

# Poly(ethylene terephthalate)/Polypropylene Reactive Blends through Isocyanate Functional Group

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**ABSTRACT:** To evaluate the compatibilization effects of an isocyanate group on poly(ethylene terephthalate)/polypropylene (PET/PP) blends through a reactive blend, PP grafted with 2-hydroxyethyl methacrylate-isophorone diisocyanate (PP-*g*-HI) was prepared and blended with PET. In view of the blend morphology, the presence of PP-*g*-HI reduced the particle size of the dispersed phase by the reduced interfacial tension between the PP and PET phases, indicating the *in situ* copolymer (PP-*g*-PET) generated during the melt blending. The DSC thermograms for the cooling run indicated that the PET crystallization in the PP-*g*-HI rich phase was affected by the chemical reactions of PET and PP-*g*-HI. The improved mechanical properties for the PET/PP-*g*-HI blends were shown in the measurement of the tensile and flexural properties. In addition, the water absorption test indicated that the PET/PP-*g*-HI blend was more effective than the PET/PP blend in improving the water resistance of PET. The positive properties of PET/PP-*g*-HI blends stemmed from the improved compatibilization of the PET/PP blend. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1056–1062, 2001

**Key words:** compatibility; reactive blend; polypropylene; poly(ethylene terephthalate); isocyanate group

## INTRODUCTION

Polymer blends are an efficient way to formulate new materials with tailored properties. The major problem of polymer blends is immiscibility from the inherent thermodynamic incompatibility. Satisfactory performance in immiscible polymer blends is usually attained by compatibilization that minimizes interfacial tension and improves interfacial adhesion between the polymers.<sup>1,2</sup> Among the many compatibilization techniques, reactive melt blending methods that graft or block copolymers as compatibilizers formed *in situ* by the reaction between functional units in the blends have been widely used.<sup>3–6</sup>

Blending of polyolefins with engineering plastics such as poly(ethylene terephthalate) (PET)

and polyamide (PA) could be a useful method for enhancing either the moisture resistance of PET and PA or the oil resistance of polyolefins. The use of maleic anhydride (MAH)<sup>7–9</sup> grafted polyolefin was shown to be effective for the reactive compatibilization of PA with polyolefin blends. However, the use of a maleated polyolefin does not provide much compatibilization between the PET and polyolefin phases. PET lacks the presence of the highly nucleophilic amine end groups, which are found in PA. Therefore, PET and polyolefin based blends and alloys would be intensified as a result of the availability of high purity recycled PET resins if an effective compatibilization of PET with polyolefin could be achieved.<sup>10</sup>

Many attempts to form compatible blends of PET with polyolefins resorted to the use of a highly electrophilic monomer grafted polyolefin copolymer. Glycidyl methacrylate (GMA) contains an epoxide, which is highly electrophilic and capable of reacting with weakly nucleophilic spe-

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cies, such as the carboxyl or hydroxyl end groups of PET. Akkapeddi and VanBuskirk found that GMA grafted PE acts as a good compatibilizer PET with various polyolefins.<sup>11</sup> Dagli and Kamdar found that ethylene-GMA copolymer was an effective compatibilizer in the blends of high-density PE with PET.<sup>12</sup> Other than the above highly electrophilic monomer, isocyanate (NCO) groups were suggested in our previous work.<sup>13</sup>

In this study peroxide initiated, free-radical solution grafting of NCO groups onto polypropylene (PP) was conducted. We carried also out mixing of PP having an NCO functionality with PET having a COOH/OH functionality to investigate the *in situ* compatibilization of blends through a chemical reaction during the melt blending process. The effect of compatibilization on the PET/PP blend was demonstrated in the results for the morphological, thermal, mechanical, and water absorption properties.

## EXPERIMENTAL

### Materials

The PP was a nonreactive homopolymer obtained from Hyosung T&C Co. It had a melt flow index (MFI) of 0.5 dg/min (ASTM D1238, 230°C, and 2.16 kg). Bottle grade PET ( $M_n = 28,500$ , Samyang Co.) was used that had end group concentrations of 46.3 mol/1000 kg OH and 29.1 mol/1000 kg COOH, and it was dried for 48 h under a vacuum at 80°C. The NCO functional monomer (HI) was prepared by the reaction of 2-hydroxyethyl methacrylate (HEMA, Aldrich Chemical) with isophorone diisocyanate (IPDI, Aldrich Chemical) with a molar ratio of 0.95 : 1. The detailed conditions of reaction of the HEMA with IPDI for the synthesizing of HI was described in the literature.<sup>13–15</sup> Dicumyl peroxide (DCP, Aldrich Chemical) was used as a radical initiator.

