

Alternating Copolymers as Compatibilizer for Blends of Poly(ethylene terephthalate) and Polystyrene

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ABSTRACT: Compatibilization of blends of poly(ethylene terephthalate) (PET) and polystyrene with alternating copolymers of maleic anhydride and isobutylene (IM) and its partly phenol substituted product (PIM) has been studied. The characterization techniques applied were dynamic mechanical analysis, differential scanning calorimetry, scanning electron microscopy, and tensile testing. In all compositions studied, morphological observations demonstrated that the addition of approximately 5 wt % of copolymers led to the domain size reduction of dispersants. The PIM copolymer was most effective in reducing the domain size, whereas the IM copolymer was less satisfactory. The blends containing PIM also gave the more enhanced ultimate strength than those of other systems. The noncrystalline PIM copolymers lowered the tensile modulus of the blend as much as 60% even in the polystyrene-rich region and varied linearly with values of quenched PET modulus throughout the compositions, indicating the formation of homogeneous amorphous phase. Based on the experimental observation that the reduced domain size with PIM copolymer, a compatibilization mechanism of the blend with PIM alternating copolymer is proposed and discussed in terms of the interactions between ester groups of PET and PIM (transesterification), and the possible formation of intermediate π -complex between the π -electron deficient aromatic ring of PIM and π -electron rich aromatic ring of PS. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1998–2007, 2000

Key words: PS; PET; blends; compatibilizer; alternating copolymer

INTRODUCTION

As is well known, the commercial significance of both poly(ethylene terephthalate) (PET) and polystyrene (PS) is confirmed by the large number of producers throughout the world. In particular, PET is an extensively used thermoplastic because of a combination of unique physical, mechanical and permanent properties, and processability. Also, as an engineering plastic, it offers, among

others, excellent high temperature properties, creep resistance, and solvent resistance.

Currently, on the other hand, the problem of environmental pollution and raw material conservation encourage the recycling of plastics waste. Among them, the availability of large amounts of recycled PET mainly from the packaging industry warrants studies of its blends with other plastics wastes that may also be recyclable. In addition, although they are known to be immiscible, the potential synergistic effects of combining a high modulus thermoplastic with a ductile one are good enough to draw attention not only for the development of a cost effective compatibilizing strategy but also for achieving favorable cost/per-

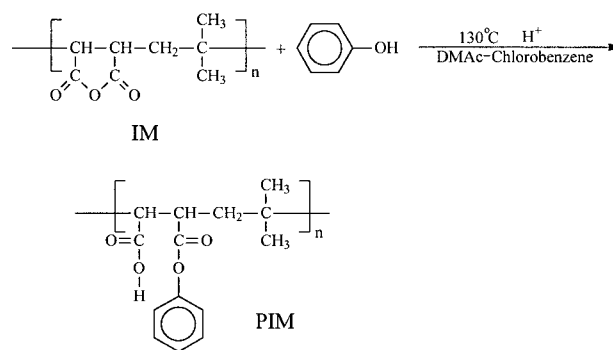
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formance balances suitable for materials replacement or new market applications. Therefore, a blending of PET and PS is considered to be highly desirable. However, essentially no such commercial products are so far known to exist and very few studies on this system have been reported previously. Undoubtedly, this is because of the incompatibility of the given system, and hence an exploitation of a new compatibilizer is indispensable.

An enhancement in the degree of compatibility between the constituent components has been known by an addition of a block or graft copolymer as a compatibilizer to those immiscible polymer blends.¹⁻⁶ Previous work on the PET/PS blend includes a report by McKay,⁵ who found that the addition of PS-block-polycaprolactone copolymer exhibited discrete glass transition of the blend system, but increased the extent of dispersion of the homopolymer components within one another quite effectively. Kim and Lee⁶ also studied the effect of poly(styrene-co-glycidyl methacrylate) copolymer as an *in situ* compatibilizer on the morphology and rheological properties of the immiscible poly(butylene terephthalate) and PS, and reported that the viscosity at low shear rates increased but the degree of shear thinning was not pronounced and the finer morphology was obtained when more than 5 phr copolymer was added to the blend system. However, given the fact that the PET/PS binary blend is incompatible, those research efforts led to the result that there still remains an unacceptable level of properties and costs.

In this work, the mechanical, thermal, and morphological features of the PET/PS blend mixed with two chemically different alternating copolymers as the compatibilizers, maleic anhydride and isobutylene (IM) and its partly phenol substituted product (PIM), are examined. The reason for selecting the alternating copolymer as the compatibilizer is to avoid the shortcomings met usually by those block or graft copolymers, that is, they are in the microphase separated state at mixing temperature, or they may stay in a homopolymer phase as a micelle when added, rather than move to the interface, or making their dispersion difficult near the interface between two phases due to high viscosity. Furthermore, an expectation that the interactions between polar groups (ester or anhydride group), or possible formations of aromatic π -complexes between the PS and benzene ring connected to the ester group, or the secondary valence forces acting between non-



Scheme I Synthetic route for the preparation of phenol substituted IM copolymer.

polar groups can enhance the compatibility between the constituent polymers, and hence the compatibilizer is designed to have the structures having maleic anhydride and isobutylene unit (IM), and partially phenol substituted units in IM copolymer. Three blend systems, PET/PS/IM, PET/PS/PIM, and PET/PS, are melt blended and characterized in terms of compatibilizing effect, blend morphology, and the resultant mechanical performance.

