PBA and PS/PBAAA blends. PBA and PEO have similar solubility parameters (calculated from "group molar attraction constants"),[11] 9.2 and 9.4 $(cal/cm^3)^{1/2}$, respectively, indicating partial miscibility. However, we have found no reports on PBA-PEO miscibility in the literature.

In a previous article we reported the use of PS grafted with PEO as a compatibilizer for PS/PA-6

and PS/PA-12 blends.[6] In that study a combination of DSC and IR analysis was successfully used for probing specific interactions and miscibility in systems containing hydrogen bonding carbonyl groups. These methods have also been used previously to confirm interactions and miscibility in systems containing carboxylic acid and ether groups. Lee et al.[7] used IR spectroscopy to study hydrogen bonding in poly(ethylene-co-methacrylic acid) blends containing poly(vinyl methyl ether) and poly(ethylene oxide-co-propylene oxide). They found two distinct carbonyl stretching regions for carboxylic acid dimer and for carboxylic acid–ether oxygen interactions. When the weight fraction of the ether-containing polymer was increased, the relative absorption of carbonyls involved in acid–ether interactions increased. The authors concluded that the blends were extensively mixed at the molecular level in the amorphous state. Pilar et al.[8] studied the phase structure of partly miscible PEO/PSAA blends. By DSC they found that the presence of PEO lowered the T_g of the copolymer. Also, two separate PEO melting endotherms were observed instead of one for pure PEO.

A study of binary blends of PBA/PEO and PBAAA/PEO was carried out to probe the miscibility of PEO side chains in PBA and PBAAA. The IR spectrum in Figure 1 shows the carbonyl region of PBA blended with 0 and 50 wt % PEO. In Figure 2, the same region of PBAAA blended with 0, 50, and 80 wt % PEO is shown. The dominating ab-
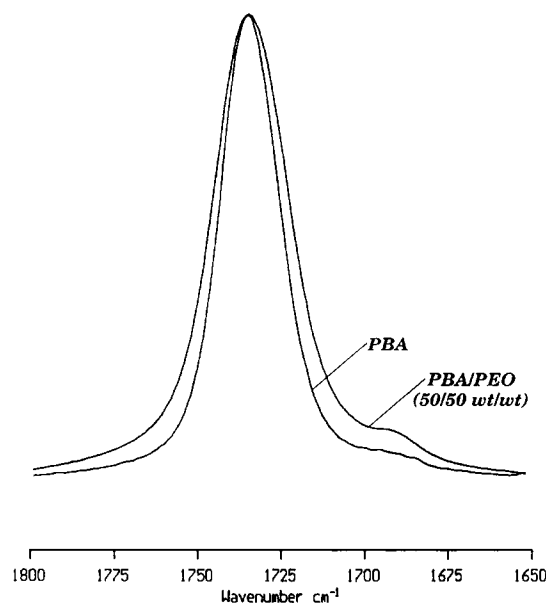

Figure 1   IR spectra in the carbonyl region of pure PBA and PEO/PBA (50/50 w/w).
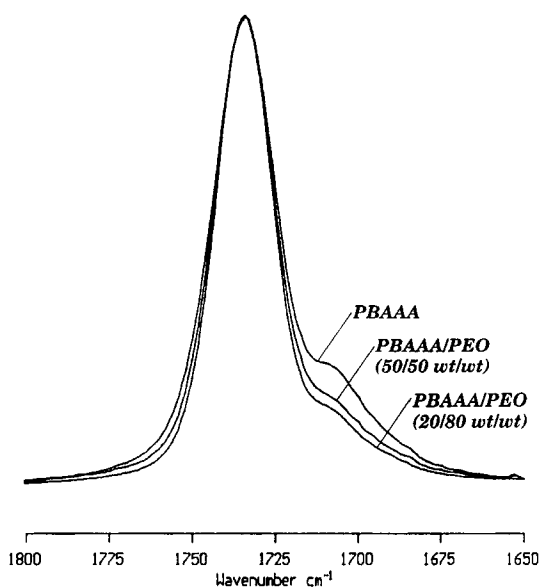
Figure 2 IR spectra in the carbonyl region of pure PBAAA and of PBAAA/PEO blends. In this region contributions from ester carbonyls (at 1735 cm^{-1}) and carboxylic acid dimer carbonyls (at 1710 cm^{-1}) are visible. The presence of PEO clearly decreases the IR absorption from carboxylic acid dimers, indicating hydrogen bonding between amide hydrogens and ether oxygens.

