

Reactive Reinforcement of the Interface of Poly(ether sulfone)/Poly(phenylene sulfide) Polymer Blend by PMR-POI

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ABSTRACT: The effect of polymerization of monomer reactant-polyimide (POI) as the interfacial agent on the interface characteristics, morphology features, and crystallization of poly(ether sulfone)/poly(phenylene sulfide) (PES/PPS) blends were investigated using a scanning electron microscope, FTIR, WAXD, and XPS surface analysis. It was found that the interfacial adhesion was enhanced, the particle size of the dispersed phase was reduced, and the miscibility between PES and PPS was improved by the addition of POI. It was also found that POI was an effective nucleation agent of the crystallization for PPS. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1297–1306, 2002

Key words: poly(ether sulfones); blends; polyimide; interfaces

INTRODUCTION

Blending existing polymers together has long been known to be an effective, low-cost way of developing novel materials. However, the vast majority of polymer pairs are mutually immiscible and, when blended, display very poor mechanical properties due to their coarse, heterogeneous morphology and weak adhesion. In recent years, this problem has been addressed by incorporating a compatibilizer or interfacial agent, which can reduce the interfacial tension and promote adhesion between phases, into incompatible blends.^{1–5}

Interfacial adhesion plays an important role in the mechanical properties of polymer blends. Several methods to promote interfacial adhe-

sion have been proposed, such as using preformed block or graft copolymers⁶ and random copolymers.⁷ The block copolymer chains form interphase junctions through which stress can be transferred, thus resulting in substantial reinforcement of the interfaces. The interaction between a block copolymer and homopolymers can be either via a van der Waals bond^{8,9} or via hydrogen bonds,¹⁰ but present evidence suggests that entanglement, rather than the details of intermolecular bonding, plays a dominant role. Another more efficient way to increase the interfacial strength is by reactive blending.¹¹ Here, the reactive interfacial agents have specific functional groups and are able to generate *in situ* formation of block or graft copolymers at the interface during the blend preparation through the reaction of functional group incorporation into the blend components. Reactive compatibilization has been proved to be an effective means for morphology control^{12–18} and interfacial tension reduction.^{19–22}

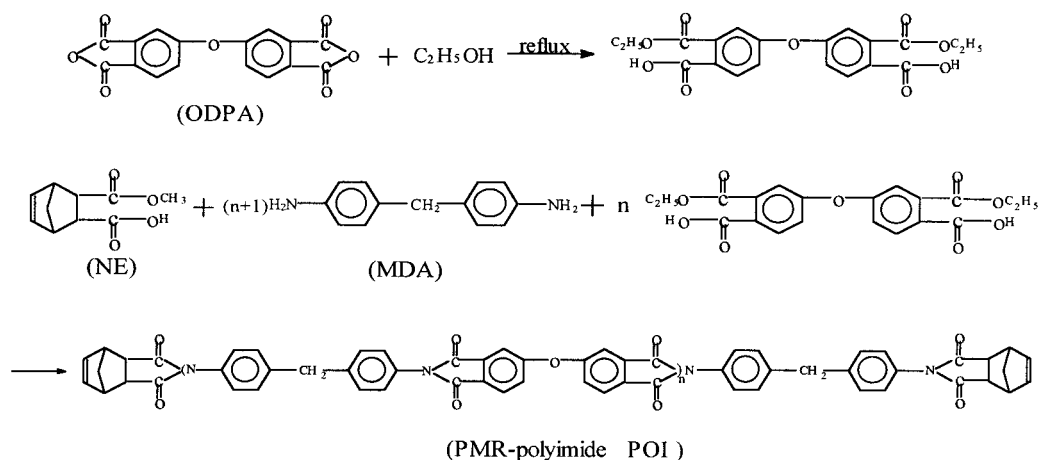
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However, the cost of premade block or graft copolymers and the limitation of reactive processing in the *in situ* formation of block copolymers are hindrances to broaden the application of this technique, and these made us consider new compatibilization strategies.^{23,24} For engineering plastics, for example, poly(ether ether ketone) (PEEK), poly(ether sulfone) (PES), and poly(phenylene sulfide) (PPS), it is not easy to design and synthesize suitable block or graft copolymers or to make each pair have appropriate functional groups. Here, we introduced thermally *in situ* crosslinkable polymerization of a monomer reactant-type polyimide [polymerization of monomer reactant (PMR)-polyimide (POI)] precursor²⁵ as the interfacial agent which will have a crosslinking or grafting reaction with PEEK, PES, and PPS during melt blending.



The precursor can form a crosslinked network or graft with PPS and PES by thermally induced radical polymerization through the double bonds at each end of the molecule. Also, the molecular weight can be controlled by changing the mol ratio of the three ingredients to ensure that the precursor exhibited satisfactory mobility in the melt blending. In this experiment, the mol ratio of ODPA, MDA, and NE was 2:3:2, and the average molecular weight of the precursor was 1434. ODPA and NE were purified before use; MDA and ethanol were used as received.