EXPERIMENTAL

Materials

The PS used in this study was a commercial grade ($M_w = 3.60 \times 10^5$ g/mol, $M_w/M_n = 2.41$) of Miwon Petrochemical Co., Korea. The PET was a semicrystalline polyester and was obtained as a commercial grade resin with no additives from SKI Ltd., Korea. The intrinsic viscosity $[\eta]$ of PET found in the mixed solvent of phenol and tetrachloroethane (60 : 40 volume ratio) was 0.78 dL/g at 25°C. The isobutylene-alt-maleic anhydride copolymer (Isopan 04,⁷ $M_w = 5.5 \sim 6.5 \times 10^4$ g/mol) was kindly donated by the Kuraray Co., Japan. The phenol used for the modification of the copolymer was purchased from the Tedia Co., USA, and was used without further purification. Other solvents were purified by simple distillation before use.

Preparation of Phenol Substituted Copolymer (PIM)

The procedure of phenol substitution reaction at the maleic anhydride unit of the copolymer is given schematically in the following Scheme I. A

typical synthetic procedure is as follows. The IM copolymer (10 g) was dissolved in a 200 mL of mixed solvent of *N,N*-dimethyl acetamide (DMAc) and chlorobenzene (100 : 100 volume ratio). After complete dissolution of IM, catalytic amounts of sulfuric acid and excess amounts of phenol (the molar ratio of IM/phenol was 1 : 2.5) were added with vigorous agitation. Reaction was continued for 48 h, maintaining a temperature of 130°C and stirring. The reaction mixture was then cooled to room temperature and poured into large quantity of *n*-hexane. The precipitated fibril-form of reaction product was separated by filtration and dried under reduced pressure at 40°C.

Preparation of Blends

Both the component polymers and compatibilizer were dried in a forced air convection oven at 80°C overnight. The dried materials were tumble-blended and fed into a Brabender counter-rotating screw extruder operating at a temperature profile of 230-250-260°C in sequence of hopper, melting zone, and die, respectively. The residence time of the melt mixture was about 5 min under the screw speed of 60 rpm. The extrudate was air cooled, pelletized, and dried.

Specimens for tensile tests were injection-molded with a dumbbell molder (Model CS-183; Custom Scientific Instruments, Inc., USA) set at $265 \pm 5^\circ\text{C}$.

Characterization and Analysis

$^1\text{H-NMR}$ (Bruker AM-300 Spectrophotometer) was used to determine the substitution degree of phenol to the anhydride group of IM copolymer. The solvent used was dimethylsulfoxide- d_6 (DMSO- d_6) containing 0.4 vol % of tetramethylsilane. On the theoretical bases that the integrated intensity of an absorption on the proton NMR spectrum depends only on the molar concentration of the substance times the number of nuclei per molecule responsible for the peak, the content of phenol group in the copolymer is estimated by the following equations derived from the values of arithmetic mean of the integrated intensities of characteristic proton absorptions per mol of the phenol groups,

$$I_{\text{PH}} = \frac{\frac{I_{4,o}}{n_{4,o}} + \frac{(I_{4,m} + I_{4,p})}{(n_{4,m} + n_{4,p})}}{2} \quad (1)$$

$$I_{\text{IM}} = \frac{I_3}{n_3} \quad (2)$$

where I_{PH} is the intensity of phenol, n is the number of nuclei responsible for the peak, o , m , and p indicate respectively the ortho, meta, and para positions of aromatic protons. Thus, the wt % of the phenol groups substituted can be written as the following:

$$w_{\text{PH}} = \frac{I_{\text{PH}} \cdot M_{\text{PH}}}{I_{\text{PH}} \cdot M_{\text{PH}} + I_{\text{IM}} \cdot M_{\text{IM}}} \times 100 \quad (3)$$

where w_{PH} is the wt % of phenol and M is the molecular mass of phenol and the repeating unit of IM copolymer.

The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet spectrophotometer in the wave number range of $4000 \sim 400 \text{ cm}^{-1}$. The KBr pellet method was used. Dynamic mechanical response was established by means of a DuPont Model 983 dynamic mechanical analyzer (DMA). Storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) of the blends and pure polymers were measured at 1 Hz over the temperature range of 30 to 120°C with a heating rate of 5°C/min. The size of the bar shaped specimen, prepared by injection molding, was 45-mm long, 12.5-mm wide, and 3-mm thick, and the instrument was calibrated to account for the instrument losses and end-corrections of specimen length. The glass transition temperatures (T_g 's) of the blend samples of various compositions were also measured with a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-7) equipped with an intracooler. All T_g measurements were made with 10 mg of samples at a scan rate of 10°C/min in the range of 30 ~ 270°C under nitrogen atmosphere. The data obtained from the second scanning were accepted.

To confirm the phase homogeneity, the morphology of the fracture surfaces of the blends was examined using a scanning electron microscope (Model S-2250N; Hitachi Co., Japan), operated with a high-tension voltage of 15 kV. The stress-strain behaviors of blends were observed by tensile testing. An Instron (Instron Co. Series IX Automated Material Testing System 1.16) operated with a chart speed of 5 pts/s, and a crosshead speed of 3 mm/min was used. Tests were performed at 25°C and 60% relative humidity, and data were taken as averages of at least 10 measurements.