Table III   Summarized DSC Data for Pure Polymers and PEO Blends

Sample	T_g (°C)	T_c (°C)	T_{melt} (°C)	ΔH_f[a] (PEO) (J/g)
PS	100	—	—	—
PEO	—	55	64	139
PBA	−50	—	—	—
PBA/PEO (50/50 w/w)	−57	51 (−5)	65	126
PBAAA	−36	—	—	—
PBAAA/PEO (50/50 w/w)	−60	20 (−37)	53	18

Temperatures in parentheses originate from small crystallization exotherms (see Fig. 3).

[a] Values are based on the PEO weight of the samples.

sorption peak in this region is positioned at 1735 cm^{-1}, and is ascribed to ester carbonyls present in both PBA and PBAAA. This band was used as an internal reference to compensate for differences in film thickness. Absorption from carbonyl groups in AA dimers is seen as a shoulder at 1710 cm^{-1}. The small absorption band at 1690 cm^{-1} is present in both PBA and PBAAA spectra and arises from BA units. It is evident from Figure 2 that the absorption band at 1710 cm^{-1} decreases considerably on addition of PEO to PBAAA, which is a consequence of a decrease in the concentration of acid dimers because of the introduction of PEO ether oxygens as hydrogen bond acceptors. Because of the large absorption from ester carbonyls in the region 1760–1710 cm^{-1}, no absorption bands from free carboxylic acid groups or from carboxylic acid groups interacting with ether oxygens could be resolved.

DSC data obtained from the PBA and PBAAA blends with PEO are summarized in Table III, and PEO crystallization exotherms and melting endotherms are shown in Figure 3. As compared to the pure polymers, the glass transitions of PBA and PBAAA were 7° and 24°C lower, respectively, in the PEO blends. PBAAA also influenced the crystallization of PEO that took place over a broad temperature range. Moreover, the PEO melting point was
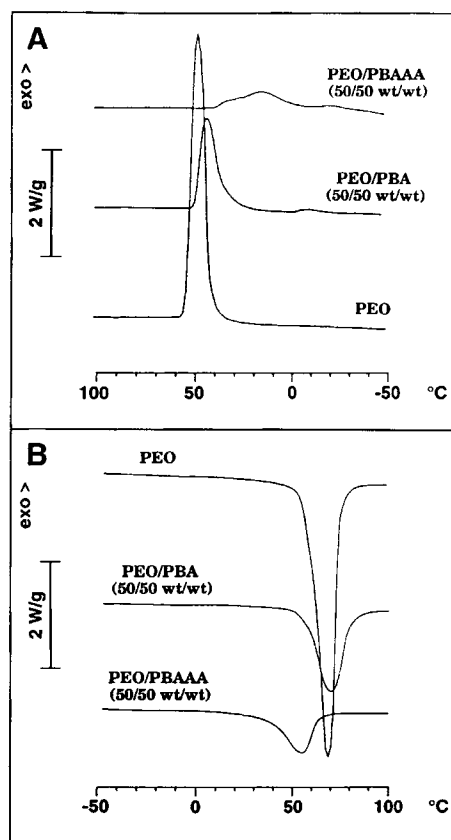

Figure 3 DSC traces from (A) PEO crystallization exotherms and (B) the corresponding melting endotherms for pure PEO, PEO/PBA (50/50 w/w), and PEO/PBAAA (50/50 w/w). (Values given for w/g are based on the total sample weight.)