### Graft Copolymerization

The functionalization of the PP was carried out in four-neck round-bottom apparatus equipped with an overhead stirrer, condenser, thermometer, and nitrogen gas inlet. The PP (20 g) and xylene (200 g) were put into the vessel and heated with agitation, followed by the immediate addition of HI (1 g) and DCP (0.1 g). The reaction was continued for 2 h at 120°C under a nitrogen stream in order to prevent oxidation of the PP. After the reaction was finished the reaction mixture was cooled to

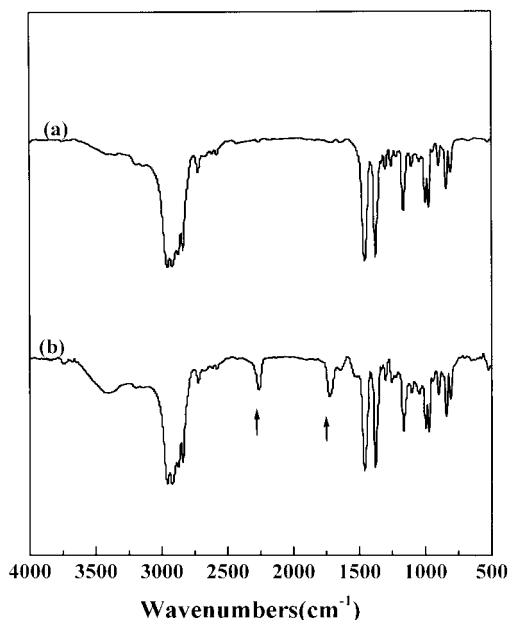
80°C and washed with pure xylene several times; precipitated in a large amount of acetone at room temperature during 12 h to eliminate the xylene, unreacted HI, and initiator; and finally dried in a vacuum. The functionalized PP had an MFI of 7 dg/min (ASTM D1238, 230°C, and 2.16 kg), and the grafting extent of HI was characterized by <sup>1</sup>H-NMR spectroscopy (Unity Inova NMR 300, Varian). The MFI of the grafted PP was significantly higher than the homopolymer PP as a result of chain scission during the grafting reaction.<sup>16</sup>

### Blend Preparation

Because of degradation of PP during the grafting reaction, we used another PP (Hyosung T&C Co., MFI = 7 dg/min, ASTM D1238, 230°C, and 2.16 kg) with the same MFI value as PP-g-HI to equivalently compare PET/PP blends with PET/PP-g-HI blends. The blends were prepared in an internal mixer (Rheomix 900, Haake) at 265°C. The rotor speed was 50 rpm, and the blending was carried out under a nitrogen blanket to prevent oxidative degradation. After mixing for 5 min, the blends were slowly cooled at room temperature. The blend ratios of the PET/PP and PET/PP-g-HI were 10/90, 30/70, 50/50, 70/30, and 90/10 by weight.

### Measurements

The morphology of the blends was observed by SEM (JSM-35CF, Jeol) from a cryogenically fractured (in liquid nitrogen) surface. The thermal behaviors of the blends were investigated using DSC (DSC-7, Perkin-Elmer). The DSC measurements were carried out in an N<sub>2</sub> atmosphere by heating from 50 to 280°C at 10°C/min and cooling to 50°C. Two minutes were allowed between the heating and cooling scan. All of the specimens for mechanical testing were prepared using a Mini Max molder (SC-183 MMX, Custom Scientific Instruments, Inc.) at 260°C with a mold temperature of 95°C. Prior to molding, samples were dried in a vacuum oven at 80°C for 24 h. Tensile properties were investigated with an Instron machine at room temperature, following the procedures described in ASTM D638. The amount of water absorbed by the blend samples (50 × 10 × 1 mm) were determined following the ASTM D570 procedure. All of the specimens for the water absorption testing were obtained by compression molding in a heated press. The blend sample prepared earlier was heated to 270°C and kept for 5 min