Sample Preparation

The premixing of POI with polymers was carried out by soaking the PES and PPS powder into a POI ethanol solution homogeneously. After most

EXPERIMENTAL

Materials

PES powder was purchased from the Xinghua Chemical Plant of the Jilin University (Changchun, Jilin, China). The inherent viscosity was 0.38 dL/g. The PPS used was a commercial grade p-3 manufactured by the Sichuan Factory of High Performance Engineering Plastics (Zigong, Sichuan Province, P.R. China). All PESs and PPSs were dried at 90°C for 12 h in a vacuum oven to remove the absorbed water.

The thermally crosslinkable PMR-POI precursor was prepared in the laboratory using three monomeric ingredients of 4,4'-oxydipthalic anhydride (ODPA), 4,4'-methylenedianiline (MDA), and the monomethyl ester of norbornene anhydride (NE). The chemical structure is

of the ethanol evaporated at room temperature, the POI-coated powder was dried at 70°C for 12 h in a vacuum oven. The PES/PPS (70/30) and PES/PPS/POI (70/30/5) blends were prepared by melt blending the coated or uncoated PES and PPS powders in a Brabender internal mixer at 290°C, 50 rpm, for 10 min. To characterize the reaction between POI and the two bulk polymers, PES/POI (90/10) and PPS/POI (90/10) blends were also prepared by the same method described above.

To observe the effect of POI on the interface characteristics of PPS/PES blends directly, PPS and PES powders were compression-molded into disks with a thickness of 1.5–2 mm. Thin film of POI was prepared by the spin-coating of 5 wt % of an ethanol solution of POI directly onto the PPS and PES disks. After the ethanol evaporated thoroughly at

room temperature, the coated PPS and PES disks were brought into contact so that the spin-coated film was located between the two polymers. Also, samples without POI at the interface were also made. These specimens were isothermally annealed in the hot stage at 250°C for different times. The temperature was chosen because it is well above the glass transition temperature of the PPS and PES, but still below the melting point of the PPS.

Morphology

The morphology of the blends and interfaces of the adhesive joint specimens were observed with a scanning electron microscope (JXA-840A) at an accelerating voltage of 25 kV. Both the blended samples and the adhesive joint specimens were fractured at the liquid nitrogen temperature; the latter were fractured in the direction perpendicular to the interface, then coated with a thin layer of gold before observation.

XPS Surface Analysis

Films about 0.5–1 μm in thickness of PPS were spun-cast from a diphenyl ether solution onto silicon wafers and dried in a vacuum oven at 80°C; then, a layer of the PES or PES/POI (100/7.5) solution blends was cast from dichloromethane directly onto the PPS-coated wafers. These bilayer films were annealed at 250°C for various times to allow the reaction to occur. After cooling to room temperature, the samples were drenched in dichloromethane, which is a good solvent for PES but cannot swell PPS; then, they were analyzed by a VG ESCALAB MK-II X-ray photoelectron spectroscopy using a $\text{MgK}\alpha$ source.

Purification and Characterization of Grafting and/or Crosslink Copolymers of PES–POI and PPS–POI

The PES/POI (or PPS/POI) blend (1–1.5 g) was packed in filter paper and put in a Soxhlet extractor and extracted with dichloromethane (or diphenyl ether) for 24 h, then dried in a vacuum oven at 80°C until its weight was constant. The gel content was calculated by the following equation:

$$\text{Gel content (\%)} = \frac{W_s - W_n}{W_p} \times 100$$

where W_s , W_n , and W_p represent the total weight of the polymer and the filter paper after extraction, the weight of the filter paper, and the weight of the polymer, respectively.

The gels of the PES/POI and PPS/POI blends were analyzed by a BIO-RAD FTS-135 Fourier transform infrared spectrophotometer. Its resolution was 4 cm^{-1} and the number of scans was 16. To prove that the residual POI had been removed from the blends during extraction, the solution after extraction was cast onto a silicon wafer; then, a VG ESCALAB MK-II X-ray photoelectron spectroscopy was adopted to examine whether the unreacted POI existed.

Crystallization of the Blends

Wide-angle X-ray diffraction (WAXD) profiles of PES/PPS and PES/PPS/POI blends were obtained by using a RIGAKU D/Max II X-ray diffractometer with $\text{CuK}\alpha$ Ni-filter radiation. The measurement condition was 40 kV, 20 mA.

RESULTS AND DISCUSSION

Characterization of Grafting and/or Crosslink Copolymers of PES–POI and PPS–POI

The gel content of PES/POI (90/10) and PPS/POI (90/10) blends were 11.17 and 17.83%, respectively. Figures 1(a) and 2(a) show the XPS spectra of the filtrate of the extracted PES/POI and PPS/POI blends, with a characteristic peak at 399.68 eV that resulted from the 1s electron of the nitrogen atom in unreacted POI molecules. For neat PES and PPS, no signal was detected in this range.

For comparison, FTIR spectra were collected from both neat POI, PES, and PPS and the gel of PES/POI and PPS/POI blends. Figures 3(c) and 4(c) show the spectrum of POL. In Figure 3(b), an additional peak at 1717 cm^{-1} corresponding to the carbonyl stretch appears, indicating that POI molecules are introduced onto the molecular chains of PES via the reactive melt blending, because the unreacted POI has been removed from the sample. However, in Figure 4, more characteristic peaks of POI that were not observed in the spectrum of neat PPS appear in the spectrum of the PPS/POI gel. Their intensities are higher than those in the spectrum of the PES/POI gel, which means that more POI molecules react with the molecular chains of PPS than with those of PES.

