

Thermally Crosslinkable Poly(phenylene sulfide)/Poly(ether sulfone)/Polymerization of Monomer Reactant–Polyimide Blends

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ABSTRACT: The effects of thermally crosslinkable polymerization of monomer reactant–polyimide (POI) on the miscibility, morphology, and crystallization of partially miscible poly(ether sulfone) (PES)/poly(phenylene sulfide) (PPS) blends were investigated with differential scanning calorimetry and scanning electron microscopy. The addition of POI led to a significant reduction in the size of PPS particles, and the interfacial tension between PPS and crosslinked POI was smaller than that between PES and crosslinked POI. During melt blending, crosslinking and grafting reactions of POI with PES and PPS homopolymers were detected; however, the reaction activity of POI with PPS was much higher than that with PES. The crosslinking and grafting reactions were developed further when blends were annealed at higher temperatures. Moreover, POI was an effective nucleation agent of the crystallization of PPS, but crosslinking and grafting hindered the crystallization of PPS. The final effect of POI on the crystallinity of the PPS phase was determined by competition between the two contradictory factors. The crosslinking and grafting reactions between the two components was controlled by the dosage of POI in the blends, the premixing sequence of POI with the two components, the annealing time, and the temperature. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2906–2914, 2002; DOI 10.1002/app.10287

Key words: compatibilization; high performance polymers; polyimides; thermally crosslinkable polymer blends

INTRODUCTION

The blending of polymers is an established method of producing polymer materials with unusual combinations of desirable properties. Because most polymer pairs are immiscible, they form multiphase systems with weak physical and chemical interactions across the phase boundaries. The addition of properly designed block or

graft copolymers, acting as compatibilizers, to immiscible polymer blends is an efficient way to stabilize the phase morphology and improve the interfacial adhesion.^{1–6} These compatibilizers are thought to be localized mainly at the interface between the two immiscible polymers and thereby induce local miscibility.¹ Recently, increasing effort has been directed toward the creation of block or graft copolymers *in situ* by the addition of a suitable functionalized polymer that can react with blend components, with their inherent chemical reactivity based on end-capping or grafting reactions, such as a maleic anhydride-functionalized polymer blending with polyamides.^{7,8}

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The mechanisms of compatibility include the generation of chemical bonds, the formation of interpenetrating or semi-interpenetrating polymer networks, the enhancement of interfacial adhesion, the reduction of interfacial tension, the suppression of coalescence, and the even dispersion of dispersed phase particles. Among these factors, the main advantage of using compatibilizers in polymer blends is the suppression of coalescence achieved through stabilization of the interface.^{2,3} Entanglement and intermolecular bonding are responsible for this advantage to a large extent.^{4,5}

The cost of premade block copolymers and the limitations of reactive processing in the *in situ* formation of block copolymers are incentives for considering new compatibilization strategies.^{9–11} For high-performance polymers such as poly(ether ether ketone), poly(ether sulfone) (PES), and poly(phenylene sulfide) (PPS), it is not easy to design and synthesize suitable block or graft copolymers or to give each pair the appropriate functional groups. Therefore, studies on the interfaces of high-performance polymer blends are seldom reported. Recently, some good results have been published concerning small molecules such as bismaleimide¹² and

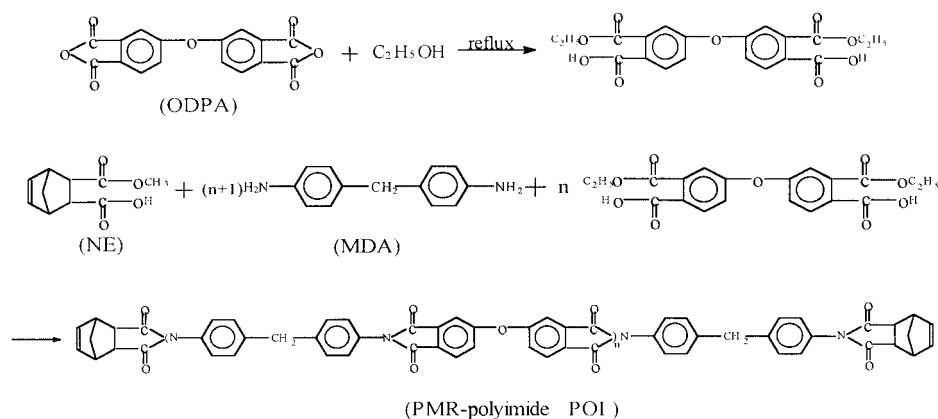
diepoxides¹³ that can crosslink and graft with polymers as compatibilizers. Here we introduce the thermally crosslinkable polymerization of monomer reactant–polyimide (POI) precursor¹⁴ as the interfacial agent involved in crosslinking and grafting reactions with PES and PPS during melt blending.

