# Maleic Anhydride Grafted Thermoplastic Elastomer as an Interfacial Modifier for Polypropylene/Polyamide 6 Blends

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**ABSTRACT:** A maleic anhydride grafted thermoplastic elastomer (TPE<sub>g</sub>) was prepared. The effect of the TPE<sub>g</sub> on the morphology and performance of polypropylene (PP)/polyamide 6 (PA-6) blends was studied. The final properties of the blends were tuned through variations in the TPE<sub>g</sub>/PA-6 ratios and TPE<sub>g</sub> and PA-6 percentages in the blends. Scanning electron micrographs showed that the TPE<sub>g</sub> greatly improved the homogeneity of the blends, and this led to better mechanical performance. The nonisothermal crystallization behaviors of PP and PA-6 in the blends, revealed by differential scanning calorimetry, were different from those

of pure PP and PA-6. The crystallization temperature and rate of PP were promoted by the PA-6 component because of its nucleating effect, whereas stepwise crystallization was detected for PA-6 in the PP/PA-6 blends when the TPE<sub>g</sub> was added. On the basis of these observations, a schematic model was proposed for these blends. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1806–1815, 2004

Key words: elastomers; polyamides; poly(propylene) (PP); blends

## INTRODUCTION

It has been estimated that the usage of polymers, regarded as the fastest growing structural materials, will grow 10% annually in the future. Polymer blends and alloys, which have been estimated to have increased 9% annually during past years, are widely used because of their excellent mechanical, thermal, and chemical properties (or some other specific properties) and their friendly processing conditions. The properties of polymer blends are intimately related to the characteristics of the components, the compositions, and the morphologies. During the past decades, much work has been dedicated to reaching a desired morphology through optimization of the processing conditions, including the process temperature, residence time, shear rate, and elongation draw, or through the reduction of the interfacial energy with an interfacial agent.<sup>1</sup>

Polypropylene (PP) and polyamide (PA) blends have been widely studied because these blends can combine the good thermal and mechanical properties of PA and the excellent processability and resistance to moisture of PP. However, the differences in the polarity and crystal structure of PP and PA can result

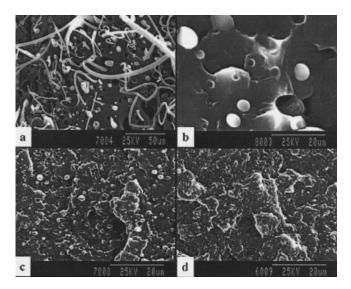
in bad compatibilization between the two components. To obtain more homogeneous PP/PA blends through the addition of either interfacial active block copolymers or functionalized components, which react with the blends during the process, has become the dream of many researchers. For instance, the formation of bonds between maleic anhydride-g-polypropylene  $(PP_{\sigma})$  and polyamide 6 (PA-6) was investigated by Bidaux et al.<sup>2</sup> Reinforced PP was prepared by the blending of 70 vol % PP and 30 vol % PA-6 in the presence of compatibilizers, such as PPg and maleic anhydride grafted rubbers.<sup>3</sup> The rheological properties, crystallization, and morphology of isotactic PP/ PA-6 compatibilized with PPg were investigated.<sup>4</sup> Static mechanical and falling weight impact tests were performed on PP/PA-6 blends compatibilized with PPg.<sup>5</sup> Heino et al.<sup>6</sup> studied the fracture toughness of PA-6/PP blends to which SEBS-g-MA had been added. The compatibility of PP/PA-6 and PP/polyamide 6,6 with styrene-ethylene-butylene-styrene (SEBS) as an interfacial agent was found to be poor, but it became very good when SEBS-g-MA was used.<sup>7</sup> A copolymer consisting of PP grafted with phenol formaldehyde was found to be suitable for PP/PA-6 blends.8

In our laboratory, comprehensive studies have been performed on polymer composites and blend materials in the past decades. Rigid fillers in the polymers have been found to produce high-modulus, highstrength polymer composites, but they cannot improve the toughness. However, elastomers added to

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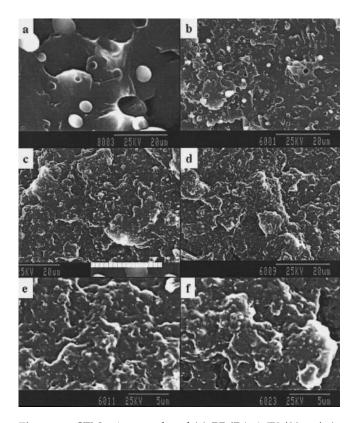


**Figure 1** SEM micrographs of (a,b) PP/PA-6 (70/30 w/w), (c) PP/TPE<sub>g</sub> (75/25 w/w), and (d) PP/PA-6/TPE<sub>g</sub> (55/30/15 w/w/w).