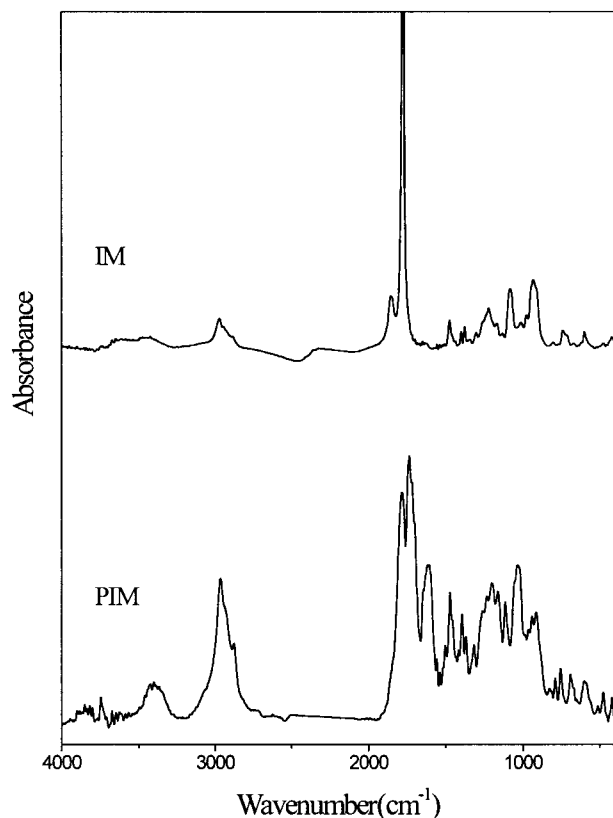


Figure 1 IR spectra of copolymer IM and PIM.

RESULTS AND DISCUSSION

Modification of Cyclic Anhydride Group in IM Copolymer by Phenol

Reactions that break the O—H bond of the hydroxy group are common reactions of phenol, which usually lead to the formation of esters with cyclic anhydrides in the presence of acidic catalyst. The intention, therefore, has been to prepare a copolymer containing monosubstituted phenolate group by a condensation reaction with continuous elimination of by-product, the water.

Figure 1 compares the FTIR spectra of the phenol substituted copolymer (PIM) and pure IM copolymer. Evidently, the PIM exhibits weaker carboxylic acid anhydride C=O stretching band at $1870 \sim 1820 \text{ cm}^{-1}$, but shows formations of a new broad carboxylic acid band at $3300 \sim 3500 \text{ cm}^{-1}$ and a medium benzoate ester band at 1110 cm^{-1} , which indicates that the anhydride rings in the IM copolymer have been broken and partly substituted with phenol groups. The substitution degree (wt % of phenol) of the reaction product was estimated from the intensities of aromatic

proton absorptions appearing in the $^1\text{H-NMR}$ spectrum, illustrated in Figure 2. The IM copolymer shows its broad methine protons at δ 3.0 and 3.2 ppm, methylene proton at δ 1.8 and 2.2 ppm, and methyl proton at around δ 1.0 ppm, whereas the PIM reveals weak aromatic proton absorptions at δ 6.8 and 7.3 ppm, indicating the substitution of aromatic groups in the IM copolymer chain. The degree of phenol substitution, estimated on the basis of eq. (3), was found as 25% by weight. This low value of substitution is probably the consequence of steric hindrance of the phenol group to approach the nucleophilic carbonyl carbon of anhydride ring mainly because of the interference of bulky isobutylene unit in the neighborhood. Moreover, the possibility that those anhydride rings in the chain are partly underexposed because of the flexible chain conformation of the IM copolymer (the exponent value of Mark-Houwink equation is 0.77 in DMF at 30°C ⁷) might have led the substitution degree of phenol to be low. It is thus considered that those unreacted anhydride rings are opened by acid catalyst and remain in the form of carboxylic acids.

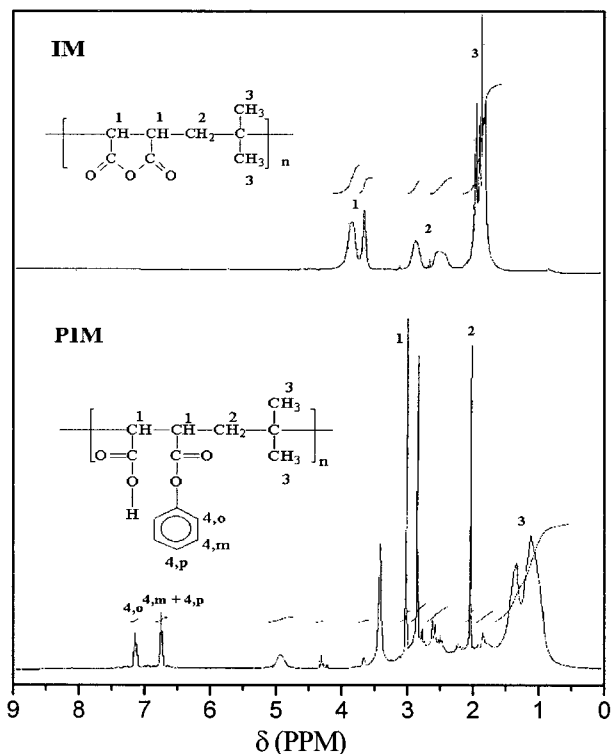


Figure 2 $^1\text{H-NMR}$ spectra of copolymers IM and PIM.