EXPERIMENTAL

Materials

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

The thermally crosslinkable POI precursor was prepared in our laboratory with three monomeric ingredients: 4,4-oxydiphthalic anhydride (ODPA), 4,4-methylene dianiline (MDA), and the mono-methyl ester of norbornene anhydride (NE). The chemical structure was as follows:



The precursor formed crosslinked networks or grafts with PPS and PES by thermally induced radical polymerization through the double bonds at each end of the molecule. Moreover, we controlled the molecular weight by changing the molar ratio of the three ingredients to ensure that the precursor exhibited excellent mobility in melt blending.

ODPA and NE were purified before use, and MDA and ethanol were used as received.

Sample Preparation

The premixing of POI with polymers was achieved by PES and PPS powder being sopped into a POI ethanol solution homogeneously. After most of the ethanol had evaporated at room temperature, the powder coated with POI was dried at 70°C for 12 h in a vacuum oven. A Brabender internal mixer (OHG DUISBURG, Germany) was employed to prepare the blends and determine their rheological properties during blending. Both

the shear rate and mixing temperature were controlled. Typically, a 70-g sample was mixed at 50 rpm for about 10 min at 290°C. The torque and melting temperature (T_m) as functions of the mixing time were measured. The same processing procedure was followed for the homopolymers. The hot blends were removed from the chamber of the mixer, rapidly cooled to room temperature, and stored in a desiccator until testing.

Thermal Analysis

The thermal behavior of the samples was determined with a PerkinElmer DSC-7 differential scanning calorimeter (USA) under an atmosphere of N_2 from 50 to 300°C.

Morphology Observations

The morphology of the blends was investigated with press-molded samples. Transverse sections of the specimens were obtained via fracturing in liquid nitrogen, and then the surfaces were coated with gold for viewing with a JEOL JXA-840 scanning electron microscope (Japan) operated at 20 kV. The apparent diameter of each particle in the field of view was measured. The volume fraction of the domains was calculated under the assumptions that the dispersed domain was spherical and that each particle had been cut at its equator.

Contact-Angle Measurements

For smooth surfaces, the commercial powders of PPS and PES were dissolved in diphenyl ether (220°C) and dichloromethane, respectively, to make 20 mg/mL solutions. At the same time, a 2% POI solution was prepared. Silicon wafers were selected as substrates for polymer films. The substrates were rinsed with distilled water for 10 min and dried at 70°C for 1 h in a vacuum oven.

After the cleaning procedure, a few of drops of polymer solution were placed on the silicon substrate immediately. The solution spread, and the solvent was allowed to evaporate slowly in a vacuum oven for 12 h at room temperature. The POI films were crosslinked during annealing at 280°C for 5 h. Then, the films were stored in a desiccator until testing.

For the conventional determination of contact angles by the sessile drop method, the goniometer G-H (Erma Optical Works Co. Ltd., Japan) was used. The testing liquids were distilled water and purified glycol.

RESULTS AND DISCUSSION

Morphology

Scanning electron microscopy (SEM) micrographs of the cryogenically fractured surfaces in Figure 1 show the effect of adding POI on the morphology development of PPS/PES blends. The binary blends of 70/30 and 75/25 PES/PPS had a coarse morphology, with domain sizes as large as 3 μm [Fig. 1(a,b)]. From the large voids left on the fracture surface, where the particles had separated from the matrix, and the smooth surfaces of the exposed PPS particles, no evidence of adhesion between the matrix and the dispersed phase was detected. However, for the ternary blends, the presence of POI significantly reduced the size of the dispersed domain and showed good interfacial adhesion [Fig. 1(c,d)] because POI played a role as a compatibilizer in the immiscible blend. It can be also seen in Figure 1 that the domain size of the dispersed phase decreased as the contents of POI increased.