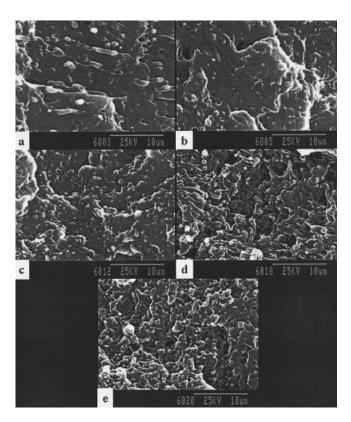
the polymers easily increase the toughness but greatly reduce the stiffness. For the production of materials with high toughness, strength, and modulus, a thermoplastic matrix/elastomer/rigid filler system has been designed. Two kinds of phase structures can be expected in these blends: (1) the filler and elastomer separately dispersed in the matrix and (2) the filler as a core and the elastomer as a shell. Matonis<sup>11</sup> pointed out that it was doubtful that a mixture of separately dispersed phases of a filler and a elastomer, exhibiting two different and distinct responses to an applied load, could result in a composite with desirable properties. The encapsulation method was suggested.9 Three factors can greatly affect the performance of this filler core/elastomer shell/thermoplastic matrix polymer composite: (1) the thickness of the elastomer shell, (2) the properties of the material in this shell phase, and (3) the interfacial adhesion of the various phases.<sup>10-15</sup> A careful consideration of these factors can produce stiffer and tougher materials. We want to extend this idea to PP/PA-6 blends and make PP matrix/elastomer interlayer/PA-6 core blends. To reach this goal, the design of the elastomer interlayer is crucial. Our work on high-density polyethylene (HDPE)/ethylene-propylene-diene monomer (EPDM)/carbon black (CB) composites has shown that bad interfacial adhesion results in separated CB and EDPM phases in the HDPE matrix.<sup>16</sup> When an interfacial modifier is used, CB is capsulated in EDPM, and this forms a core-shell structure. The resulting blends have much better mechanical properties. Lu et al.<sup>17</sup> studied rubber-particle-toughened nylon 6 with styrene/maleic anhydride copolymers, styrene/acrylic acid copolymers, ethylene/acrylic acid as a compatibilizer.<sup>17</sup> The interfacial adhesion was found to be intimately related

to the final properties. A good compatibilizer should have both good reactivity with nylon 6 and miscibility with the core. The lack of either characteristic in a potential compatibilizer will presumably lead to a failure to provide an adequate dispersion of the core phase or interfacial adhesion. Our work has further shown that a soft interlayer of a certain thickness and good interfacial adhesion will improve the adhesion and mechanical properties.

We have developed a maleic anhydride grafted thermoplastic elastomer (TPE<sub>g</sub>) consisting of maleic anhydride grafted poly(octene ethylene) (POE) rubber and a semicrystalline polyolefin. The incorporation of a semicrystalline polyolefin with POE not only improves the extruding processability and makes the resulting extrudate (TPE<sub>g</sub>) easily pelletized but also lowers the cost. TPE<sub>g</sub> has been shown to be an excellent elastomer for toughening PA-6. The POE part in TPE<sub>g</sub> is an excellent interlayer for the PP/POE/talc ternary composite.<sup>18–21</sup> In this work, we used TPE<sub>g</sub> as the interfacial agent for PP/PA-6 blends and studied its effect on the compatibility, morphology, and mechanical performance of the blends. The idea of using a soft elastomer as an interlayer for two rigid plastics was demonstrated.



**Figure 2** SEM micrographs of (a) PP/PA-6 (70/30 w/w), (b) PP/PA-6/TPE<sub>g</sub> (64/30/6 w/w/w), (c) PP/PA-6/TPE<sub>g</sub> (58/30/12 w/w/w), (d) PP/PA-6/TPE<sub>g</sub> (52/30/18 w/w/w), (e) PP/PA-6/TPE<sub>g</sub> (46/30/24 w/w/w), and (f) PP/PA-6/TPE<sub>g</sub> (40/30/30 w/w/w).



**Figure 3** SEM micrographs of (a) PP/PA-6/TPE<sub>g</sub> (64/30/6 w/w/w), (b) PP/PA-6/TPE<sub>g</sub> (58/30/12 w/w/w), (c) PP/PA-6/TPE<sub>g</sub> (52/30/18 w/w/w), (d) PP/PA-6/TPE<sub>g</sub> (46/30/24 w/w/w), and (e) PP/PA-6/TPE<sub>g</sub> (46/30/24 w/w/w).

#### **EXPERIMENTAL**

## Materials

For TPE<sub>g</sub>, the grafted maleic anhydride content, with respect to the blend, was about 1 wt %. POE (Engage 8445) was supplied by Dow Chemical China, Ltd. (Beijing, China). Its octane content and melt-flow rate were 9.5% and 3.5 g/10 min, respectively. TPE denotes a POE rubber/semicrystalline polyolefin (60/40) blend. PP (PP2401; Yanshan Petroleum & Chemical Co.) and PA-6 (Shanghai No. 18 Nylon Factory, Shanghai, China) were used as received.