Glass Transition Evidence

The thermal transition behaviors of blends are observed both by the DMA and DSC measurements, and their dynamic spectra and thermograms are shown in Figures 3 and 4, respectively. Also the potentially observable transitions including T_g for blends, PET, and PS, as well as crystallization exotherm (T_{cr}) and melting endotherm (T_m) for PET are summarized in Table I. Because of the ambiguity of the T_g s of the constituents determined by the DSC and $\tan \delta$ for the PET-rich phases, the transition temperatures read by the loss modulus (E'') are used for most considerations of compositional effects. In this report, the notations used for the sample codes indicate the weight ratios (g/g) of component polymers and

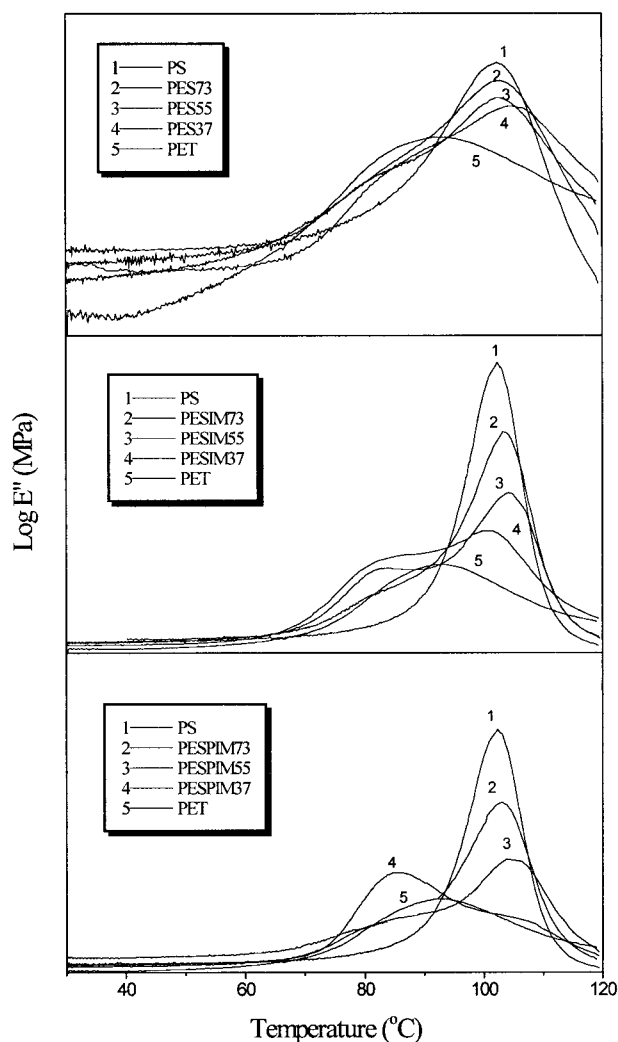


Figure 3 Loss modulus spectra for PS, PET, and blends.

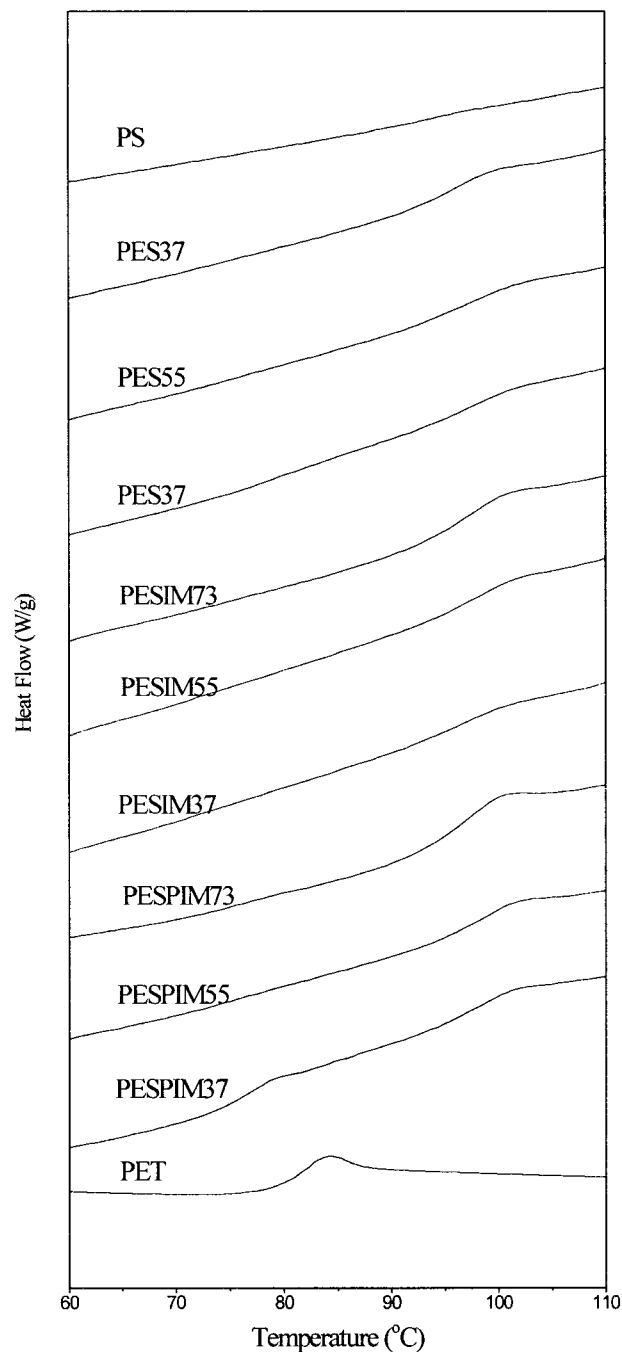


Figure 4 DSC thermograms of blends and component polymer.

compatibilizer; for example, PESIM73 indicates 70 PS/30 PET/5 PIM by weight ratio.