Morphology generation during the mixing of polymer components involves a balance between the competing processes of fluid drop breakup and coalescence. Taylor¹⁵ studied the deformation and disintegration of Newtonian fluids. Tokita¹⁶ derived an expression for describing the particle size of a dispersed phase in polymer blends. At equilibrium, when breakup and coalescence are balanced, the equilibrium particle size (D) may be expressed as follows:

$$D = \left(\frac{24P_r v}{\pi r_{12}} \right) \left(\phi + \frac{4P_r E}{\pi r_{12}} \phi^2 \right) \quad (1)$$

where r_{12} , v , E , and P_r refer to the interfacial tension, stress field, bulk breaking energy, and probability that a collision will result in coalescence, respectively. Equation (1) predicts that the equilibrium particle size decreases when the stress field becomes larger, the interfacial tension becomes smaller, and the volume fraction of the dispersed phase is smaller. As shown in Figure 1(c,d), because a decrease in the interfacial tension resulted from the addition of 5 wt % POI, the average domain size was reduced to approximately 1/10 in comparison with those in the non-compatibilized blend systems with the same composition.

Interfacial Tension

The components of the surface tensions (r^d and r^p) of polar polymers can be calculated from two sets

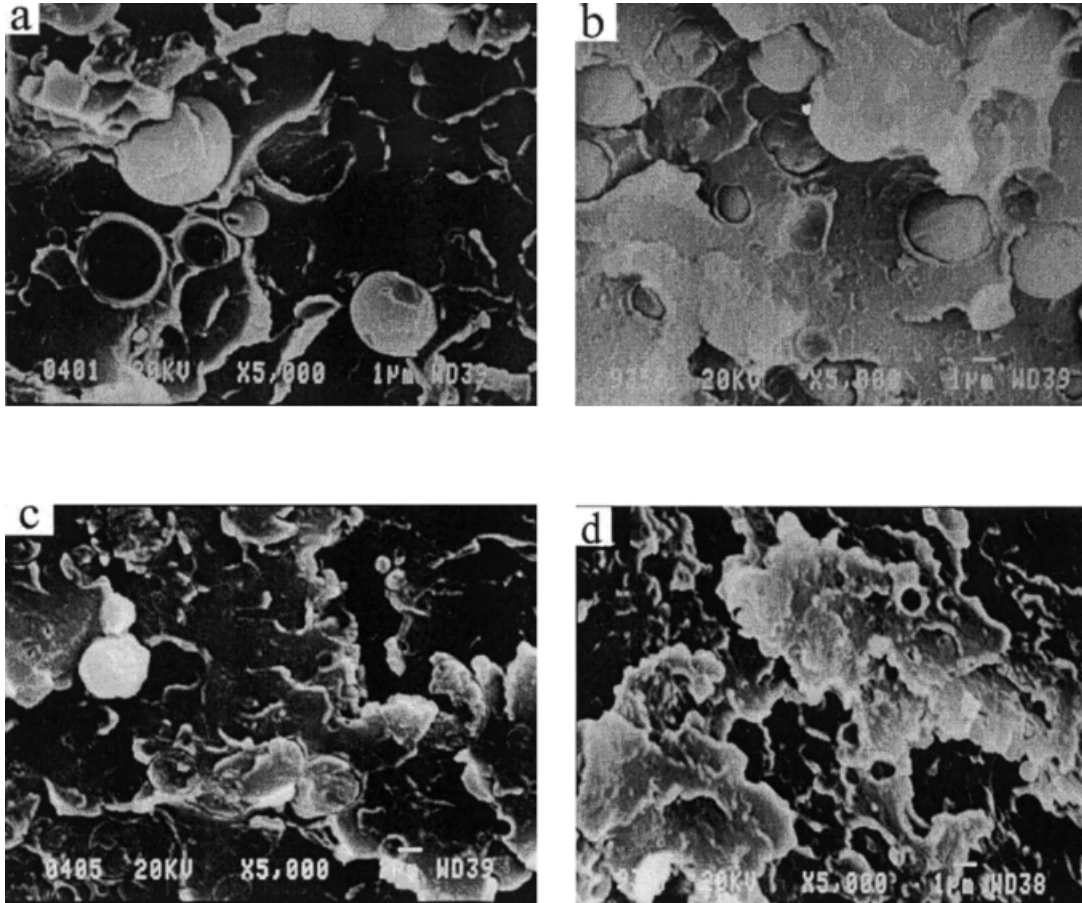


Figure 1 SEM micrographs of (a) 70/30/0, (b) 75/25/0, (c) 70/30/1.5, and (d) 75/25/5 PES/PPS/POI blends.