### **Blend** preparation

The blends were prepared by melt extrusion with a  $\phi$  30 twin-screw extruder (SHJ-30, Nanjing Plastic Machinery Co., Ltd., Nanjing, China) at 250 rpm. The barrel temperature was 220°C. The blends were pelletized, dried, and injection-molded into standard tensile, flexural, and Izod impact test specimens with an injection-molding machine (SZ-160/80 NB, Ningbo Plastics Machinery Co., Ltd., Ningbo, Zhejiang Province, China) at 220°C

#### Mechanical testing

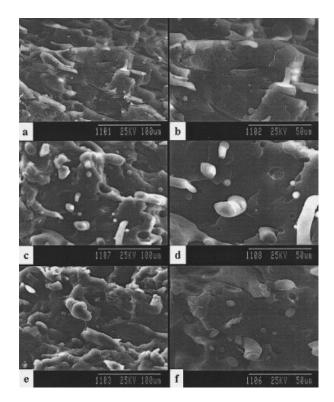
The tensile and flexural tests were carried out on a universal tensile tester (Instron 1122, Instron, Ltd., England) according to National Standard Test Methods GB 1040-79 and GB 1042-79, respectively. The two test methods were very similar in their sample dimensions and test conditions to ASTM D 638 and ASTM D 790, respectively. The notched Izod impact strength was measured with an impact test machine (Custom Scientific Instruments CSI-127C, Atlas Electric Devices Co.) according to GB 1843-80, which is similar to ASTM D 256.

### Thermal analysis

Nonisothermal scans were carried out on a PerkinElmer DSC-7 differential scanning calorimeter at a heating or cooling rate of  $20^{\circ}$ C/min from 25 to 260°C under an N<sub>2</sub> purge. The nylon samples were dried *in vacuo* at 80°C for 12 h before the analysis.

# Morphological observations

The impact-fractured surfaces of the blends samples at room temperature were observed with a Hitachi S-530 scanning electron microscope. The surfaces were coated with gold.



**Figure 4** SEM micrographs of (a,b) PP/PA-6/TPE (64/ 30/6 w/w/w), (c,d) PP/PA-6/TPE (52/30/18 w/w/w), and (e,f) PP/PA-6/TPE (46/30/24 w/w/w).

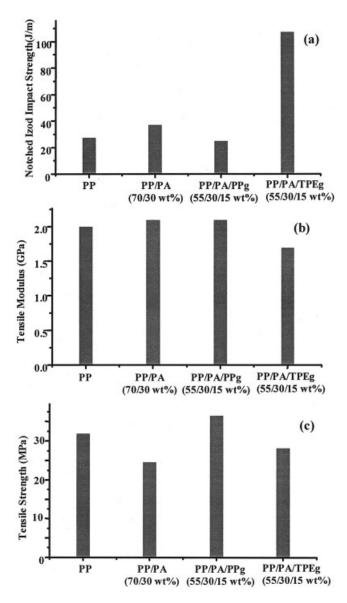


Figure 5 Mechanical properties of PP and PP/PA-6 blends.

#### Dynamic mechanical analysis

A dynamic mechanical analyzer (DMA-7, PerkinElmer) was used to measure the dynamic mechanical properties of the blends. The specimens were  $3 \text{ mm} \times 10 \text{ mm} \times 1.5$  mm. Before the measurements were taken, the specimens were dried in a vacuum oven for 12 h at 80°C. Temperatures from -170 to  $160^{\circ}$ C were used in a three-point bending mode at a vibration frequency of 1 Hz and at a heating rate of 5°C/min in a nitrogen atmosphere.

## **RESULTS AND DISCUSSION**

# Morphology

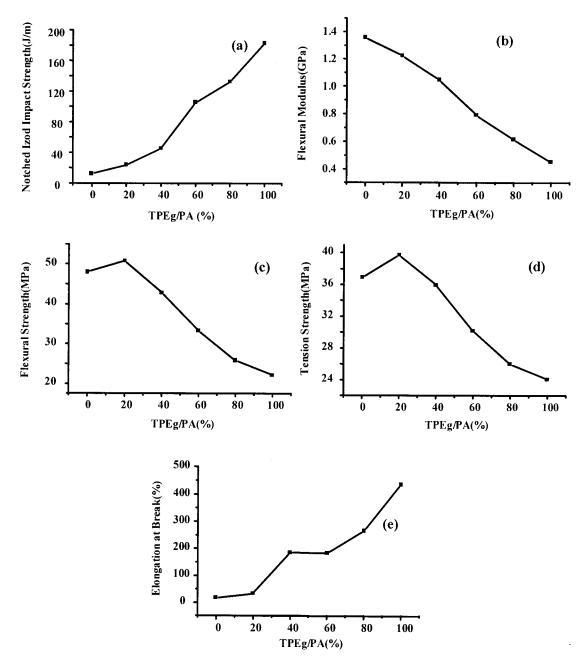
To test the efficiency of  $TPE_g$  as a compatibilizer for PP/PA-6 blends, we investigated the microstructures of the blends with scanning electron microscopy