As Table I exhibits, the T_g s of PET read from the dynamic spectra appear, as usual, as slightly higher than those measured by DSC. The PS and PET phases in the blends are showing discrete glass transitions indicative of the immiscibility of

Table I Summary of Thermal Transition Temperature for Polystyrene/Poly(ethylene terephthalate)/Poly(isobutylene-*alt*-maleic anhydride), Polystyrene/Poly(ethylene terephthalate)/Phenol Substituted Poly(isobutylene-*alt*-maleic anhydride) Blends Measured by DSC and DMA

Sample Code	Blend Composition (wt %)	T_g (PET) ^a (°C)	T_g (PS) ^a (°C)	T_g (PET) ^b (°C)	T_g (PS) ^b (°C)	T_{cr}	T_m
PS/PET							
PS	100 : 0		98		102		
PES91	90 : 10	74	97	82	102	^c	252
PES73	70 : 30	74	96	82	103	119	253
PES55	50 : 50	75	94	83	102	118	254
PES37	30 : 70	76	94	83	103	121	256
PES19	10 : 90	77	95	84	103	122	258
PET	0 : 100	81 ^d 69 ^e		91		175	256
PS/PET/IB-a-MA							
PESIM91	90 : 10 : 5	72	96	81	102	^c	252
PESIM73	70 : 30 : 5	74	95	82	103	116	253
PESIM55	50 : 50 : 5	76	95	83	104	120	254
PESIM37	30 : 70 : 5	73	94	83	101	122	256
PESIM19	10 : 90 : 5	72	93	82	100	123	256
PS/PET/IB-a-PMA							
PESPIM91	90 : 10 : 5	68	96	81	101	^c	252
PESPIM73	70 : 30 : 5	70	95	82	102	120	252
PESPIM55	50 : 50 : 5	73	95	84	104	122	255
PESPIM37	30 : 70 : 5	72	94	83	101	124	256
PESPIM19	10 : 90 : 5	70	93	82	99	125	256

^a Obtained from DSC.^b Obtained from E'' of DMA.^c Transition not observed.^d Crystalline.^e Quenched (amorphous).

the components in all compositions studied. However, the overall trends of T_g variations of the blends after the addition of copolymers appear different than that of the uncompatibilized blend. In particular, when the blend is compatibilized with the PIM copolymer, it can be seen from Table I that the T_g s of the two components are shifted somewhat closer to one another, which is an indication that the addition of PIM copolymers to the blend enhanced the degree of dispersion of the homopolymer components. This can likely be attributable to the potential specific interactions of PIM copolymer with ester groups of PET and aromatic rings of the PS chain, such as transesterification or intermediate aromatic π complex formation, although it has been impossible to provide experimental evidence.

On the other hand, Table I demonstrates some peculiar features in the T_g variations of both the blends containing compatibilizer and simply melt blended. For the melt blends, the T_g of PET increased monotonously with an increase of PET

content, whereas those blends containing copolymer PIM or IM revealed a peculiar trend of T_g variation, that is, the T_g increased with the content of PET up to 50 wt % but depressed gradually with the increment of PET content. The monotonic increase in T_g of the melt blends is considered to be attributed to the enhanced crystallinity of PET along with the increased quantity of PET. However, in the case in which the copolymers were added, the occurrence of phase inversion of the blend at around 60 wt % of PET may have favored the compatibility of the blend, which in turn suppressed the crystallization of PET and finally led to depression of T_g as the PET content increased. This phenomenon can also be readable from the crystallization temperatures (T_{cr}) listed in Table I.

For the case of PS T_g of those blends compatibilized, there exists a trend that an increase in the PET contents results in a decrease in the blend T_g , which is an indication that there are intimate molecular interactions between the co-

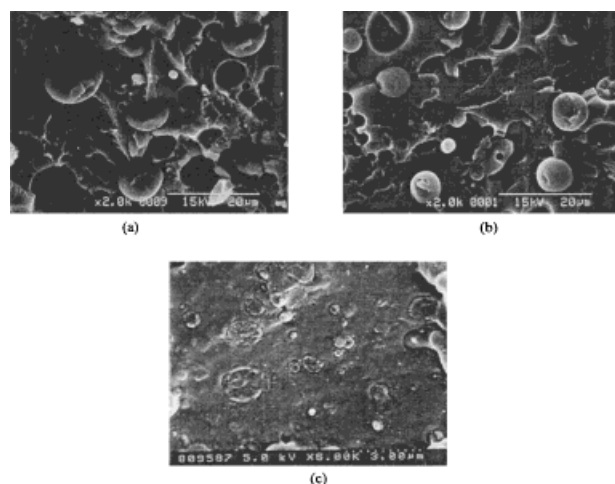


Figure 5 Scanning electron micrographs of blends; 80PET/20PS. (a) PES82 (original magnification, $\times 2000$); (b) PESIM82 (original magnification, $\times 2000$); and (c) PESPI82 (original magnification, $\times 6000$).