of contact-angle data obtained from different test liquids (water and glycol) with eqs. (2) and (3), and interfacial tension values between two polymers can be calculated with eq. (4), which was proposed by Wu:¹⁷

$$\cos \theta = \frac{2}{r_l} [(r_l^d r_s^d)^{1/2} + (r_l^p r_s^p)^{1/2}] - 1 \quad (2)$$

$$r_s = r_s^d + r_s^p \quad (3)$$

$$r_{12} = r_1 + r_2 - \frac{4r_1^d r_2^d}{r_1^d + r_2^d} - \frac{4r_1^p r_2^p}{r_1^p + r_2^p} \quad (4)$$

where θ is the contact angle; r_l is the surface tension of the testing liquid and r_s is the surface tension of the solid surface (polymer films in our experiment); the superscripts d and p represent the dispersion component and polar component of

surface tension, respectively; and r_{12} is the interfacial tension.

The results are listed in Tables I and II. For a solid surface to be obtained, POI was annealed at 280°C for 5 h, and crosslinked POI (PI) was made. Because lower interfacial tension led to better miscibility between two phases, we concluded that the affinity of PI to PPS was better than the affinity of PI to PES. The morphology evidence proved that POI was a good compatibilizer for the PES/PPS blend, but the calculated value of interfacial tension for PPS/PES was smaller than that

Table I Surface Tension of PES, PPS, and PI

	PES	PPS	PI
r_s^d (10^{-3} N/m)	19.377	17.1	10.26
r_s^p (10^{-3} N/m)	14.4	7.07	11.77
r_s (10^{-3} N/m)	33.77	24.17	22.03

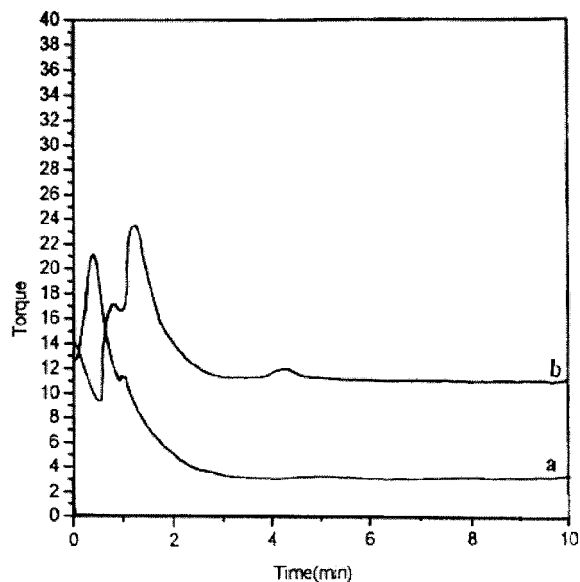
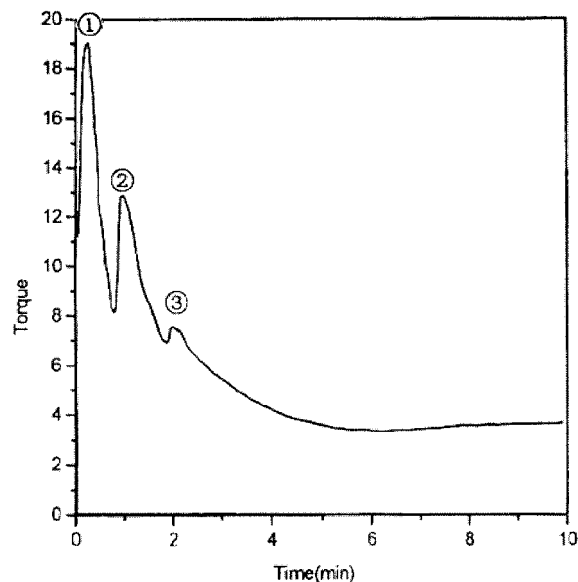
Table II Interfacial Tension Between Different Component Pairs

	PI/PPS	PI/PES	PPS/PES
r_{12} (10^{-3} N/m)	2.82	3.06	2.62

of PPS/PI and PES/PI. This should be attributed to the differences in the mixing entropy, mobility, and interfacial properties between the small molecule POI and PI. The advantage of the POI precursor is its good mobility due to its low molecular weight, so it is easier and faster to diffuse from the interface to bulk polymers or from bulk polymers to the interface than PI or traditional compatibilizers such as block or graft copolymers. After POI molecules penetrated the bulk polymers, the *in situ* formation of the PPS/POI/PES graft copolymer acted as an interfacial emulsion and evidently affected the morphology development of the blends.