Morphology

SEM images of the blends are shown in Figure 5. For binary blends [Fig. 5(a)], the average particle

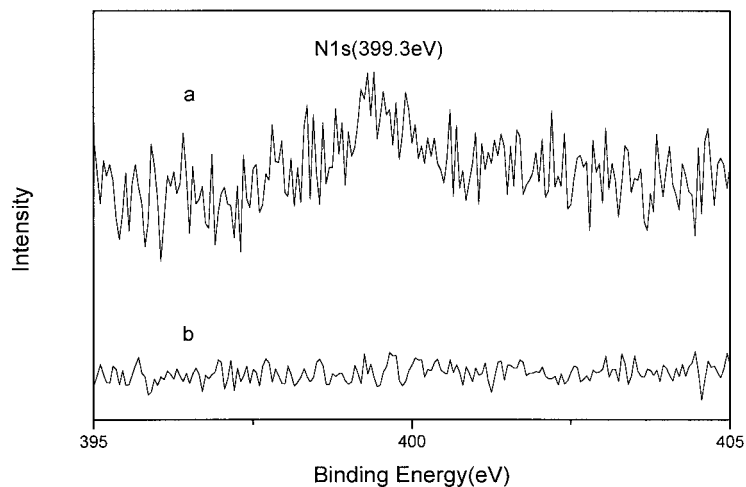


Figure 1 XPS spectra of (a) filtrate of the extracted PES/POI blend and (b) neat PES.

size of the dispersed phase of PPS is about $3 \mu\text{m}$ in diameter, the detachment of the PPS phase from the PES matrix is observed, and there is no indication of adhesion between the two components. When 5 wt % of POI was added to the system, the domain size of the dispersed phase was reduced to less than $1 \mu\text{m}$, as shown in Figure 5(b). This micrograph, in which the strong plastic deformation of the matrix was observed and the shear deformation of PPS particles accompanied it, is an indication of the improved adhesion at the interface between the PPS and PES phases.

Figure 6 shows the micrographs of the interface region of the PES/POI/PPS adhesive joint after isothermally annealing at 250°C for various

times. The original sample consists of three layers: PPS and PES disks and POI spun-coated in the middle. The samples without POI at the interface had no interface adhesion at all even after heating for more than 5 h. The PPS and PES disks separated completely when quenched in liquid nitrogen. The cryogenically fractured morphology of the interface region of the three-layer samples is presented in Figure 6. Three distinctive features can be seen in all the micrographs of Figure 6. The PPS phase exhibits a macroscopically smooth surface with irregular features, which are typical of brittle failure. The fracture surface of the PES phase is fully covered with striations because of the ductile property of the material. Also, an independent interface region

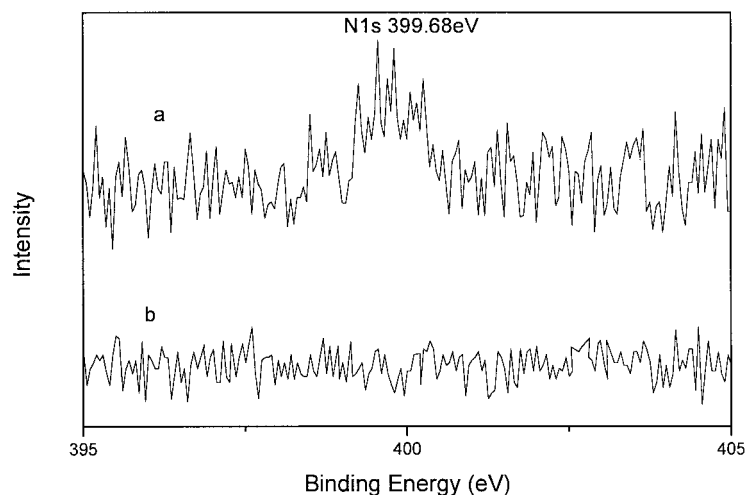


Figure 2 XPS spectra of (a) filtrate of the extracted PPS/POI blend and (b) neat PPS.

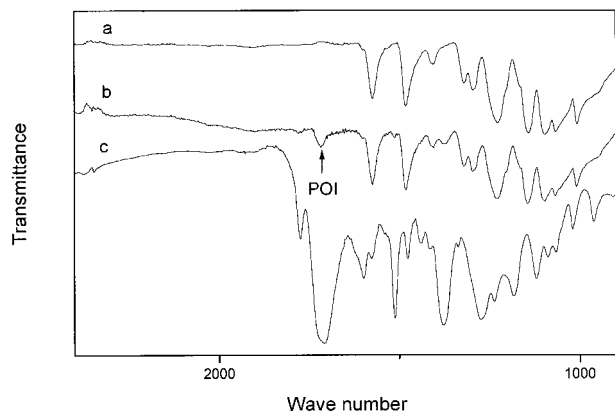


Figure 3 FTIR spectra of (a) neat PES, (b) the gel of the PES/POI blend and (c) POI.