polymers and PS and thus result in enhancement of compatibility between PS and PET. However, in the case of PET 50 wt %, both the blends of PESIM 55 and PESPI 55 show an exceptional behavior of T_g variations, that is, the smaller decay in T_g than other compositions has occurred. A decisive explanation of this peculiar behavior is not available at present, but is probably due to the consequence of the uncertain settlement of the matrix and dispersed phase in the blend at the given composition. For a typical immiscible system, it is known that such behavior can often be observed.⁸

Phase Morphology

As is well known, taking SEM micrographs of fracture surfaces of blends and observing their morphology, particle sizes, and degree of dispersion often proves to elucidate the compatibility between the blend components or to define the effectiveness of a compatibilizer. SEM micrographs for those blend samples selected from the PS- and PET-rich compositions with constant content of copolymer are presented in Figures 5–7 and compared. The SEM micrographs are obtained from the cryoscopic fracture surfaces.

Looking first at Figure 5 in which the PET-rich blends are depicted, it can be seen that a considerably different phase morphology can exist according to the existence and kinds of copolymer. In the case in which the copolymer is absent, a

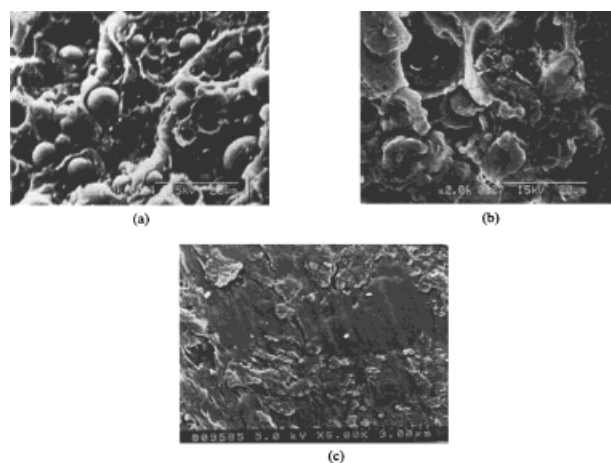


Figure 6 Scanning electron micrographs of blends, 20PET/80PS. (a) PES28 (original magnification, $\times 2000$); (b) PESIM28 (original magnification, $\times 2000$); and (c) PESPI28 (original magnification, $\times 6000$).

spherical-domain (PS)/matrix (PET) morphology [Fig. 5(a)], indicating the phase separation, is seen. The average domain size of the disperse phase is about $10 \mu\text{m}$ and the interfacial adhesion between the domains and matrices turns out very poorly, but the addition of 5 wt % of IM copolymer [Fig. 5(b)] yields a phase morphology showing a partly coalesced structure in which the PS domains have almost disappeared. Surprisingly, as Figure 5(c) exhibits, the addition of a phenol-modified copolymer (PIM) produced a phase of further coalescence of the PS spheres, and thus

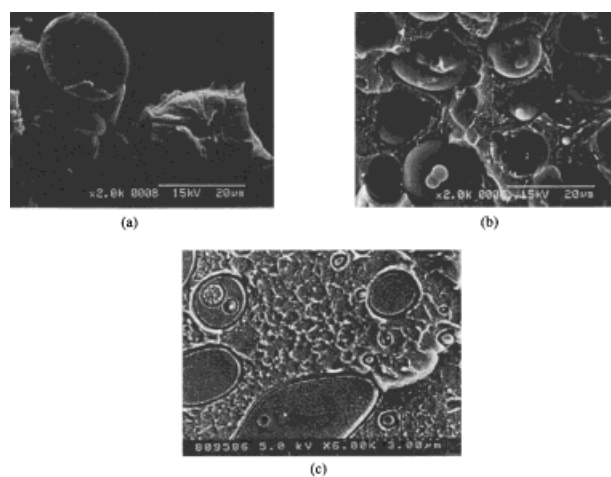


Figure 7 Scanning electron micrographs of blends, 50PET/50PS. (a) PES55 (original magnification, $\times 2000$); (b) PESIM55 (original magnification, $\times 2000$); and (c) PESPI55 (original magnification, $\times 6000$).

both phases come to be continuous in which the interphases between the domains and the matrices can hardly be definable. This result can be ascribed to the effects of transesterification between the pendant carboxylic acid groups of PIM and the ester groups of PET, and the possible intermediate π -complex formations between π -electron deficient aromatic ring of the PIM and π -electron rich benzene ring in the PS.

In Figure 6(a), the SEM micrograph of 20 PET/80 PS containing no copolymer, PS is the continuous phase and PET appears as large sized spheres, indicating that the phases are completely separated as in the case of the PET-rich system. The addition of 5 wt % of IM copolymer, however, does not change much of the phase morphology from that of blends with no copolymer, though the numbers of spheres are slightly decreased, as Figure 6(b) reveals. This means that the IM copolymer has little affinity with PS. Nevertheless, as in the case of PET-rich blends, the addition of 5 wt % PIM copolymer to the blends containing 80% PS is responsible for a deep modification of the morphology, that is, the discrimination of PS and PET phases is almost impossible and the interfacial adhesion between the spheres and continuous phase becomes unquestionable, as can be seen in Figure 6(c). In fact, with the exception of a few irregular parts in the micrograph, the phase is remarkably homogeneous. This result emphasizes again the importance of aromatic interactions for the promotion of compatibility.