Rheological Behaviors

Figures 2 and 3 and Table III show the Brabender data and curves illustrating changes in torque during the mixing process at 290°C for the components PPS and PES and the blends 100/4 PPS/POI, 100/4 PES/POI, 75/25 PES/PPS, 75/25/5 PES/PPS/POI, and 70/30/1.5 PES/PPS/POI, respectively. The high loading peaks resulting from

**Figure 2** Torque-time curves of (a) 75/25/0 and (b) 75/25/5 PES/PPS/POI blends.**Figure 3** Torque-time curve of a 70/30/1.5 PES/PPS/POI blend with the following blend sequence: (1) PES, (2), POI, and (3) PPS.

the melt fracturing of cold samples were recorded before complete fusion of the materials; after the mixing period exceeded 5 min, both the torque and temperature leveled off, indicating that an equilibrium state was reached. It is obvious that with the addition of POI into the systems, the torque value at the equilibrium state was increased with respect to the values for the blends without POI with the same composition. The second peak in the curve of Figure 3 was caused by the addition of a 0.5M POI ethanol solution. In a normal case, when a melting polymer was blended with a liquid component that had no interaction with it, the torque dropped because of the decrease in the friction among the polymer chains caused by the addition of the liquid component. However, in our experiment, the addition of POI not only caused the high loading peak during the melt blending but also the increase in the equilibrium-state torque value. Furthermore, the torque value at the equilibrium state of PPS blended with POI went up 5 times (from 0.4 to 2.4

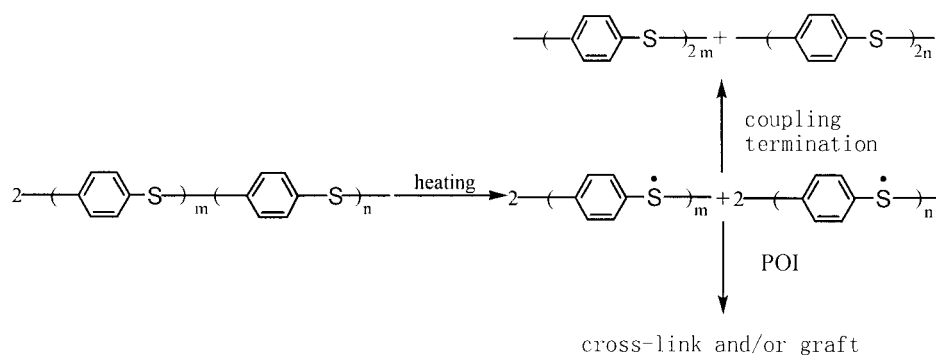
Table III Effect of POI on the Torque Value at Equilibrium of Pure Components

	Neat PPS	PPS/POI (100/4)	Neat PES	PES/POI (100/4)
Torque (Nm)	0.4	2.4	5.6	6.0

Nm), but it only increased 7% (from 5.6 to 6.0 Nm) when the same dosage of POI was blended with PES. The reactivity of POI with PPS was higher than that with PES.

The increase in torque and the difference in reactivity should be attributed to the reaction mechanism of POI. As we know, POI is a precursor with a low molecular weight; it can

crosslink itself and graft with bulk polymers that can generate radicals at high temperatures, and so a strengthened interface and enhanced viscosity can be created through the formation of chemical bonds. The reaction between PPS and POI during melt blending or annealing can be described by the following mechanism:



Many rheological empirical or semiempirical equations have been reported and reviewed that describe the relationship of the morphology, composition, rheology, and processing steps in polymer blends. Utracki¹⁸ suggested that the log-additivity rule might be used to classify the flow behaviors of polymer blends:

$$\log T = \sum W_i \log T_i \quad (5)$$

where T and T_i are the torque at the equilibrium state of the blends and the component i and W_i is a measure of composition, usually expressed as the weight or volume fraction of the component. Equation (5) makes it possible to distinguish a positive deviating blend, a negative deviating blend, and a positive–negative deviating blend with a sigmoidal dependence. A comparison of the variations in the torque of the blends as a function of the composition measured experimentally and those calculated readily from eq. (5) can provide us with very interesting information about the morphology of blend melts during mixing.