11°C lower in the PBAAA blend than in pure PEO. The influence of PBA on the thermal properties of PEO was less pronounced. The substantial PEO melting point depression in the PBAAA/PEO blend is a strong indication of miscibility.[12] However, the polymers can only be partially miscible because PEO, PBA, and PBAAA all had distinctly separate transitions in the blends.

Morphology of PS/PBA and PS/PBAAA Blends

PS/PBA (80/20 w/w) and PS/PBAAA (80/20 w/w) blends with various amounts of graft copolymer SEO18 were prepared by melt mixing at 190°C. Compression molded sample bars were freeze fractured in liquid N_2 and the BA polymer phase domains were removed by etching the fracture surfaces with butanol prior to SEM analysis. Figure 4 shows SEM micrographs of etched freeze fracture surfaces of PS/PBA blend samples containing 0 and 5 wt % of SEO18, respectively. The graft copolymer seems to have no effect on the blend morphology because no significant differences in PBA domain sizes could be noted. On the other hand, in PS/PBAAA blends the domain sizes depended strongly on the graft copolymer content. In Figure 5 SEM micrographs of PS/PBAAA blends with 0, 1, 3, and 5 wt % SEO18, respectively, are shown. The average domain size decreased from about 10 μm in the uncompatibilized blend to about 3 μm with 1 wt % SEO18 added. With an addition of 3 wt % the domain size was further reduced to about 1 μm. At 5 wt % of SEO18, no further decrease in the average domain size was obtained. This saturation effect was similar to that previously found for PS/PA-6 and PS/PA-12 blends compatibilized by graft copolymer SEO18. The saturation effect, which has also been observed by others,[13,14] can be understood from a theory derived by Taylor[15] for Newtonian dispersed systems in shear flow. Initially, the graft (or block) copolymer reduces the interfacial tension in the blend, thereby causing a decrease in the domain size of the dispersed phase. The final domain size is determined by a balance of shear forces, causing domain breakup, and interfacial tension, working against deformation and domain breakup. Graft copolymer additions beyond the saturation concentration, that is, the concentration at which the blend interface is completely covered with graft copolymer, will not result in any further reduction in interfacial tension or in domain size.

The limited miscibility of the PEO side chains of the graft copolymer in the PBA phase noted above apparently makes the graft copolymer unsuitable as
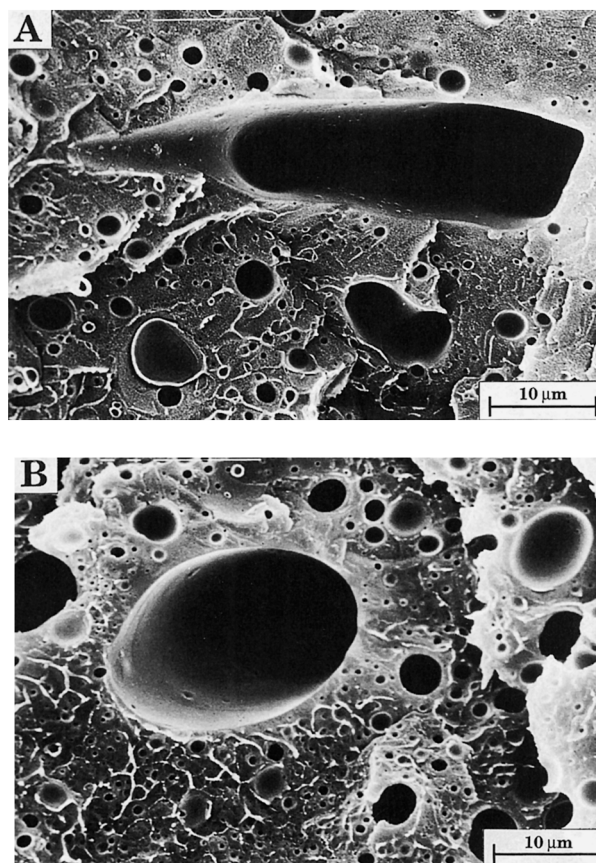

Figure 4 SEM micrographs of etched freeze fracture surfaces of PS/PBA blends containing (A) 0 wt % SEO18 and (B) 5 wt % SEO18. The samples were prepared by compression molding.

a compatibilizer in PS/PBA blends. When AA units are introduced into the polyacrylate, as in PBAAA, the miscibility with the PEO side chains increases considerably as noted above. An increased interfacial coverage of the graft copolymer is achieved, and consequently a reduction of the interfacial tension and a reduction of the domain size in the blend is obtained.