**Figure 1** IR spectra of homopolymer PP (spectrum a) and grafted PP (PP-g-HI, spectrum b).

between the plates without any applied pressure, allowing for complete melting. After this period, a pressure of 2500 psi was applied at the same temperature for 2 min. The sample was then slowly cooled in the press to room temperature in 30 min. In this test the dried specimens were immersed in distilled water at 50°C for 24 h. We measured the weight of the wetted samples after wiping off all surface water with a dry cloth. The water absorption (%) was evaluated from the following definition:

water absorption(%)

$$= \frac{\text{weight wetted sample} - \text{weight dried sample}}{\text{weight dried sample}} \times 100 \quad (1)$$

## RESULTS AND DISCUSSION

### Functionalization of PP

The presence of grafted HI in the PP was confirmed by FTIR spectroscopy. Figure 1 shows the FTIR spectra for HI incorporated in the PP chain. It was possible to observe the C=O peak (about 1730 cm<sup>-1</sup>) of HEMA. In addition, the NCO group was also observed at 2270 cm<sup>-1</sup> for C=N. This was clear evidence of the presence of an NCO functional group in the PP.

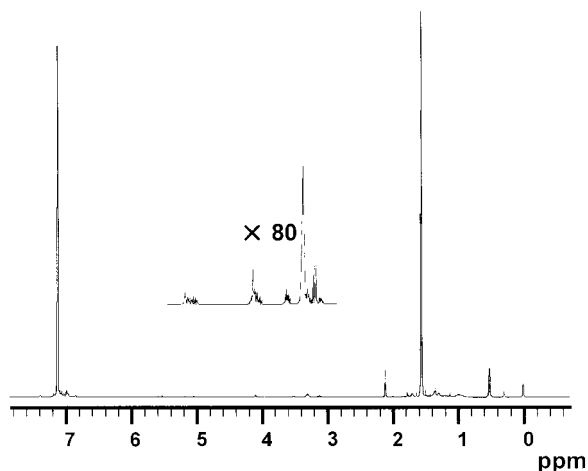
<sup>1</sup>H-NMR spectroscopy (Fig. 2) of the purified product in deuterated benzene solution was used to determine the extent of grafting. The extent of grafting was calculated from the ratio of the integral of the peaks between 3.10 and 5.22 ppm (for the hydrogen atoms on the HI) to the integral of the peaks between 0.5 and 2.11 ppm (for the six hydrogen atoms of the PP). The amount of HI in the PP-g-HI was 1.79 wt %.

### Morphology

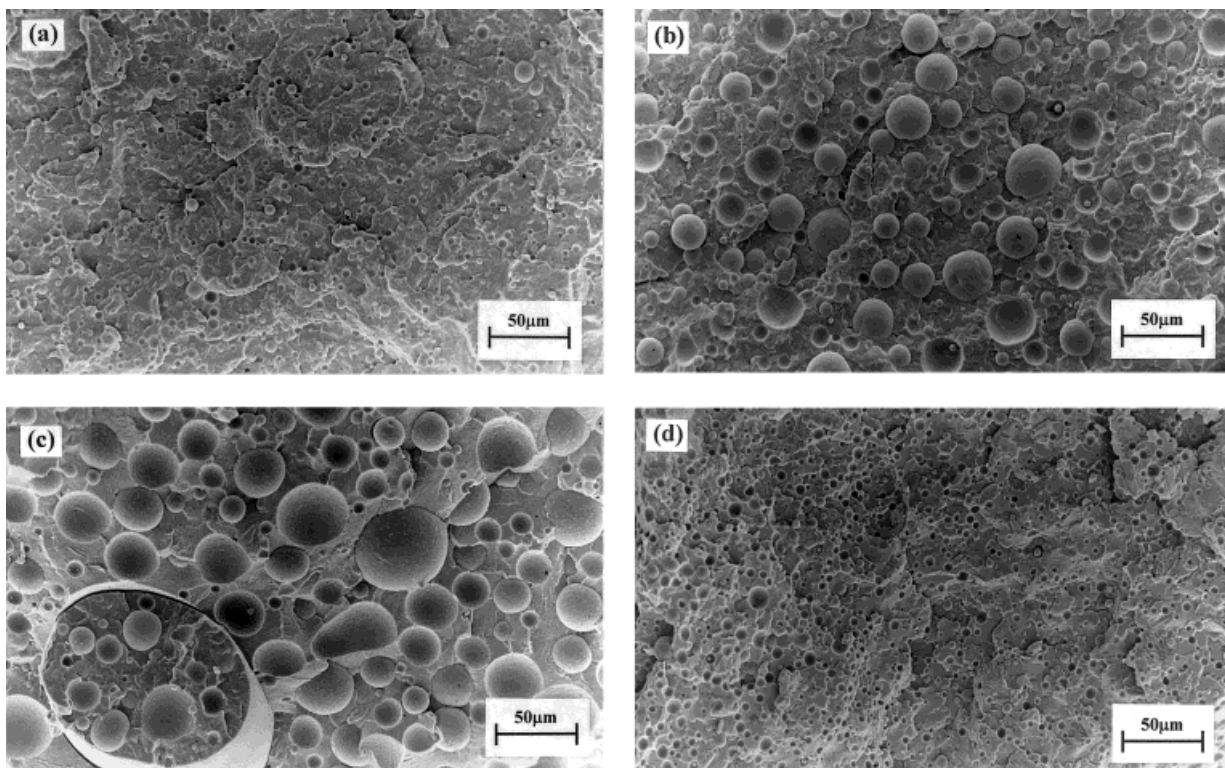
The SEM observations of the surface fractures of the blends show an evolution of the morphology. In Figure 3 the photomicrographs of the cryogenically fractured surfaces of the uncompatibilized (PET/PP) blends are displayed for various compositions. They show morphologies typical of immiscible blends. As indicated, PP and PET are immiscible and their phases are grossly separated. The phase morphologies of PET/PP blends are very poor and the dispersed phases are large and coarse because of the inherent immiscibility.