Figure 2(a) shows for the 75/25 PES/PPS blend that the plateau value of torque (2.8 Nm) was lower than the calculation value from eq. (5) (2.89 Nm). This result was in agreement with the conclusion that PES and PPS had partial miscibility as reported by Shibata et al.¹⁹ When 1.5 wt % POI was added to the system (as shown in Fig. 3), the

equilibrium-state torque value of the blend increased to 3.4 Nm; for the sample in which PES and PPS powder was premixed with 5 wt % POI (see the Experimental section) and then annealed at 180°C for 2 h to cure POI to some extent, the torque–time curve is reported in Figure 3. The torque value of the equilibrium state grew to about 11 Nm, and the second, smaller peak that appeared 4 min into the blending process was the characteristic curve of physical or chemical interactions among the components. We supposed that POI was dispersed homogeneously in the PPS and PES phases, and we considered the data in Table III to be the approximate torque values of the pure components. Then, we calculated the theoretical value of the sample [Fig. 2(b)] with eq. (5); it was 4.95 Nm, equal to 45% of the experimental value. Such a distinct departure not only resulted from the interaction between two components but also should be ascribed to chemical crosslinking reactions, grafting reactions, or both between blending components with the addition of POI. Furthermore, the difference between the torque values of Figures 2(b) and 3 resulted both from the dosage level of POI in the blend and the pretreatment process of the materials (PES and PPS powder was premixed with POI and then annealed at 180°C for 2 h to cure POI to some extent); in our opinion, the latter was more important.

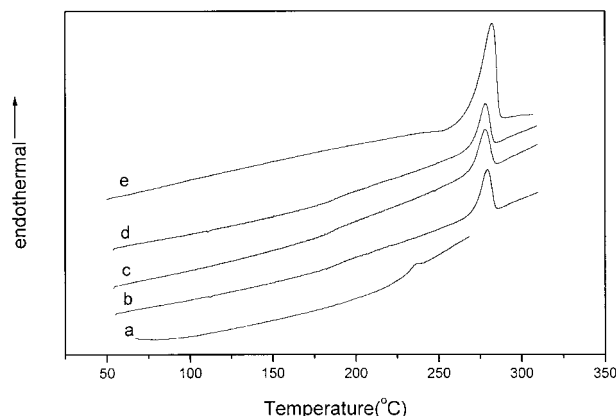


Figure 4 DSC traces of neat PPS, neat PES, and PES/PPS/PI blends: (a): neat PES, (b) 70/30/0 PES/PPS/POI, (c) 70/30/1.5 PES/PPS/POI (PI premixed with PES), (d) 70/30/1.5 PES/PPS/PI (PI premixed with PPS), and (e) neat PPS.

Thermal Analysis

The differential scanning calorimetry (DSC) thermograms of the blends are shown in Figure 4, and the transition parameters are summarized in Table IV. The degree of crystallinity (χ_c) for PPS was calculated with a heat of fusion (ΔH) of 80 J/g for 100% crystalline PPS. Only one glass-transition temperature (T_g) was detected in all the blends. For the 70/30 and 75/25 PES/PPS blends, the T_g measured by DSC was about 8.7°C higher than

the one predicted by the Fox equation, which also proved the partial miscibility of the PES/PPS blend. There are three reasons we could not detect the T_g of the PPS phase. First, the PPS phase was in the minority in the blend; second, because PES and PPS were partially miscible, some PPS molecule mingled with the PES rich phase; and third, PPS was a semicrystalline polymer. Therefore, the small quantity of amorphous PPS remaining as the independent disperse phase in the blends made it difficult to detect T_g under the resolution of DSC.