Thermal Properties

Summarized DSC data for the different polymers and blends are given in Table IV. The T_g of PBA ($-47°C$) in the binary blend with PS remained essentially unchanged as compared to that of the pure polymer. The addition of graft copolymer to the PS/PBA system did not influence the T_g of the PBA phase either. In contrast, the T_g of PBAAA ($-36°C$) increased by 6°C in the blend with PS. As noted in the table, the T_g's of extracted PBA and PBAAA from the binary PS blends were virtually identical
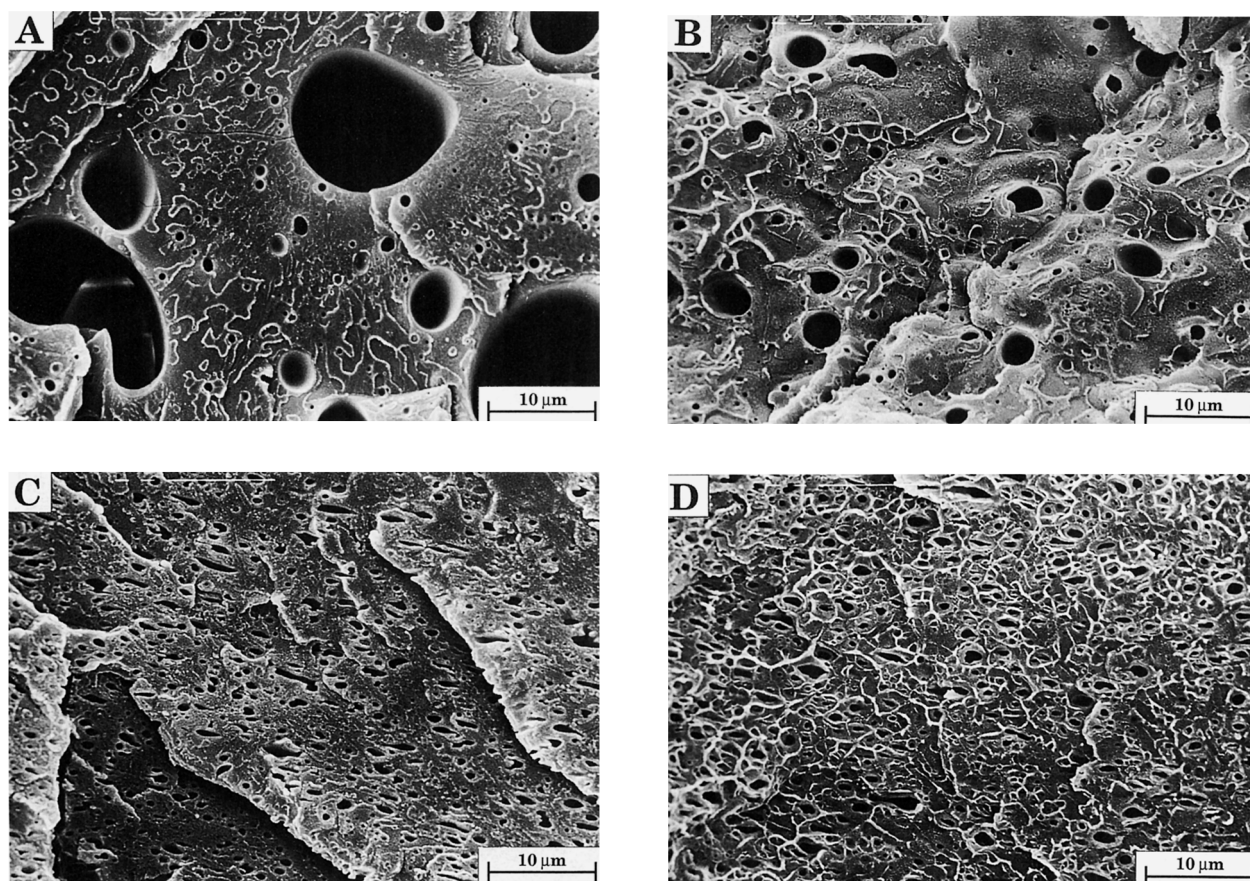
Figure 5 SEM micrographs of etched freeze fracture surfaces of PS/PBAAA blends containing (A) 0 wt %, (B) 1 wt %, (C) 3 wt %, and (D) 5 wt % SEO18. The samples were prepared by compression molding.