The photomicrographs of the PET/PP-g-HI blends are represented in Figure 4. The dispersions of the PET/PP-g-HI blends were much finer than those of the PET/PP blends. Also, the microdispersions of the PET/PP-g-HI blends exhibited much more homogeneous phase structures than those of the PET/PP blends.

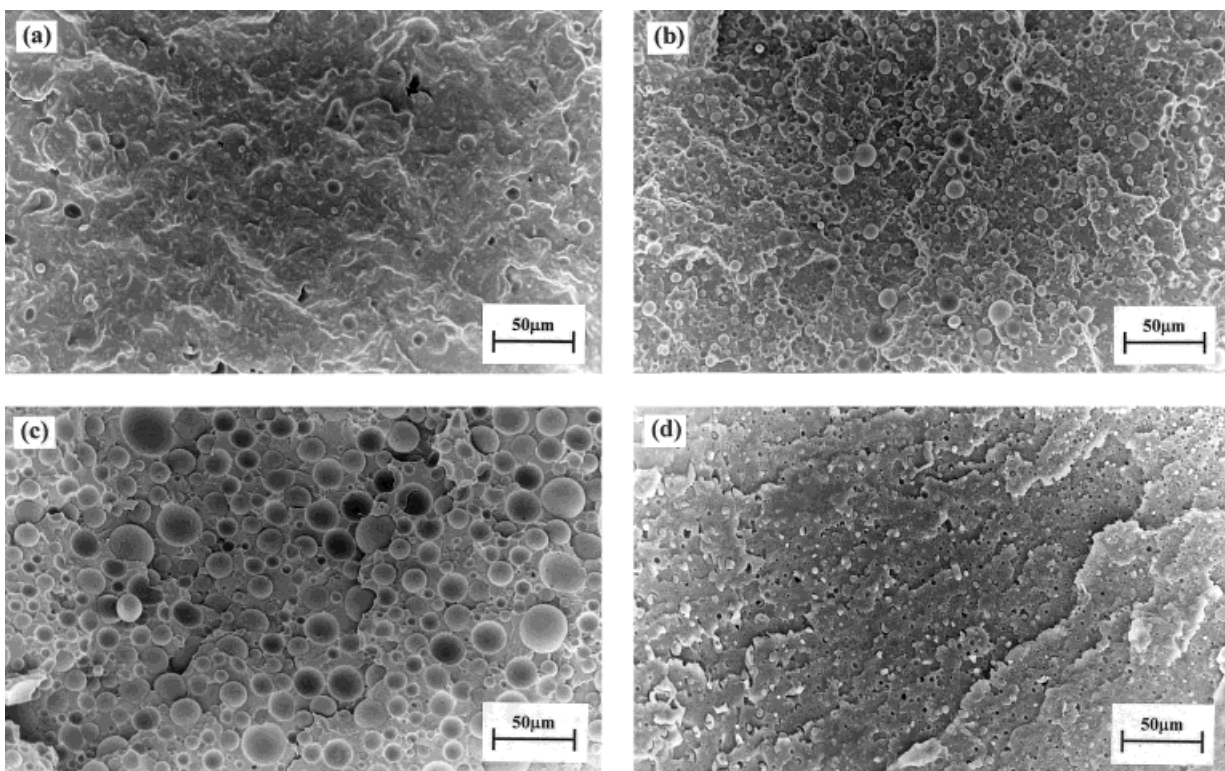
It is generally known that the morphologies of polymer blends depend on the shear history in the mixer, the viscosity ratio, and the interfacial tension between the matrix and minor components. In particular, the interfacial tension between two polymers is very important for phase morphology, and compatibilization plays a major role in low-