(SEM). The microstructures of PP/PA-6, PP/TPE<sub>g</sub>, and PP/PA-6/TPE<sub>g</sub> are illustrated in Figure 1. Each micrograph was taken at the surface with a thin coating of gold after the impact test. PP and PA-6 had poor compatibilization because of the differences in the polarity and crystal structure. In the PP/PA-6 blends without  $TPE_{g}$ , PA-6 domains with diameters of 7–10  $\mu$ m were dispersed in the continuous PP matrix. The long PA-6 fibers shown in the micrographs were formed because of the elongation during the impact test. Partial PA-6 phases were completely dislodged, leaving dark voids in the matrix [Fig. 1(a,b)]. Big cracks can be clearly seen between the PP and PA-6 phases. Although they had similar backbone structures, TPE<sub>o</sub> had only moderate compatibilization with PP [Fig. 1(c)].  $TPE_g$  particles were dispersed in the PP matrix with diameters of  $3-4 \ \mu m$  (3.5  $\ \mu m$  on average). Many TPEg particles were exposed, and this indicated only moderate adhesion between PP and TPEg. Our early work showed that POE had good miscibility with PP. Therefore, the diminished miscibility between PP and TPE<sub>g</sub> must have resulted from the functionalization of POE by the succinic anhydride groups, which raised the polarity, charge, and hydrophilicity.

With the addition of 15 wt % TPE<sub>g</sub> to PP/PA-6, the morphologies changed obviously. No PA-6 fibers existed again. The PA-6 particle size was reduced to 1  $\mu$ m, and the particle size range was very small. The particles were dispersed quite uniformly over the matrix [Fig. 1(d)]. TPE<sub>g</sub> greatly improved the dispersion of the PA-6 phase. During the blending process, the succinic anhydride groups of TPE<sub>g</sub> reacted with the amino groups of PA-6, and this resulted in grafted copolymers, which had a strong tendency to be anchored at the PP/PA-6 interface. Most of the succinic groups of TPE<sub>g</sub> were incorporated into PA-6, and the miscibility between PP and TPE<sub>g</sub> was improved because of the disappearance of the polarity groups in TPE<sub>g</sub>.

The microstructures of PP/PA-6 blends with various amounts of TPE<sub>g</sub> are shown in Figure 2. Increasing the amount of TPE<sub>g</sub> changed the following features: (1) PA-6 fibers found in uncompatibilized PP/PA-6 [Fig. 1(a)] disappeared when TPE<sub>g</sub> was used [Fig. 2(b)], (2) the PA-6 domain size was reduced when the TPE<sub>g</sub> content was increased, (3) the PA-6 domains size was smaller when more TPE<sub>g</sub> was used, and (4) PA-6 was dispersed more and more uniformly through the addition of more TPE<sub>g</sub>. These features well reflected how TPE<sub>g</sub> could improve the dispersion of PA-6 in the PP matrix.

Figure 3 provides a close look at the microstructures with higher resolution micrographs. For blends with less than 24 wt % TPE<sub>g</sub>, the impact-fractured surfaces were very smooth, this being characteristic of brittle polymers. The impact energy was mainly dissipated

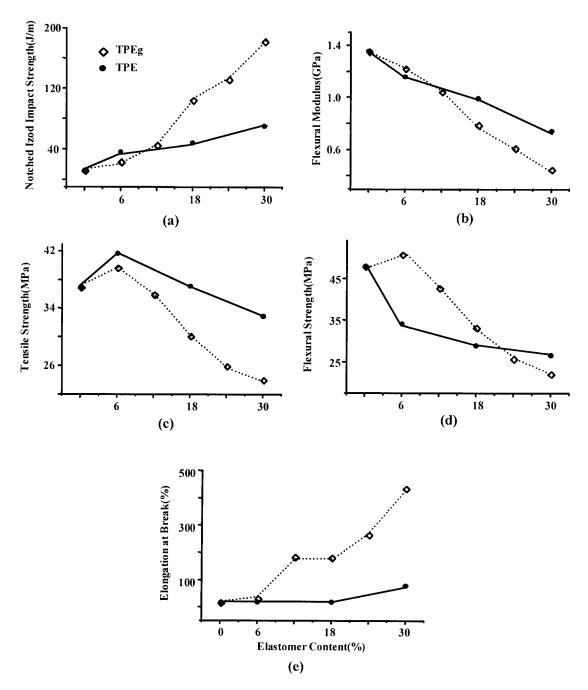


**Figure 6** Effects of the  $TPE_g/PA-6$  ratio on the mechanical properties of  $PP/PA-6/TPE_g$  blends (all blends had 30 wt % PA-6).

through matrix crazing. For blends with 24 and 36 wt % TPE<sub>g</sub>, profuse cavitation and matrix shear yielding can be observed.