Figure 7(a–c) illustrates those SEM micrographs obtained from the blends of 50 PET/50 PS containing different kinds of copolymers. In these blends, it has been regarded that PET forms the continuous phase because of the difference in melt rheological characteristics of the PET and PS resins.⁸ It can be seen from Figure 7(a) that the dispersed PS domain appears as a large cylindrical phase, suggesting the complete immiscibility, but the addition of small amounts (5 wt %) of IM makes the shape of the PS domain become spherical, as Figure 7(b) reveals. Interestingly, again, the addition of 5 wt % of phenol modified copolymer (PIM) to the 50 : 50 blend is responsible for a deep modification of the morphology [Fig. 7(c)]. Clearly, the SEM image demonstrates that the dispersed PS macrodomains contain subinclusions of PET microdomains, which leads us to conclude that the two component polymers become partly miscible because of the emulsifying effect of the PIM.

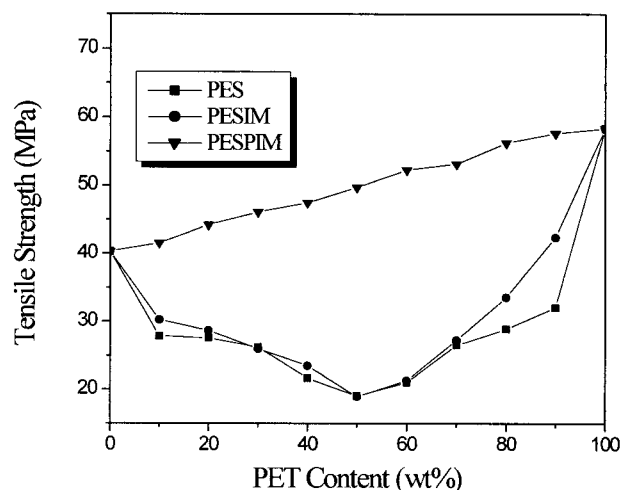


Figure 8 Tensile strength variations of PET/PS, PET/PS/IM, and PET/PS/PIM blends as a function of PET content.

The results of SEM microscopy thus far observed indicate that although the two major blend components, PET and PS, are immiscible, they can be emulsified to a considerable extent by incorporating a phenol modified maleic anhydride-isobutylene alternating copolymer.

Mechanical Performance

Recently, it has been shown that the measurement of tensile strength is a sensitive tool to evaluate the extent of compatibility of blends.⁹ The compatible systems demonstrate similar synergism in tensile strength as found in the PPO-PS system^{10–12} and the partially compatible blends exhibit a sigmoidal dependence of tensile strength on composition as observed recently for blends of polyvinyl chloride with copolymers of vinyl chloride and vinyl acetate,¹³ and for the blend of a poly(aryl ether) and poly(α -MS/AN) (69 : 31).¹⁴ Totally phase separated blends of PPO and various copolymers with compositions greater than 67.8 mol % 4-chlorostyrene show signs of deterioration in strength, especially at low PPO blend content.¹⁵

Plots of tensile strength at break and Young's modulus of blends across the composition range are shown in Figure 8 and 9, respectively. Evidently, the tensile strength values of blends compatibilized with the copolymer PIM lie above the tie line levels, showing a reinforced physical response,¹⁶ whereas either the system containing IM copolymer or the noncompatibilized system

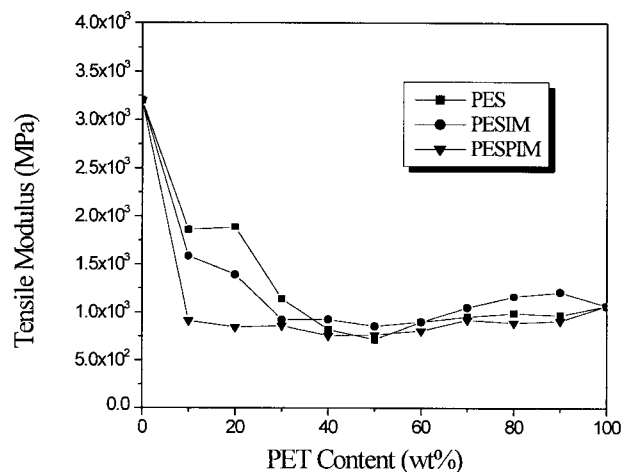


Figure 9 Tensile modulus variations of PET/PS, PET/PS/IM, and PET/PS/PIM blends as a function of PET content.

exhibits large negative deviations. Although it may be dangerous to consider the changes of mechanical properties as evidence for the compatibilization, about 200% enhancement of tensile strength of the PET/PS/PIM system can be regarded, as usual, as a confirmation of compatibilization.¹⁷