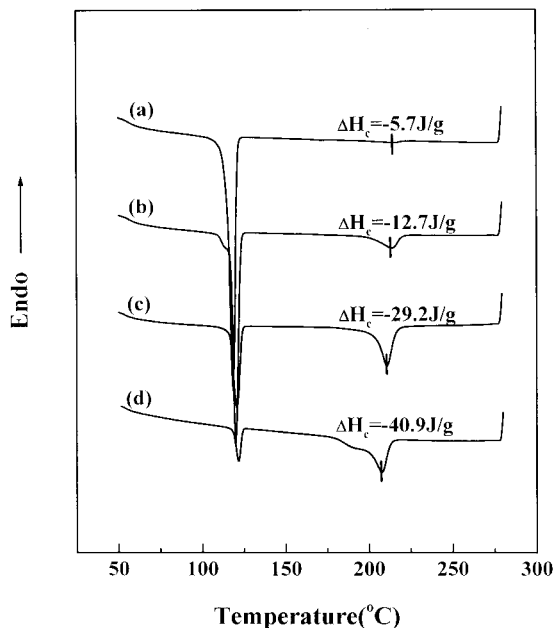
**Figure 2** A <sup>1</sup>H-NMR spectrum of HI grafted PP.



**Figure 3** SEM micrographs of the cryogenically fractured surfaces of the PET/PP blends: (a) 10/90, (b) 30/70, (c) 70/30, and (d) 90/10.



**Figure 4** SEM micrographs of the cryogenically fractured surfaces of the PET/PP-*g*-HI blends: (a) 10/90, (b) 30/70, (c) 70/30, and (d) 90/10.



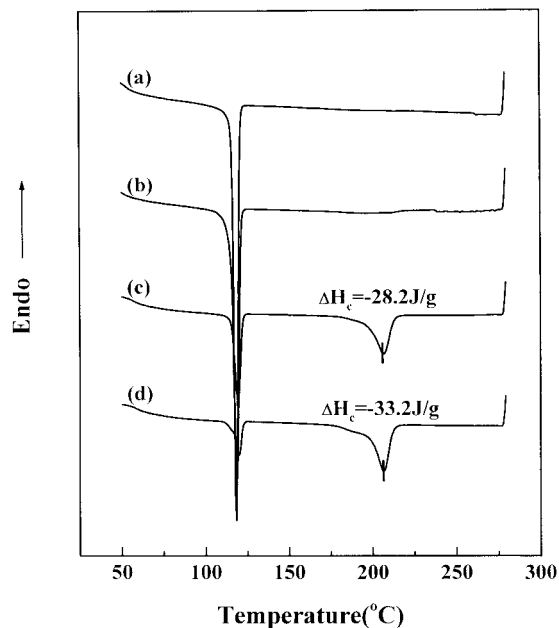
**Figure 5** DSC cooling thermograms of the PET/PP blends: (a) 10/90, (b) 30/70, (c) 70/30, and (d) 90/10.

ering interfacial tension or enlargement of interface adhesion, thereby forming a finer morphology.<sup>17</sup>

In our experiment the reaction of OH (or COOH) and NCO in the PET/PP-*g*-HI blends during the melt blending allowed the lowering of the interfacial tension of the blends over the PET/PP blends because of the generation of the *in situ* copolymer (PP-*g*-PET). From this effect we could observe the finer dispersions, as well as some adhesions of the phases, in the PET/PP-*g*-HI blends. From this result we confirmed that the compatibility of PET/PP blends could be improved by a modification of PP with HI.