For PP/PA-6/TPE blends, the phase structures were quite different. Three phases, including continuous, fibrous, and spherical phases, were clearly found in the blends (Fig. 4). We attributed the continuous matrix to PP and the fibers to PA-6 based on PP and PA-6 compositions in the blend. Uncompatibilized PP/PA-6, having PA-6 fibers, provided further proof of this. The spherical particles were mainly attributed

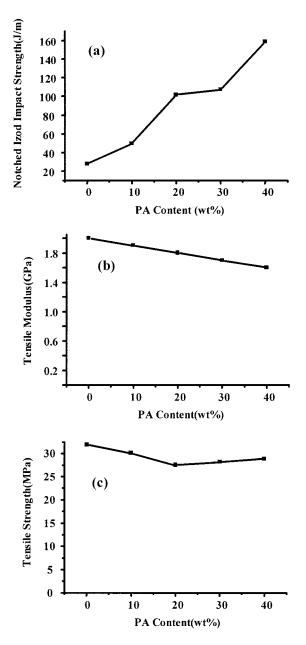
to TPE because the number and total volume of this phase rose as the TPE content increased. Partial particles may have been PA-6; the diameters of the PA-6 fibers and the dispersed particles did not change much as more TPE was used. The interface between PP and PA-6 was kept clear. Although TPE had good miscibility with PP, TPE could not react with PA-6 because of the lack of succinic anhydride groups. As a result, TPE could not form a core–shell structure with PA-6 and improve the dispersion of PA-6 in the PP matrix. A typical isolated three-phase structure was formed.



**Figure 7** Effect of the TPE<sub>g</sub> (TPE) content on the mechanical properties of PP/PA-6/TPE<sub>g</sub> (TPE) blends (all blends had 30 wt % PA-6).

#### Mechanical properties

As an interfacial modifier,  $TPE_g$  could affect the final properties of the blends in three ways. First,  $TPE_g$ improved the dispersion of the PA-6 domains, reduced the PA-6 domain size, and reduced the dispersed particle–particle distance. These could influence the toughness of the blends. As shown in many rubber-toughened pseudoductile polymers, there is a critical particle–particle distance. Blends with dispersed particle–particle distances less than this critical distance will transform from brittle polymers into ductile polymers. In our PP/PA-6/TPE<sub>g</sub> blends, PA-6 surrounded with a TPE<sub>g</sub> elastomer layer could act as a particle, toughening the PP matrix. Therefore, the improved dispersion could significantly change the toughness of PP. Second, TPE<sub>g</sub> increased the interfacial adhesion of PP and PA-6. The succinic anhydride groups in TPE<sub>g</sub> reacted with the amino groups of PA-6. POE in TPE<sub>g</sub> was dissolved in the PP matrix. Third, the thick soft TPE<sub>g</sub> layer contributed to the final



**Figure 8** Effects of the PA-6 content on the mechanical properties of  $PP/PA-6/TPE_g$  blends (the  $TPE_g/PA-6$  ratio was fixed at 1/2 for all the blends).

mechanical properties, increasing the toughness and lowering the modulus. In the following paragraphs, we examine the effectiveness of  $\text{TPE}_{g}$  as an interfacial modifier and then characterize the effects of the interlayer structure on the mechanical properties.

To test the efficiency of  $\text{TPE}_{g}$  as an interfacial agent for the PP/PA-6 blends, we characterized the mechanical properties of the PP/PA-6 blends. Figure 5 illustrates the notched Izod impact strength, tensile modulus, and tensile strength of different samples. PP/ PA-6 consisted of 70 wt % PP and 30 wt % PA-6. The TPE<sub>g</sub>-compatibilized PP/PA-6 was 55 wt % PP, 30 wt % PA-6, and 15 wt % TPE<sub>g</sub>. The properties of PP<sub>g</sub>compatibilized PP/PA-6 are listed as well.

PP and PA-6 were brittle polymers with notched Izod impact strengths of 28 and 19 J/m, respectively. Simply blending PP and PA-6 did not improve the mechanical properties. With respect to pure PP, the notched Izod impact strength and tensile modulus only slightly increased, whereas the tensile strength was actually reduced. The difference in the polarity and crystal structure of PP and PA-6 led to a high interfacial energy and bad adhesion between the two components. The mechanical properties confirmed the poor compatibilization of PP and PA-6, as shown in the SEM micrographs.

Adding 15 wt % TPE<sub>g</sub> into the PP/PA-6 blends increased the notched Izod impact strength to 110 J/m, which was nearly 3 times that of unmodified PP/PA-6. The tensile strength was also improved from 25 to 28 MPa. However, the blend with a 110 J/m notched impact strength was still brittle, and this agreed well with the smooth impact-fractured surface shown in Figure 1(d).

 $PP_g$  was used as a stiff interfacial agent in this study. As expected, the tensile modulus and strength improved, but the toughness deteriorated.