In contrast, however, all three blend systems demonstrate tensile moduli as negative deviations, especially notable in the composition range in which rigid PS is the continuous phase, as can be seen from Figure 9. Also found is that the PIM containing system gives not only the lowest values of moduli even in the PS-rich composition region, but also an almost linear trend of variations of moduli throughout the composition range with values nearly the same as that of pure PET, indicating little effect of the blend composition on the tensile modulus of the blend containing 5% PIM. This result well agrees with that of the phase morphology demonstrated by the blend PET(20)/PS(80)/PIM(5) [Fig. 6(c)], which has shown good adhesion between the matrices and the domains. Thus, the lowering of the modulus of PS even at the PS-rich blend region can likely be attributable to the reduction of crystalline character of the PET by the addition of noncrystalline PIM copolymer, which in turn yields increased ductility of the PET, and then the improved adhesions and domain dispersion must have led the phase to the homogeneous and stabilized phase, giving decreased values of PS modulus. This tensile modulus performance also gives strong support that the PIM copolymer acts as an effective compatibilizer for PET and PS blending.

The question remains as to why the PIM copolymer appears effective for the blending of PET and PS. This can be considered firstly to be a result of conformational similarities (flexible chain polymers, $\langle R^2 \rangle_o^{1/2}/M$ for PS is 670×10^{-4} nm, for PET is 840×10^{-4} nm) between the component polymers and the compatibilizer (PIM), which can accentuate the tendency for the intimate mixing of the different segments of those polymers by the favorable entropic gain. This increment of segmental contacts, in turn, can allow some specific interactions to occur between PET and PIM chains such as transesterification¹⁸ or Claisen-type condensation,¹⁹ yielding a new block copolymer or a β -keto ester. Likewise, an intermediate π -complex formation between π -electron deficient aromatic ring due to the electron withdrawing effect of carbonyl carbon in the PIM ester group and π -electron rich benzene in PS, giving the reinforced affinities between PIM and PS, can also be anticipated.²⁰ Although no experimental evidences can be provided at present, the isobutylene groups in the PIM main chain also are believed to be effective in promoting the interactions with PS either by weak London dispersion force or entanglement.

CONCLUSIONS

In the immiscible PET and PS systems, a phenol modified alternating copolymer of maleic anhydride and isobutylene (PIM) is experimentally evidenced as an effective compatibilizer for improving adhesive properties and domain dispersions, and consequently stabilizes the phase morphologies of the PET and PS blends. For most of the blends, the addition of small amounts of copolymer PIM (5 wt %) demonstrated synergism in mechanical performance of the blend relative to that of the corresponding noncompatibilized blend.

The effectiveness of PIM is discussed in terms of the possible interactions between ester groups of PET and functional groups of PIM, and the intermediate π -complex formation between PS aromatic rings and those attached to the ester group of PIM.

Those experimental evidences so far obtained lead us to conclude that the blends of PET and PS compatibilized with small amounts of PIM alternating copolymer are considered to be potential for substantial applications.

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REFERENCES

1. Giudice, L. D.; Cohen, R. E.; Attala, G.; Berninotti, F. *J Appl Polym Chem* 1985, 30, 4034.
2. Brown, H. R. *Macromolecules* 1989, 22, 2859.
3. Creton, C.; Kramer, E. J.; Hadjiioannou, G. *Macromolecules* 1991, 24, 1846.
4. Fait, R.; Jerome, R.; Teyssie, Ph. *J Polym Sci Polym Phys* 1989, 27, 775.
5. McKay, I. D. *J Appl Polym Sci* 1991, 43, 1593.
6. Kim, J. K.; Lee, H. *Polymer* 1996, 37, 305.
7. Kuraray Co., Kuraray Isopan, 1995.
8. Li, T.; Topolkaev, V. A.; Hiltner, A.; Baer, E.; Ji, X. Z.; Quirk, R. P. *J Polym Sci Part B* 1995, 33, 667.
9. Fried, J. R.; MacKnight, W. J.; Karasz, F. E. *J Appl Phys* 1979, 50, 6052.
10. Yee, A. F. *Polym Eng Sci* 1977, 17, 213.
11. Kleiner, L. W.; Karasz, F. W.; MacKnight, W. J. *J Polym Eng Sci* 1979, 19, 519.
12. Freid, J. R. Ph.D. Dissertation, University of Massachusetts, 1976.
13. Dimitrov, M.; Foldes, E. *Int Polym Sci Technol* 1979, 6(10), T/1-T/5.
14. Oblabisi, O.; Farnham, A. G. *Adv Chem Ser* 1979, 176, 559.
15. Freid, J. R.; Hanna, G. A.; Kalkanoglu, H. *Polymer Compatibility and Incompatibility*; Solc, K., Ed.; MMI Press Symposium Series: New York 1980; Vol. 2; p. 237.
16. Choi, H. J.; Park, S. H.; Kim, J. K.; Jun, J. I. *J Appl Polym Sci* 2000, 75, 417.
17. Brown, H. R.; Char, K.; Deline, V. R.; Green, P. F. *Macromolecules* 1993, 26, 4155.
18. Li, H.-M.; Wong, A. H. *Characterization of Extruded Films Based on Blends of PET and PTMT*; Solc, K., Ed.; MMI Press Symposium Series; New York, 1982; Vol. 2, p. 395.
19. Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4th Ed.; Prentice Hall International, Englewood Cliffs, NJ, 1983.
20. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper & Roe: New York, 1981; Chapter 7; p. 566.