#### Thermal Analysis of Blends

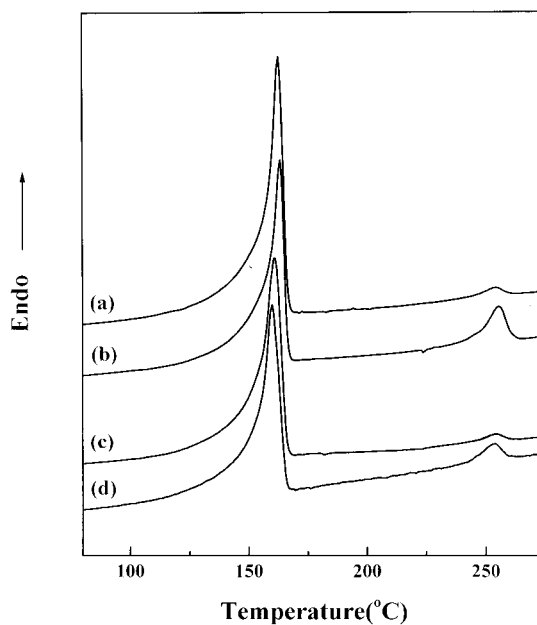
Typical DSC thermograms of the PET/PP and PET/PP-*g*-HI blends for a cooling run at 10°C/min are shown in Figures 5 and 6, respectively. At a given blend composition, the heats of crystallization ( $\Delta H_c$ ) of PET in the PET/PP-*g*-HI blend were decreased compared with those in the PET/PP blend. Moreover, the crystallization peaks disappeared in the PET/PP-*g*-HI 10/90 and 30/70 blends [see Fig. 6(a,b)]. The disappearance of the crystallization peaks at the usual crystallization temperature ( $T_c$ ) for PET suggested that the whole PET crystallization coincidentally took place at the usual  $T_c$  for PP in the PET dispersed phase. The crystallization of PET at the  $T_c$  for PP



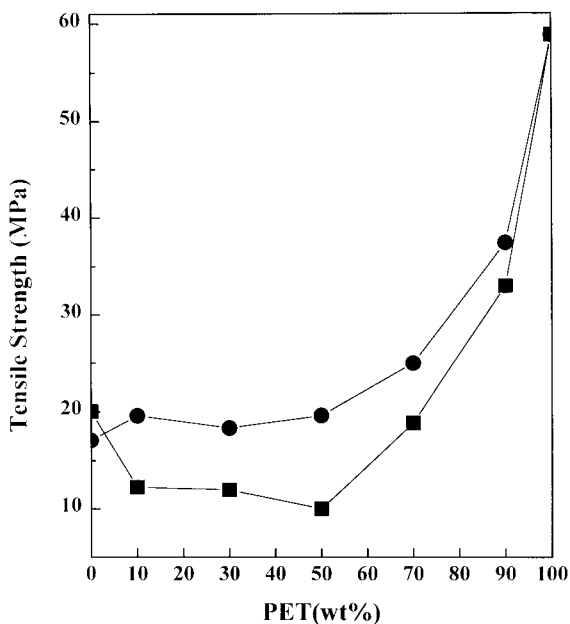
**Figure 6** DSC cooling thermograms of the PET/PP-*g*-HI blends: (a) 10/90, (b) 30/70, (c) 70/30, and (d) 90/10.

did not mean that PET cocrystallizes with PP, because each component showed a separate melting endotherm (see in Fig. 7).

Thus, the chemical reactions between NCO groups present in the PP-*g*-HI and COOH (or OH) groups of PET caused the generation of an *in situ*



**Figure 7** DSC heating thermograms of the (a,b) PET/PP blends and (c,d) PET/PP-*g*-HI blends: (a) 10/90, (b) 30/70, (c) 10/90, and (d) 30/70.