In the PP/PA-6/TPE<sub>g</sub> blends, TPE<sub>g</sub> was expected to surround the dispersed PA-6 domains and be located at the interface of PP and PA-6. Therefore, the TPE<sub>g</sub>/PA-6 weight ratio would determine the thickness and structure of the interlayer. Large amounts of TPE<sub>g</sub> could produce more succinic anhydride to react with

| TABLE I                                     |  |  |  |  |  |  |
|---|--|--|--|--|--|--|
| Nonisothermal Crystallization of PP and PA- | 6 in the PP/PA-6/TPE <sub>g</sub> Blends |  |  |  |  |  |

|                            |                       | 5     |                    |                      | 5     |                    |                      |
|----------------------------|-----------------------|-------|--------------------|----------------------|-------|--------------------|----------------------|
| Sample                     |                       | PP    |                    | PA-6                 |       |                    |                      |
|                            | Composition<br>(wt %) | (°C)  | $\Delta H_c$ (J/g) | Crystallinity<br>(%) | (°C)  | $\Delta H_c$ (J/g) | Crystallinity<br>(%) |
| PP                         | 100                   | 116.9 | -98.7              | 47.19                |       |                    |                      |
| PP/PA-6                    | 70/30                 | 120.2 | -105.5             | 50.44                | 191.2 | -55.67             | 34.80                |
| $PP/TPE_{g}$               | 75/25                 | 116.7 | -106.0             | 50.71                |       |                    |                      |
| PP/PA-6/TPEg               | 64/30/6               | 121.7 | -103.5             | 49.27                | 187.7 | -67.30             | 42.08                |
| PP/PA-6/TPEg               | 52/30/18              | 118.5 | -116.9             | 55.90                | 185.8 | -6.28              | 3.93                 |
| PP/PA-6/TPE <sup>°</sup> g | 40/30/30              | 117.8 | -152.0             | 72.67                | 186.7 | -1.34              | 0.84                 |

|                                       | Nonisotherm                  | al Crystalliz           | zation of PP a             | nd PA-6 in the PP       | /PA-6/TPE E             | Blends                     |                         |
|---------------------------------------|------------------------------|-------------------------|----------------------------|-------------------------|-------------------------|----------------------------|-------------------------|
|                                       |                              | РР                      |                            |                         | PA-6                    |                            |                         |
| Sample                                | Composition<br>(wt %)        | (°C)                    | $\Delta H_c$ (J/g)         | Crystallinity<br>(%)    | (°C)                    | $\Delta H_c$ (J/g)         | Crystallinity<br>(%)    |
| PP/PA-6<br>PP/PA-6/TPE<br>PP/PA-6/TPE | 70/30<br>64/30/6<br>52/30/18 | 120.2<br>121.7<br>121.7 | -105.5<br>-111.6<br>-131.4 | 50.44<br>53.34<br>62.85 | 191.2<br>191.1<br>191.2 | -55.67<br>-56.20<br>-56.07 | 34.80<br>35.14<br>35.05 |
| PP/PA-6/TPE                           | 40/30/30                     | 121.6                   | -132.5                     | 63.33                   | 191.0                   | -51.37                     | 32.12                   |

TABLE II onisothermal Crystallization of PP and PA-6 in the PP/PA-6/TPE Blends

PA-6. It had more POE dissolved in the PP matrix as well. As a result, large amounts of  $\text{TPE}_{g}$  increased the interfacial interaction. Large amounts of  $\text{TPE}_{g}$  formed a thick soft interlayer as well. The layer improved the toughness and reduced the modulus. Figure 6 shows the influence of the  $\text{TPE}_{g}$ /PA ratio on the final mechanical properties. All the blends had 30 wt % PA-6. The  $\text{TPE}_{g}$ /PA-6 ratio increased the notched Izod impact strength linearly. However, the  $\text{TPE}_{g}$  elastomer made a negative contribution to the tensile and flexural properties.

Figure 7 further shows the effects of the  $\text{TPE}_{g}$  percentages in the blends on their final performance. PA-6 was fixed at 30 wt % in all the blend samples. The ungrafted TPE is presented as well.  $\text{TPE}_{g}$  improved the notched Izod impact strength linearly, whereas TPE only slightly changed the properties.

The PA-6 content in the blends was another important factor affecting their properties and price, and it is studied in Figure 8. The notched Izod impact strength, tensile modulus, and strength were plotted versus the PA contents in the PP/PA-6/TPE<sub>g</sub> blends.  $TPE_g/PA-6$ was fixed to be 1/2, at which ratio there was enough  $TPE_g$  to compatibilize PP/PA-6. The notched impact strength grew linearly with respect to the PA-6 content. The tensile strength and modulus only slightly changed.

These results show that  $TPE_g$  acted as a high-efficiency interfacial agent for the PP/PA-6 blends. The  $TPE_g/PA-6$  ratios and  $TPE_g$  and PA-6 percentages in the blends were intimately related to the final properties. The careful design of PP, PA-6, and  $TPE_g$  produced blends with expected properties, whereas ungrafted TPE polymer altered the blends slightly.