between the PPS and PES phases was detected significantly, which showed a combined morphology of the irregular patchy brittle fracture surface and striations; perhaps it resulted from the reaction among PPS, PES, and POI. The width of the interface region in Figure 6(c,d) was about $30\ \mu\text{m}$, which was larger than three times of that of Figure 6(a,b). The molecules of POI diffused into the PPS and PES phases and the expansion of diffusion depended on the temperature and annealing time. The chemical reactions between POI and PPS and PES were introduced; some small striations also turned up in the PPS fracture surface, which means improvement of its toughness. Apparently, the interfacial adhesions of samples 6(c) and 6(d) are stronger than those of samples 6(a) and 6(b). One can conclude from these results that the temperature and annealing time are both important parameters of the diffusion and reactive ability of POI. It can also be seen in Figure 6

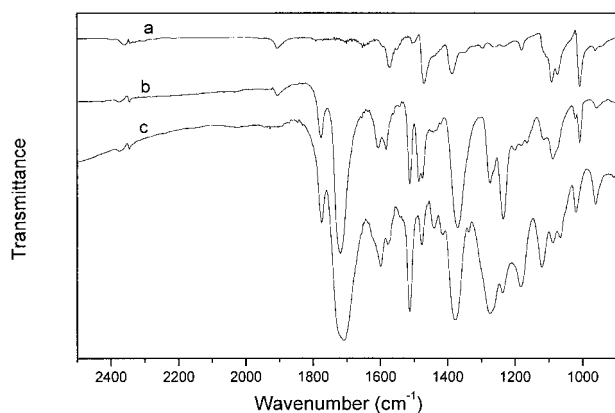


Figure 4 FTIR spectra of (a) neat PPS, (b) the gel of the PPS/POI blend, and (c) POI.

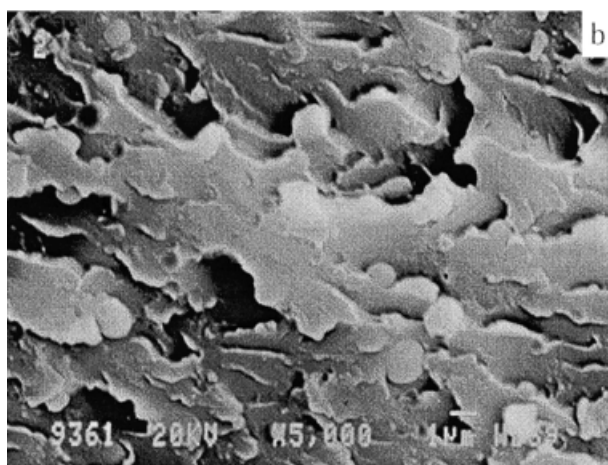
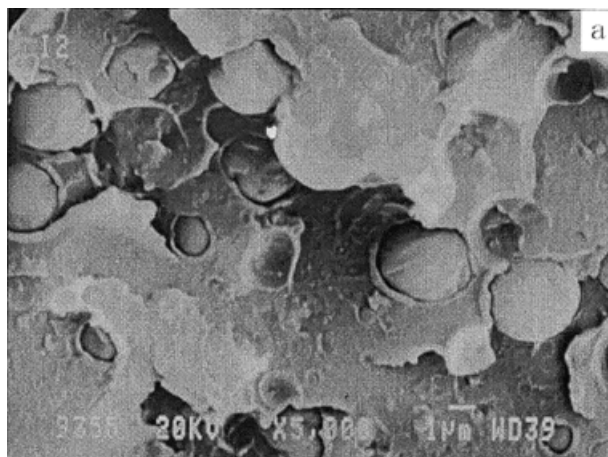


Figure 5 SEM micrograph of PES/PPS/POI blends: (a) 70/30/0; (b) 70/30/2.5.

that the interface phase penetrated deeper in the PPS phase than in the PES phase, indicating that POI molecules diffuse rapidly in the PPS phase compared with those in the PES phase.

The reinforcement of the interface is not only controlled by the reaction kinetics but it is also influenced by the diffusion kinetics. The advantage of the POI precursor is its good mobility arising from its low molecular weight, so it is easier and faster for POI to diffuse from the interface to the bulk polymers or from the bulk polymers to the interface than from traditional compatibilizers such as block or graft copolymers.

Bousmina et al.²⁶ reported that the diffusion mechanism of small molecules (solvent, for instance) in a rubbery-state polymer network of highly entangled chains can be described by the classical Fick's law expressing the time evolution of the concentration profile by the following equation²⁷:

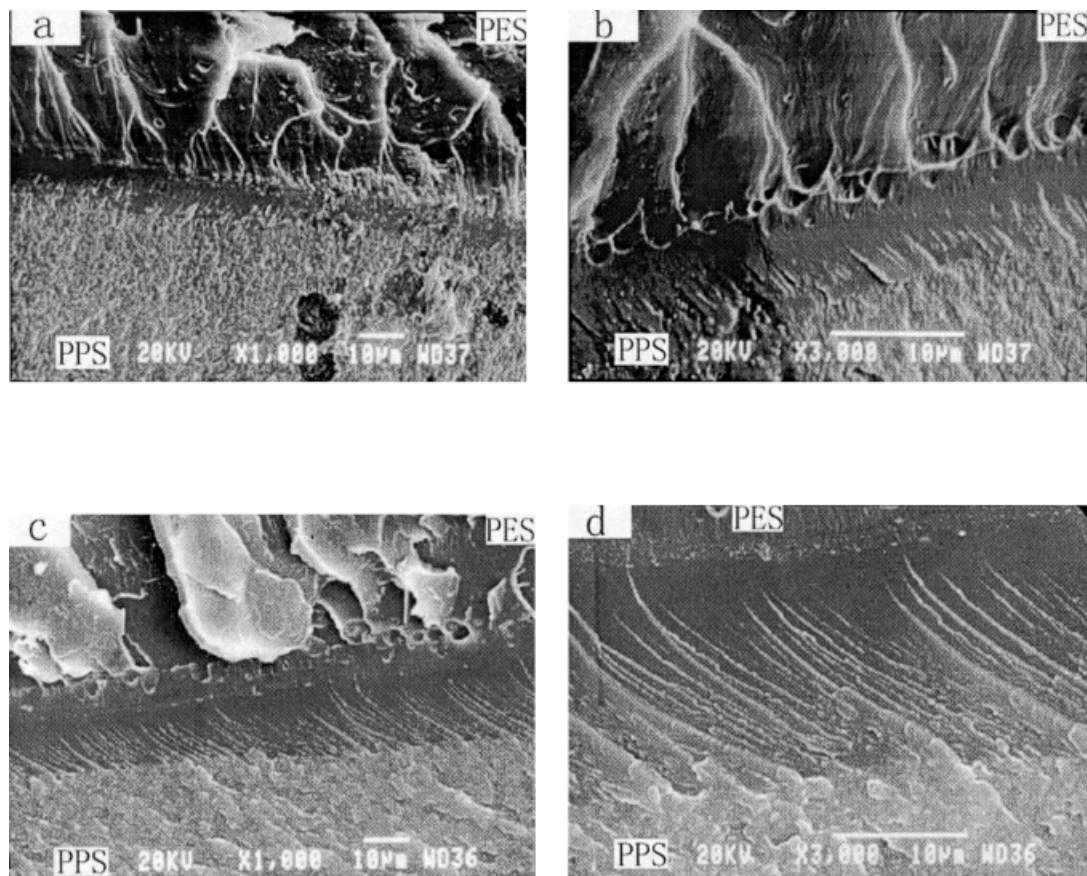


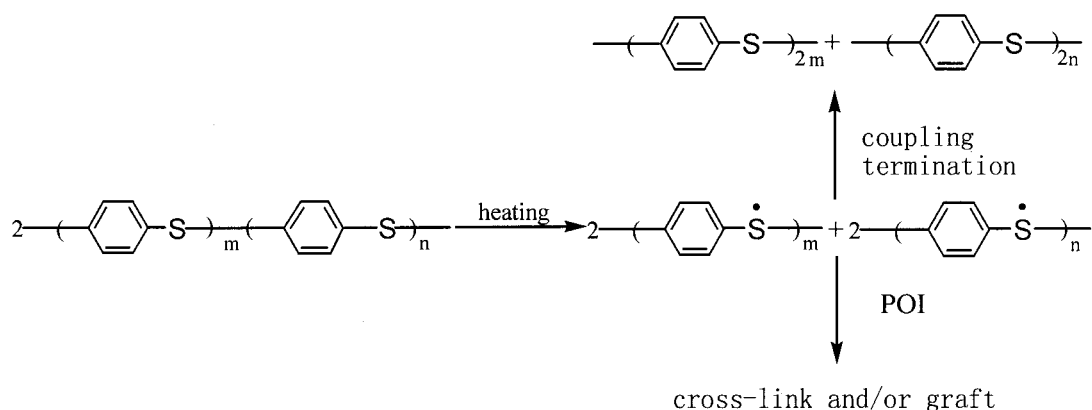
Figure 6 SEM micrograph of the interface region of the PES/POI/PPS adhesive joint prepared at (a) 250°C for 1 h (magnification $\times 1000$), (b) 250°C for 1 h (magnification $\times 3000$), (c) 250°C for 5 h (magnification $\times 1000$), and (d) 250°C for 5 h (magnification $\times 3000$).

$$\frac{\partial C}{\partial t} = \nabla D \nabla C \quad (1)$$

where D is the diffusion coefficient; ∇ , the del operator; and C , the concentration. In the glassy state, the time scale and the diffusion length scale cannot be predicted by the simple classical Fickian diffusional model. It is generally observed that, at short times, a Fickian-like front moves as \sqrt{t} , and then an abrupt transition takes place where the dynamic diffusion mechanism is of a non-Fickian type.^{28–30} The penetration of the solvent in the bulk polymer swells the chain network and thus introduces a supplementary stress that stretches the chains between entanglement junctions. This modifies the chain's relaxation mechanism, which, in turn, modifies the diffusion process of the solvent. Such behavior is described by a modified form of Fick's law:

$$\frac{\partial C}{\partial t} = \nabla [D(C)\nabla C + E(C)\nabla\sigma] \quad (2)$$

where the additional term $E(C)$ is the stress coefficient and σ is the stress induced by the penetration of the solvent that caused the swelling of the polymer network and the displacement of entanglement points. But the difference between the POI precursor and the common solvent is that, after the POI molecules have penetrated into the bulk polymers, instead of swelling the polymer network and displacing the entanglement point, POI can crosslink itself and/or graft with bulk polymers that can generate radicals at high temperature and, hence, strengthen the interface through the formation of chemical bonds. The reaction between PPS and POI during melt blending or annealing can be described by the following mechanism:



POI could be considered as a polyfunctional monomer in terms of the double bonds at both ends and its functionality is 4 regardless of its molecular weight. Any reactive material with two or more functionalities can form branching macromolecules with a high molecular weight and/or crosslinking polymeric network. The formation of an infinite network in such polyfunctional branching units will be governed by the critical branching coefficient (i.e., α_c) by its simple correlation:

$$\alpha_c = 1/(f - 1) \quad (3)$$

where f is the functionality of the branching unit. According to this theory, when POI itself reacts, it is considered a 4–4 system. Also, the critical branching coefficient of POI is 0.33, equal to its critical reactive extent (P_c). In this study, such a reactive extent was hardly reached because the concentration of POI in the blends was much lower than critical.

The concept and the mechanism of diffusion becomes much more complicated when both the diffusing agent and the medium of diffusion are highly entangled polymer chains, such as block or

graft copolymers that diffuse in the bulk polymers. It would be interpreted in terms of the chain motion and modeled by the reptation model predicted by de Gennes³¹ (tube model), meaning that the effect of the reactive reinforcement of POI on the interface of the blends is a variable function depending on the aging time. After the molecules of POI diffused into PES and/or the PPS phase and reacted with them, the location of the reacted molecules of POI in the interfaces of the blend were fixed, linked with the macromolecules, and then their diffusion became difficult.

XPS

XPS surface analysis was also used to prove the reinforcement of the interface. The sample preparation was described in the Experimental section and the result is listed in Table I and Figure 7. In Figure 7, two $S2p$ peaks were detected near 163 and 168 eV, which represent the ether sulfur (C–S–C) of PPS and the sulfone sulfur (O=S=O) of PES, respectively, caused by the different electron environments of sulfur atoms in

Table I Content of Sulfur Atom of PPS and PES on the Solvent-treated Bilayer Films

Time	PPS/PES			Time	PPS/(PES/POI)		
	S (163 eV PPS) (mol %)	S (168 eV PES) (mol %)	PES/PPS (mol/mol)		S (163 eV PPS) (mol %)	S (168 eV PES) (mol %)	PES/PPS (mol/mol)
1 h	3.42	0	0	15 min	3.36	2.02	0.60
2 h	2.52	1.25	0.49	45 min	2.96	2.24	0.76
3 h	2.55	2.46	0.97	2 h	0	4.70	—
5 h	1.64	1.52	0.93	5 h	0	4.73	—

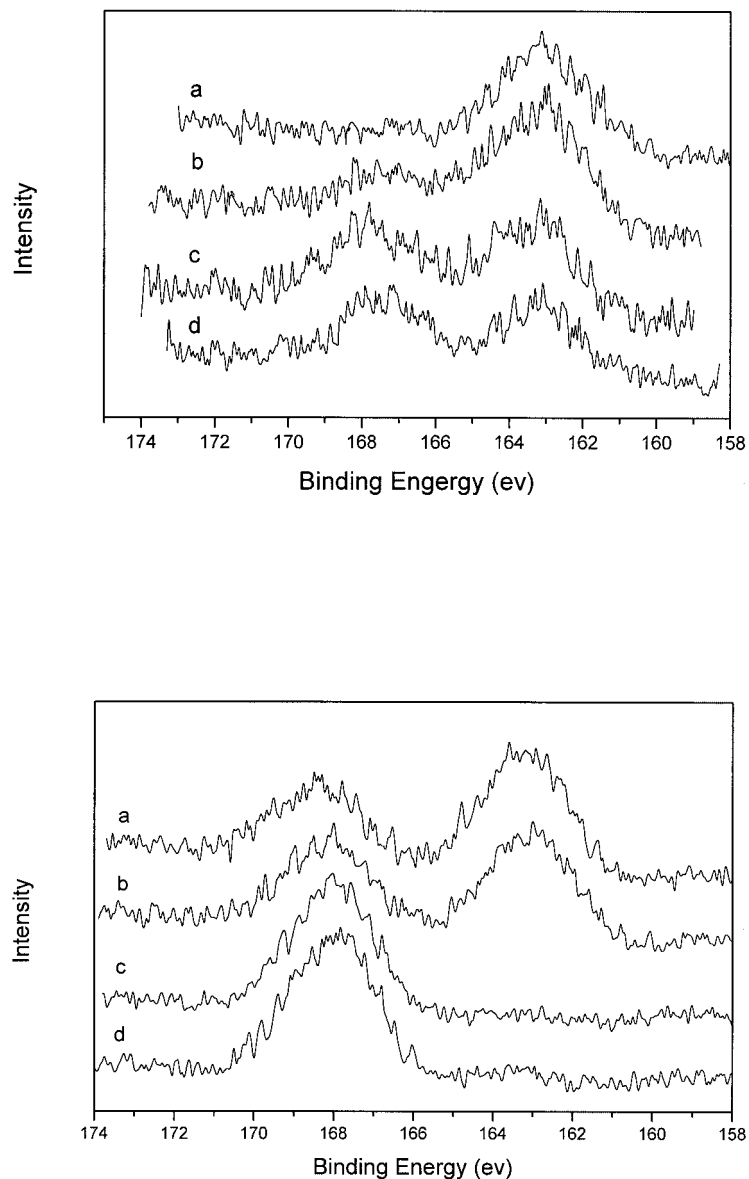


Figure 7 (1) XPS spectra of the PPS-PES bilayer films without POI after annealing at 250°C for various times and then treated by dichloromethane solvent: (a) 1 h; (b) 2 h; (c) 3 h; (d) 5 h. (2) XPS spectra of the PPS-PES bilayer films with POI preblended with PES after annealing at 250°C for various times and then treated by dichloromethane solvent: (a) 15 min; (b) 45 min; (c) 2 h; (d) 5 h.