**Figure 8** The dependence of the tensile strength on the blend composition: (■) PET/PP blends and (●) PET/PP-g-HI blends.

copolymer (PP-g-HI and COOH (or OH) groups of PET caused the generation of an *in situ* copolymer (PP-g-PET) during the melt blending. The PP-g-PET copolymers located in the PET microdispersions may act as a polymeric diluent to retard the crystallization of PET and level off the heats of crystallization of PET. It is conceivable that the chemical reaction of the interphases affected the melt crystallization.

### Mechanical Properties

Immiscible polymer blends usually have poor mechanical properties compared with those of the constituent homopolymers. However, by compatibilization that creates synergistic effects, the blends of immiscible polymers can possess enhanced mechanical properties. Figure 8 represents the tensile strengths of PET/PP (or PET/PP-g-HI) blends as a function of the content of PET. It can be easily seen that the tensile properties of the compatibilized blends are considerably improved relative to those of the uncompatibilized blends in the overall range of blend compositions. The degree of improvement is most significant for the PET content of about 50%.

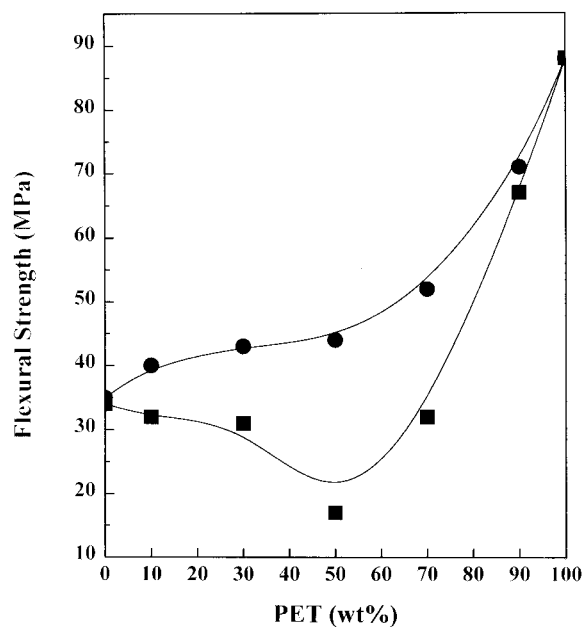
As two studies<sup>18,19</sup> pointed out, the tensile failure of a blend is attributable to the tensile failure of the adhesion between the dispersed phase and the matrix phase through a crazing or dewetting

effect. In our study the lower tensile strengths of PET/PP blends than those of PET/PP-g-HI blends were also thought to be due to the failure of the adhesion between the interphases of PET and PP.

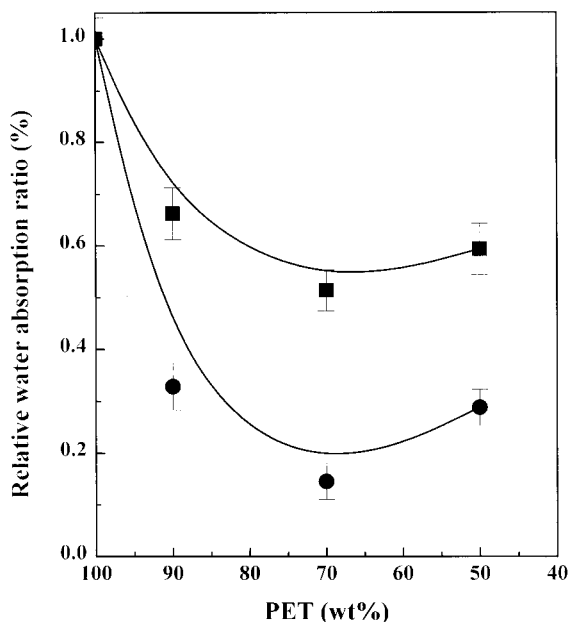
The flexural strengths of the PET/PP (or PP-g-HI) blends are given in Figure 9. The flexural strengths increased with the PET content of the blends. For the noncompatibilized (PET/PP) blend, the flexural strengths were not as good as that of the compatibilized blend in the same compositions. While the flexural strengths of the PET/PP-g-HI blends stayed almost constant, those of the PET/PP blends decreased quickly until about a 50/50 blending ratio. Obviously, this property change may have arisen from the blend morphological phase reversion at about equal compositions, representing the poor balance of properties in the incompatible blend system.<sup>20</sup> In our study the poor balances at equivalent compositions were attributed to morphological phase reversion between PET and PP.