## Thermal properties

The nonisothermal crystallization and melting of PP/ PA-6/TPE<sub>g</sub> blends were studied. The heat, temperature of crystallization, and crystallinity of PP and PA-6 are listed in Table I. In a binary polymer blend system, the crystallization temperature ( $T_c$ ) of the major component is often increased. The possible reasons accounting for this behavior are (1) the migration of nuclei across the interface from the minor component to the major component, (2) the nucleating-agent-like behavior of the existing crystal of the minor component, (3) the alternation of the chain mobility at the interface, (4) the loss of the molecular weight during the mixing process. Pure PP crystallized at 116.9°C.  $T_c$ of PP in the PP/PA-6 blend was boosted to 120°C, whereas  $T_c$  of PP in the PP/TPE<sub>a</sub> blends was kept at 116.7°C. These results indicated that PA-6 could promote the nucleation of the PP matrix, whereas  $TPE_g$ could not. For the PP/PA-6/TPE<sub>g</sub> blends, when 6 wt % TPE<sub>g</sub> was used,  $T_c$  of PP was 121.7°C, which was close to that of PP/PA-6. PA-6 had a strong nucleating effect on PP. When 18 wt %  $TPE_g$  was added,  $T_c$  of PP was 118.5°C; when 30 wt %  $TPE_g^{-}$  was added,  $T_c$  of PP was 117.8°C, which was very close to that of pure PP. These results showed that a thick TPE<sub>g</sub> layer surrounded the PA-6 phase and reduced the nucleating effect of PA-6 to PP when more than 18 wt % TPE<sub>g</sub> was added. The thick TPE<sub>g</sub> layer isolated PA-6 from the PP matrix, prevented the migration of nuclei across the interface, or weakened the nucleating effect of PA-6 to PP.

It is well known that fractionated crystallization often occurs in PP/PA blends.<sup>22–26</sup> For semicrystalline polymers, primary nucleation is usually the rate-determining step. The crystal rapidly grows over the materials once it is nucleated. In blends with a well-dispersed minor component, if the number of dispersed particles is greater than the number of general active nucleating heterogeneities ( $A_1$ ) within the blends, the nucleation in the particles without  $A_1$  can only rely on another type of heterogeneity ( $A_2$ ), for which a lower  $T_c$  is needed, or the crystallization in these particles without  $A_1$  is retarded until a homoge-

TABLE IIIDynamic Mechanical Behavior of PP and PA-6in the PP/PA-6/TPEg Blends

|   |  | 0                            |                                   |                              |
|---|--|------------------------------|-----------------------------------|------------------------------|
| Sample  | Composition<br>(wt %)                    | T <sub>g</sub> of PP<br>(°C) | <i>T<sub>g</sub></i> of PA-6 (°C) | $\Delta T_g$ (°C)            |
| PP/PA-6<br>PP/PA-6/TPE <sub>g</sub><br>PP/PA-6/TPE <sub>g</sub><br>PP/PA-6/TPE <sub>g</sub> | 70/30<br>64/30/6<br>52/30/18<br>40/30/30 | 14.2<br>25.2<br>24.5<br>18.4 | 80.8<br>82.2<br>89.9<br>98.2      | 66.6<br>57.0<br>65.4<br>79.8 |

PP/PA-6/TPE

PP/PA-6/TPE

| TABLE IV<br>Dynamic Mechanical Behavior of PP and PA-6<br>in the PP/PA-6/TPE Blends |                       |                              |                    |                   |  |  |  |  |
|---|-----------------------|------------------------------|--------------------|-------------------|--|--|--|--|
| Sample  | Composition<br>(wt %) | T <sub>g</sub> of PP<br>(°C) | $T_g$ of PA-6 (°C) | $\Delta T_g$ (°C) |  |  |  |  |
| PP/PA-6<br>PP/PA-6/TPE  | 70/30<br>64/30/6      | 14.2<br>13.2                 | 80.8<br>73.3       | 66.6<br>60.2      |  |  |  |  |

9.8

9.1

69.3

75.8

59.5

66.8

52/30/18

40/30/30

neous nucleation begins, for which a further lower  $T_c$ is demanded. The crystallization of the minor component may, therefore, take place during several steps. Sometimes, the crystallization of the minor component occurs coincidently with the major component, and the crystallization peaks of PP and PA-6 overlap. In our PP/PA-6/TPE<sub>g</sub> blends, using TPE<sub>g</sub> led to a very fine dispersion of PA-6. The crystallization of the PA-6 phase was divided into several steps. The first crystallization occurred about 5°C lower than the usual  $T_c$  of pure PA-6. The decrease in  $T_c$  may have been due to the diluting effect of PP and TPE<sub>g</sub> in the blends or due to the restricted PA-6 chain mobility from the grafting reaction with TPE<sub>g</sub>. The second crystallization took place coincidently with the crystallization of the matrix PP, in which PP and PA-6 could have a mutual nucleating effect. When more than 18 wt % TPE<sub>g</sub> was added into the blends, the first crystallization was almost completely suppressed. Meanwhile, the crystallinity of PP increased dramatically, and this was partially due to the second step of crystallization of PA-6. These differential scanning calorimetry results agreed well with the microstructures of the blends revealed by SEM and could be applied to estimate the compatibilities of the blends. However, the melting behaviors of the different blends were almost the same, and so it was concluded that the total crystallinity of PA-6 was nearly not changed for blends with different TPE<sub>g</sub> contents and that PP and PA-6 crystallized separately.