these two molecules. Table I gives the quantity of sulfur present on the surface of the solvent-treated bilayer films. It can be seen that the PES content increased with the annealing time regardless of the samples with or without the POI component because of the partly miscible property of the PPS/PES blend.³³ For samples without POI, no remaining PES was detected even after being annealed for 1 h, and after being annealed for 3 h, the ratio of PES/PPS mol/mol reached a constant value. For the

PPS/(PES/POI) blend in which PES was preblended with POI, the remaining PES content was much higher than that of the former with same annealing time. After being heated for 2 h, the washed surfaces were fully covered with PES. These results indicate that not only was the interfacial adhesion reinforced by the addition of the POI component, but also there was a reaction or strong interaction between the PES and POI molecules, although the exact mechanism is not known.

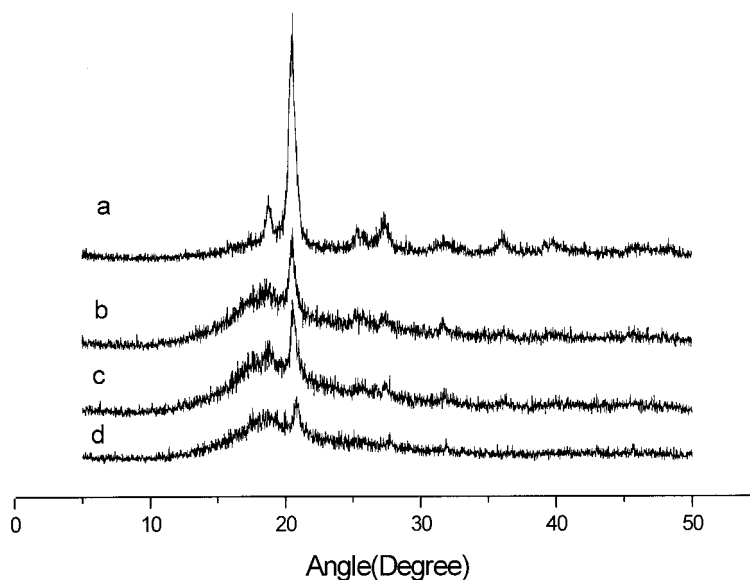


Figure 8 WAXD curves of PES/PPS/POI blends: (a) neat PPS; (b) PES/PPS/POI (70/30/1.5), POI premixed with PES; (c) PES/PPS/POI (70/30/1.5), POI premixed with PPS; (d) PES/PPS (70/30).

WAXD

Because PPS is a crystalline polymer and PES is amorphous, the crystallization behavior of the PES/PPS/POI blends can give us much interesting information. The WAXD patterns of neat PPS and PES/PPS/POI blends are presented in Figure 8. With the same composition and melt-blending condition, the difference of the WAXD curves between samples b and c was caused by the different premix processes. For sample b, PES powder was coated with POI, then blended with PPS in an intermixer, while the premixing process of sample c is the opposite. The degree of crystallinity of these four samples was calculated by using the following equations according to the integral intensity of the PPS diffraction peaks:

$$I_c = 0.79I_{110} + 1.06I_{200} + 2.07I_{112} + 2.63I_{211} \quad (4)$$

$$X_c = I_c / (I_c + 0.94I_a) \quad (5)$$

The results are listed in Table II. Shibata et al.³² studied the crystallization and melting behavior of PPS in blends with PES. They reported that the degree of crystallinity decreased with an increase of the PES content, which is in agreement with our results. But the addition of POI increased the degree of crystallinity apparently, indicating that POI was an effective nucleation agent of PPS. During melt blending, depending on its good mo-

bility, POI was separated homogeneously in the system. At the same time, a thermally induced crosslink and/or graft reaction occurred, and the reacted POI molecules could act as the nucleation agent to a certain extent. In addition, the degree of crystallinity of sample c was slightly higher than that of sample b, which resulted from different premixing processes. This indicated that the migration of POI during melt blending from one phase to the other through the interface does exist; otherwise, the POI premixed in PES would have rarely existed in the PPS phase after blending, and the degree of crystallinity of PPS would have not been improved so obviously.