with those of the pure unblended samples, $-50°$ and $-36°$C, respectively. Therefore, it seems unlikely that the observed T_g increase should be related to degradation or oxidation. Addition of graft copolymer SEO18 to the blend depressed the T_g of the PBAAA phase gradually, from $-30°$ to $-40°$C with 5 wt % added (Table IV). The shift in T_g with composition indicates a partial miscibility, as noted above for the PEO/PBAAA blend.[12] From the DSC results one may conclude that the PEO side chains

Table IV   DSC Data for PS/PBA and PS/PBAAA (80/20 w/w) Blends

| | T_g (°C) | | | T_{melt} (PEO) | ΔH_f (PEO)[a] |
Sample	PS	PBA	PBAAA	(°C)	(J/g)
PS/PBA	101	-47[b]	—	—	—
PS/PBA containing					
5 wt % SEO18	100	-46	—	53	1.2
PS/PBAAA	104	—	-30[b]	—	—
PS/PBAAA containing					
1 wt % SEO18	103	—	-33	—	—
3 wt % SEO18	103	—	-37	—	—
5 wt % SEO18	103	—	-40	54	0.7

[a] Values are based on the total sample weight.
[b] T_g of extracted PBA = $-49°$C and T_g of extracted PBAAA = $-39°$C (see Experimental section).

Figure 6 Torsional pendulum analyses of PS/PBA blends containing 0 and 5 wt % SEO18.
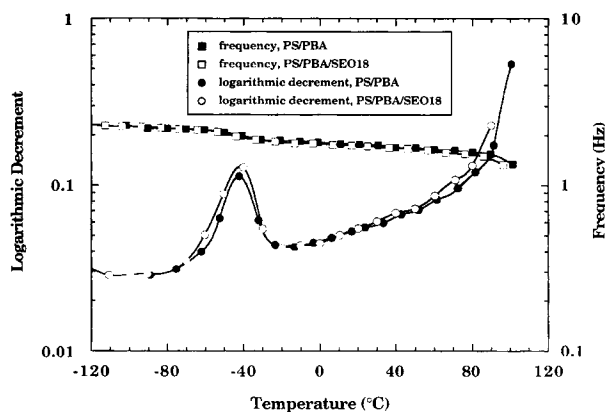

Figure 7 Torsional pendulum analyses of PS/PBAAA blends containing 0 and 5 wt % SEO18.

of the graft copolymer are partially soluble in PBAAA, but not in PBA. No significant effects on the PS glass transitions of the PS/PBA and the PS/PBAAA blends were noted.

Melting endotherms from PEO side chain crystallinity were observed at approximately 54°C in the thermograms of the PS/PBA and PS/PBAAA blends containing 5 wt % of SEO18. Similar results were previously reported for PS/PA-6 and PS/PA-12 blends (80/20 w/w) compatibilized by SEO18.[6] For these blends, PEO crystallinity was noted at SEO18 concentrations of 3 wt % and above. A transmission electron microscopy (TEM) investigation of the PS/PA-6 blends revealed that graft copolymer SEO18 at concentrations of 3–5 wt % was partly phase separated into domains in the PS phase.[16] A similar phase separation can be anticipated for the PS/PBA and PS/PBAAA blends.