It is shown in Table IV that by the incorporation of POI into the system the crystallinity of the blends was promoted, and the crystallization temperature (T_c) from the melt was raised compared with that of the pure component or the blends without POI with the same composition. PPS blended with POI crystallized at a lower degree of supercooling. From the aforementioned results, we can conclude that POI was an effective nucleant agent of PPS. Under certain dosages (≤ 5 wt %), the content of POI did affect T_c and χ_c effectively, and when the weight fraction of POI increased to 10%, χ_c declined because more PPS molecules reacted with POI and remained in the amorphous phase.

For neat PES and PPS, the effect of POI incorporation on T_g was the opposite. By the incorporation of POI into the system, the T_g values of both pure PPS and PES/PPS blends increased,

Table IV Thermal Transition Parameters of Pure Components and the Blends of PES, PPS, and POI

Sample	T_g (°C)	T_m (°C)	T_c (°C)	ΔH (J/g)	χ_c
PPS	89.5	281.5	245.1	45.6	0.57
PES	225				
PI (POI annealed at 280°C for 5 h)	169				
PPS/POI (100/1.5)	—	277.8	249.2	59.5	0.75
PPS/POI (100/4)	—	276.7	246.9	59.1	0.77
PPS/POI (100/10)	99.6	279.1	244.6	41.7	0.52
PES/POI (100/4)	206				
PES/POI (100/20)	214				
PES/POI (100/20) (annealed at 180°C for 2 h after blending)	219.5				
PES/POI (100/20) (annealed at 250°C for 8 h after blending)	226.9				
PES/PPS (70/30)	182.9	278	240.1	8.34	0.35
PES/PPS/POI (70/30/1.5) (POI premixed with PES powder)	187.7	277.7	243.8	11.42	0.48
PES/PPS/POI (70/30/1.5) (POI premixed with PPS powder)	193	278.2	245.7	12.37	0.52
PES/PPS (75/25)	189.5	278.7	241.5	7.28	0.36
PES/PPS/POI (75/25/5)	191.7	280.8	251.2	9.92	0.52
PES/PPS/POI (75/25/5)	197.5	280.2	252.8	9.03	0.47
PES/PPS/POI (75/25/5) (annealed at 250°C for 8 h)	211.4	279.8	254.2	8.08	0.42

especially after heating treatment, whereas the T_g values of PES/POI blends decreased even after annealing at high temperatures for some time. The increase in T_g for the PPS phase should be ascribed to its crosslinking and/or grafting reactions with POI, as we discussed previously, but the molecules of POI with low molecular weight mainly acted as plasticizers to PES in the PES/POI system. Although the T_g value of PES/POI blends was lower than that of pure PES, it went up as the weight fraction of POI increased because the crosslinking and grafting reactions between PES and POI occurred at the same time. The effect of the plasticization of POI in the blends was still in the highest flight between the two contrary competing factors when the weight fraction of POI reached 20%. However, the T_g value of PES/POI blends increased after the reaction was enhanced by the heating treatment.

Figure 4 shows that the T_g of the ternary blends increased because of the crosslinking reaction between POI and components during melt blending. With the same composition and melt blending conditions, the differences in the DSC traces between the samples [Fig. 4(c,d)] were controlled by the different premix processes. For the former sample, POI was premixed in PES powder and then blended with PPS in an intermixer, whereas the premixing process for the latter sample was the opposite. During blending, POI first came into contact with the heated and softened component on which it was coated, PES or PPS, according to the different premixing processes; then, to make the energy of the system as low as possible, POI diffused and migrated to the other phase, driven by the factors of mixing thermodynamics. However, in the melted blends with high viscosity, its diffusion and migration was controlled by dynamics, that is, influenced by blending conditions. Accompanied by diffusion and migration, crosslinking and grafting reactions between POI and components occurred that, in turn, hindered diffusion and migration. Therefore, the premixing process influenced the properties of the blends significantly. The difference in T_g between the samples [Fig. 4(c,d)] also indicated that the reactivity of POI with PPS was higher than that with PES. When it was premixed with PES, a considerable quantity of POI molecules migrated from the PES phase into the PPS phase, reacted with PPS, affected the T_g values of the blends, and promoted the crystallinity of PPS.

Hale et al.²⁰ reported that when poly(butylene terephthalate) (PBT)/acrylonitrile-butadiene-styrene (ABS) blends were compatibilized by methyl methacrylate, glycidyl methacrylate, ethyl acrylate terpolymers (MGE) terpolymer, the mechanical properties and rheological behavior of the ternary blends were influenced significantly by different mixing sequences. Residual acids present in emulsion-made ABS material may cause a crosslinking reaction involving the epoxide functionality of MGE terpolymer, resulting in a deleterious effect on the ABS mechanical properties and its blends with PBT. By changing the order of mixing, one can control the sequence of chemical reactions to optimize the blend properties.