### Water Absorption Properties

In Figure 10 the amount of water absorbed by the blends relative to that absorbed by the homopolymer PET is plotted with the PET content of the blends. The water absorption of pure PET was reduced by the addition of PP. The water absorption reduction of PET was approximately propor-



**Figure 9** The dependence of the flexural strength on the blend composition: (■) PET/PP blends and (●) PET/PP-g-HI blends.



**Figure 10** The water absorption of PET/PP or PP-g-HI blends relative to that of PET: (■) PET/PP blends and (●) PET/PP-g-HI blends.

tional to the PP volume content in the blends. As indicated, the compatibilized blends (PET/PP-g-HI) showed significantly improved water absorption resistance. This was due to the finer dispersed phase size, which created the increase of the total surface area for the PP phase to the PET phase. It is believed that the water resistance was enhanced by the compatibilizing effect attributable to the generation of *in situ* copolymer between the PET and PP phases.

## CONCLUSIONS

Grafting of an isocyanate functional monomer onto PP was carried out in boiling xylene as the solvent medium. The FTIR spectra of PP-g-HI showed the presence of an NCO group. Also, the extent of grafting was examined using  $^1\text{H-NMR}$  spectroscopy. In view of the blend morphology, much finer dispersions were observed in the PET/PP-g-HI blends, indicating that *in situ* generated copolymers (PP-g-PET) act as compatibilizers during the melt blending. DSC thermograms for a cooling run indicated that the PET crystallization was retarded in the PP-g-HI rich phase, because of the chemical reactions of the PET and PP-g-HI phases. The PP-g-PET copolymers locating in the

PET microdispersions may act as a polymeric diluent to retard the crystallization of PET and level off the heats of crystallization of PET. The tensile and flexural properties and water resistances of PET/PP-g-HI blends were higher than the PET/PP blends. With the above-mentioned results, it could be concluded that the compatibility of the PET/PP blends was improved by the reactive blend through NCO functionalized PP.

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## REFERENCES

1. Olabish, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic: New York, 1979.
2. Paul, D. R.; Newman, S. *Polymer Blends*; Academic: New York, 1978; Vol. 1.
3. Lambla, M.; Seadan, M. *Makromol Chem Macromol Symp* 1993, 69, 9.
4. Liu, N. C.; Xie, H. Q.; Baker, W. E. *Polymer* 1993, 34, 4680.
5. Xanthos, M.; Dagli, S. S. *Polym Eng Sci* 1991, 31, 929.
6. Frund, Z. N., Jr. *Plast Compound* 1986, 9, 24.
7. Minoura, Y.; Ueda, M.; Mizunuma, S.; Oba, M. *J Appl Polym Sci* 1969, 13, 1625.
8. Ide, F.; Hasegawa, A. *J Appl Polym Sci* 1974, 18, 963.
9. Xie, H. Q.; Feng, D. S.; Guo, J. S. *J Appl Polym Sci* 1997, 64, 329.
10. Jabarin, S. A.; Lotgren, E. A.; Shah, S. B. In *Emerging Technologies in Plastics Recycling*; Andrews, G. D., Subramanian, P. M., Eds.; American Chemical Society: Washington, DC, 1992.
11. Akkapeddi, M. K.; VanBuskirk, B. *Polym Prepr* 1993, 34, 848.
12. Dagli, S. S.; Kamdar, K. M. *Polym Eng Sci* 1994, 34, 1709.
13. Park, S. H.; Park, K. Y.; Suh, K. D. *J Polym Sci Part B Polym Phys* 1998, 36, 447.
14. Park, K. Y.; Park, S. H.; Suh, K. D. *J Appl Polym Sci* 1997, 66, 2183.
15. Park, S. H.; Bae, T. Y.; Suh, K. D. *J Macromol Sci Pure Appl Chem* 1998, 35, 1763.
16. Ho, R. M.; Su, A. C.; Wu, C. H. *Polymer* 1993, 34, 3264.
17. Xanthos, M. *Polym Eng Sci* 1988, 28, 1392.
18. Kunori, T.; Geil, P. H. *J Macromol Sci Phys* 1980, B18, 135.
19. Nielsen, L. E. *Mechanical Properties of Polymers and Composites*; Marcel Dekker: New York, 1974.
20. Locke, C. K.; Paul, D. R. *J Appl Polym Sci* 1973, 17, 2597.