Dynamic Mechanical Properties

The damping characteristics of the blends in dynamic shear were studied by torsional pendulum analysis. Compression molded sample bars were analyzed at temperatures from −120° to 100°C at a scan rate of 1°C/min. All sample bars failed at approximately 100°C due to softening of the PS matrix at the glass transition. The logarithmic decrement and frequency are shown in Figure 6 as a function of temperature for PS/PBA blends containing 0 and 5 wt % SEO18. The local damping maxima at −41°C are associated with the T_g of the PBA phases. No shift in T_g was noted for the PBA phase in the PS/PBA/SEO18 blend, as compared to the PS/PBA blend. Corresponding measurements for the PS/PBAAA blends containing 0 and 5 wt % SEO18 are presented in Figure 7, where the local damping
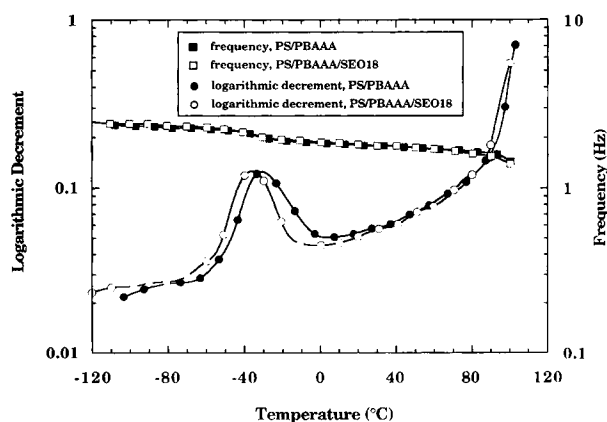
maxima at −29° and −35°C are associated with the T_g of the PBAAA phases. The dependence on the T_g of the PBAAA phases in the PS/PBAAA/SEO18 blends of the graft copolymer content is shown in Figure 8. The T_g of the PBAAA phase, as measured by torsional pendulum, was successively decreased by the addition of SEO18. Thus, both thermal and dynamic mechanical analyses showed a significant decrease in T_g with increasing graft copolymer content, analogous to that noted for the binary PBAAA/ PEO blends.

CONCLUSIONS

The compatibilizing effect of PS grafted with PEO was investigated in PS blends with PBA and PBA functionalized with 8 mol % AA (PBAAA). By adding 3 wt % graft copolymer, the PBAAA domain size in the PS/PBAAA blend could be reduced by a factor of 10. No further decrease was noted when 5 wt % was added, that is, the system seems to be satu-
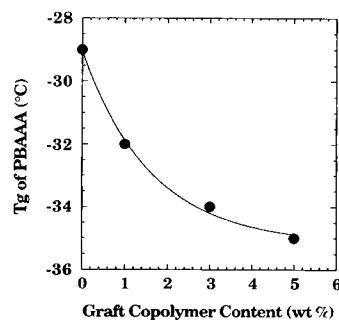

Figure 8 Variation of T_g of the PBAAA phase with the amount of graft copolymer added to PS/PBAAA/SEO18 blends as measured by torsional pendulum analysis.

rated at the 3% level. It may thus be concluded that PS/PBAAA blends can be compatibilized by the graft copolymer. PBA shows very weak interactions with PEO, and PS/PBA blends were not compatibilized by the same graft copolymer.

Thermal and dynamic mechanical analyses of PS/PBA and PS/PBAAA blends containing graft copolymer, together with DSC studies on binary PEO/PBA and PEO/PBAAA blends, all show that the presence of carboxylic acid increases the miscibility of PEO in the polyacrylate phase. The higher miscibility of PEO in PBAAA is induced by hydrogen bonding between carboxylic acid groups and the ether group, as evident from IR spectroscopy results on PEO/PBAAA blends. Finally, an important observation is that the functionalization of PBA not only increases the hydrogen bonding capability, making compatibilization possible, but it also changes thermal and other properties of the polyacrylate.

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