Because heating treatment hastened the crosslinking and grafting reactions of POI and components, as shown in Table IV, for the blends containing POI, T_g increased after annealing at high temperatures for various times. The crystallization behavior of the 75/25/5 PES/PPS/POI blend was also influenced by the heating treatment. After annealing at higher temperatures for longer time, χ_c evidently declined, but it was still higher than that of the binary blend with the same composition, whereas T_c increased slightly. The reaction between POI and PPS inhibited the folding of PPS molecular chains and kept them in the amorphous phase. The increase in T_c was attributed to the homogeneous decentralization of POI in the PPS phase resulting from heating treatment and its effective nucleation effect on the PPS molecule.

CONCLUSION

We studied the compatibilization of PES/PPS blends with POI. The particle size of the PPS phase could be reduced about 10 times by the addition of 5 wt % POI to the blends. The interfacial tension results showed that the affinity of PI to PPS was better than that to PES. The torque–time data recorded during melt mixing showed that the addition of POI to PPS, PES, and their blends led to a significant increase in the viscosity of the melt, which indicated that reactions took place between POI and the polymer during the melt-mixing process.

The DSC results indicated that the addition of POI influenced the thermal properties and crystallization behaviors of PPS, PES, and their blends. The premixing order affected the T_g val-

ues of the blends. POI was a good nucleant agent for PPS and promoted the crystallization of PPS effectively.

REFERENCES

1. Eklind, H.; Schantz, S.; Maurer, F. H. J.; Jannasch, P.; Wesslen, B. *Macromolecules* 1996, 29, 984.
2. Sundararaj, U.; Macosko, C. W. *Macromolecules* 1995, 28, 2647.
3. Macosko, C. W.; Guegan, P.; Khandpur, A. K.; Nakayama, A.; Marechal, P.; Inoue, T. *Macromolecules* 1996, 29, 5590.
4. Sha, Y.; Hui, C. Y.; Kramer, E. J.; Hahn, S. F.; Berglund, C. A. *Macromolecules* 1996, 29, 4728.
5. Dai, C.-A.; Jandt, K. D.; Iyengar, D. R.; Slack, N. L.; Dai, K. H.; Davidson, W. B.; Kramer, E. J. *Macromolecules* 1997, 30, 549.
6. Cigana, P.; Favis, D.; Albert, C.; Vu-Khanh, T. *Macromolecules* 1997, 30, 4163.
7. Tang, T.; Lei, Z. L.; Huang, B. T. *Polymer* 1996, 37, 3219.
8. Chen, G. X.; Liu, J. J. *J Appl Polym Sci* 2000, 76, 799.
9. Sun, Y.-J.; Hu, G.-H.; Lambla, M.; Kotlar, H. K. *Polymer* 1996, 37, 4119.
10. Lambla, M.; Scadan, M. *Makromol Chem Macromol Symp* 1993, 69, 99.
11. Moussaif, N.; Marechal, Ph.; Jerome, R. *Macromolecules* 1997, 30, 658.
12. Zhang, H. X.; Hourston, D. J. *J Appl Polym Sci* 1999, 71, 2049.
13. Haralabakopoulos, A. A.; Tsiourvas, D.; Paleos, C. M. *J Appl Polym Sci* 1999, 71, 2121.
14. He, T. B.; Ding, M. X. *Chin. Pat. ZL92102868.7* (1992).
15. Taylor, G. I. *Proc R Soc London Ser A* 1934, 146, 501.
16. Tokita, N. *Rubber Chem Technol* 1977, 50, 292.
17. Wu, S. H. *J Polym Sci Part C: Polym Symp* 1971, 34, 19.
18. Utracki, L. A. *Polym Eng Sci* 1988, 28, 1401.
19. Shibata, M.; Yosomiya, R.; Jiang, Z. H.; Wu, Z. W. *J Appl Polym Sci* 1999, 74, 1686.
20. Hale, W.; Keskkual, H.; Paul, D. R. *Polymer* 1999, 40, 3665.