Diffusion and reaction are two competing driving forces for the enhancement of interfacial adhesion by adding POI. Fast diffusion reduces the concentration of POI at the interface, and the POI molecules that diffused far away from the interface will have little chance to react or interact

Table II Degree of Crystallinity of Samples in Figure 4

Code	χ_c (%)
a	64.8
b	43.7
c	47.2
d	41.7

with PPS and PES across the narrow interface. Also, if a crosslink and/or graft reaction occurs too fast, the reacted molecular size will reduce the diffusion rate of POI from the bulk polymer to the interface. The parameters that affect the rates of diffusion and reaction are the temperature, the premixing process, and the initial concentration of POI. An increase in temperature will increase both the diffusion coefficient and the reaction rate. Different premixing processes will give rise to different diffusion rates because of the disparity of viscosity between PES and PPS. The viscosity of PES is much higher than that of PPS, so it is easier for POI to diffuse in PPS than in PES. The initial amount of the interfacial agent only affects the reaction rate. Therefore, the interfacial characteristics and the mechanical property of the blends can be controlled ultimately by varying these three parameters.

CONCLUSIONS

The morphologies studied show that by improving the adhesion between the dispersed-phase particles and the matrix in PES/PPS/POI blends, reducing the average dimensions of the dispersed phase, could be performed by the interfacial agent POI. Interfaces between the PES and PPS phases were reinforced. FTIR and XPS evidence suggested that there was a reaction or strong interaction among PPS, PES, and POI molecules at high temperature. From the crystallization behavior of PES/PPS/POI blends, one can conclude that POI was an effective nucleation agent of PPS and that POI can migrate from one phase to another through the interface during melt blending.

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REFERENCES

- Dedecker, K.; Groeninckx, G. *Macromolecules* 1999, 32, 2472–2479.
- Yeung, C.; Shi, A. C. *Macromolecules* 1999, 32, 3637–3642.
- Jeon, H. K.; Kim, J. K. *Macromolecules* 1998, 31, 9273–9280.
- Chapleau, N.; Favis, B. D.; Carreau, P. J. *J Polym Sci Polym Phys Ed* 1998, 36, 1947–1958.
- Pingel, E.; Markoski, L. J.; Spilman, G. E.; Foran, B. J.; Jiang, T.; Martin, D. C. *Polymer* 1998, 40, 53–64.
- Fayt, R.; Jérôme, R.; Teyssié, P. J. *J Polym Sci Polym Phys Ed* 1982, 20, 2209–2217.
- Lindsey, C. R.; Paul, D. R.; Barlow, J. W. *J Appl Polym Sci* 1981, 26, 1–8.
- Xiao, F.; Hui, C. Y.; Washiyama, J.; Kramer, E. J. *Macromolecules* 1994, 27, 4382–4390.
- Washiyama, J.; Kramer, E. J.; Hui, C. Y. *Macromolecules* 1993, 26, 2928–2934.
- Dai, K. H.; Kramer, E. J.; Freché, J. M. J.; Wilson, P. G.; Long, T. E. *Macromolecules* 1994, 27, 5187–5191.
- Xanthos, M. *Reactive Extrusion*; Hanser: Munich, 1992.
- Reactive Extrusion, Principles and Practice*; Brown, S. B.; Xanthos, M., Eds.; Hanser: New York, 1992; p 75.
- Liu, N. C.; Baker, W. E. *Adv Polym Tech* 1992, 11, 249–253.
- Xanthos, M.; Dagli, S. S. *Polym Eng Sci* 1991, 31, 929–933.
- Liu, N. C.; Baker, W. E.; Russell, K. E. *J Appl Polym Sci* 1990, 41, 2285–2300.
- Fowler, M. W.; Baker, W. E. *Polym Eng Sci* 1988, 28, 1427–1433.
- MacKnight, W. J. *Polym Eng Sci* 1985, 25, 1124–1134.
- Song, Z.; Baker, W. E. *J Appl Polym Sci* 1992, 44, 2167–2177.
- Shull, K. R.; Kellock, A. J.; Deline, V. R.; MacDonald, S. A. *J Chem Phys* 1992, 97, 2095–2104.
- Leibler, L. *Makromol Chem Macromol Symp* 1988, 16, 1–12.
- Noolandi, J.; Hong, K. M. *Macromolecules* 1982, 15, 482–492.
- Noolandi, J.; Hong, K. M. *Macromolecules* 1984, 17, 1531–1537.
- Sun, Y. J.; Hu, G. H.; Lambla, M.; Kotlar, H. K. *Polymer* 1996, 37, 4119–4127.
- Moussaif, N.; Marechal, Ph.; Jerome, R. *Macromolecules* 1997, 30, 658–659.
- He, T. B.; Ding, M. X. *China Patent ZL92 102 868.7*, 1992.
- Bousmina, M.; Qiu, H.; Grmela, M.; Klemberg-Sapieha, J. E. *Macromolecules* 1998, 31, 8273–8280.
- Crank, J. *Mathematics of Diffusion*, 2nd ed.; Oxford University: Oxford, 1975.
- Hui, C. Y.; Wu, K. C. *J Appl Phys* 1987, 61, 5137–5149.
- Witelski, T. P. *J Polym Sci Polym Phys* 1996, 34, 141–150.
- Edwards, D. A. *J Polym Sci Polym Phys* 1996, 34, 981–997.
- de Gennes, P. G. *Macromolecules* 1976, 9, 587–598.
- Shibata, M.; Yosomiya, R.; Jiang, Z. H.; Wu, Z. W. *J Appl Polym Sci* 1999, 74, 1686–1692.