The nonisothermal crystallization and melting data of PP/PA-6/TPE blends are listed in Table II. PA-6 improved the nucleation of PP.  $T_c$ , the crystallinity, and the crystallization heat increased as the PA content increases. TPE had no effect on the crystallization of PP. PP and TPE did not influence the crystallization behavior of PA-6. These findings agreed well with the isolated three-phase structure of the blends.

## **Dynamic mechanical properties**

The dynamic thermal mechanical properties are listed in Tables III and IV. Adding TPE<sub>g</sub> to the blend system raised the glass-transition temperatures  $(T_g's)$  of PP and PA-6. The physical or chemical interactions between PP, PA-6, and  $TPE_g$  at the interface reduced the mobility of PP and PA-6 and led to increases in  $T_{q}$ . Obviously, the interaction between TPE<sub>g</sub> and PA-6 was much stronger than that between PP and PA-6. The PA-6 chains reacted with TPEg, and this led to TPE<sub>g</sub>-grafted PA-6. The mobility of the PA-6 segments was significantly restricted. As a result,  $T_g$  of PA-6 was greatly improved. TPE had no strong interactions either with PP or with PA-6. TPE in the blend system increased the free volume of both PP and PA-6, producing a drop in  $T_g$ . Figure 9 shows the process pressure of the PP/PA-6/TPE<sub>g</sub> and PP/PA-6/TPE blends. When  $TPE_g$  was added, the grafting reactions between  $TPE_{g}$  and PA-6 and the entanglements between  $TPE_{g}$ and PP led to a higher viscosity, thus increasing the process pressure.

## Schematic model

On the basis of the aforementioned mechanical and thermal behaviors and the microstructures revealed by SEM, a schematic model for the  $PP/PA-6/TPE_g$ and PP/PA-6/TPE blends is presented in Scheme 1. For PP/PA-6/TPE<sub>g</sub>, TPE<sub>g</sub> had strong interactions with both PP and PA-6.  $TPE_g$  was located at the interface between PP and PA-6 as the interlayer. For samples with 30 wt % TPE<sub>g</sub> or more, most PA-6 reacted with  $TPE_g$  to form a dispersed phase. For the PP/PA-6/ TPE blend, TPE had no strong interactions with PP and PA-6. TPE formed an isolated phase in the PP matrix. These results agreed well with our initial intention to use the TPE<sub>g</sub> elastomer as an interlayer between PP and PA-6.

#### CONCLUSIONS

TPE<sub>g</sub>, an elastomer prepared and used in a former study, could greatly toughen PA-6. In this study, we

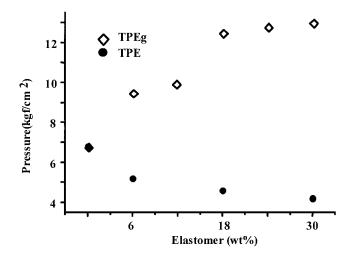
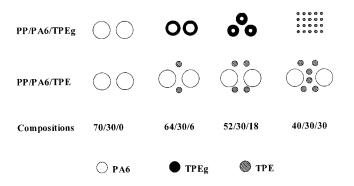


Figure 9 Processing pressure of PP/PA-6/TPE<sub>g</sub> blends with various elastomer contents (all blends had 30 wt % PA-6).



Scheme 1 Schematic microstructures for  $PP/PA-6/TPE_g$  and PP/PA-6/TPE blends.

used TPE<sub>g</sub> to improve the compatibility of PP and PA-6.  $TPE_g$  could greatly improve the toughness but only slightly reduced the tensile strength and modulus of PP/PA-6 blends when 15 wt % TPE<sub>g</sub> was added. The TPE<sub>g</sub>/PA-6 ratio influenced the interfacial structure and adhesion. SEM micrographs showed that TPE<sub>g</sub> was located at the interface of PP and PA-6 in the  $PP/PA-6/TPE_{o}$  blends, whereas for the PP/PA-6/TPEblends, a three-phase structure was formed.  $T_c$  and the rate of PP in the  $\ensuremath{\text{PP/PA-6/TPE}_g}$  blends increased with the PA-6 component because of the nucleating effect. For the minor phase PA-6, a two-step crystallization was detected. The first crystallization occurred at a temperature lower than  $T_c$  of pure PA-6 because of the dilute effect of PP and TPE<sub>g</sub> or the reduced mobility of PA-6 chains resulting from the grafting reaction. The second crystallization happened coincidently with the crystallization of PP. The strong interactions between PP, PA-6, and TPE<sub>g</sub> at the interface reduced  $T_g$  of PP and PA-6. These results show that using soft elastomers as interfacial layers between rigid components

is an effective way of preparing high-quality materials.

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