

# Polypropylene/Polypropylene-Grafted Acrylic Acid Copolymer/Ethylene–Acrylic Acid Copolymer Ternary Blends for Hydrophilic Polypropylene

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**ABSTRACT:** Ternary blends of polypropylene (PP), a polypropylene-grafted acrylic acid copolymer (PP-g-AA), and an ethylene–acrylic acid copolymer (EAA) were prepared by melt blending. The surfaces of films with different contents of these three components were characterized with contact-angle measurements. Scanning electron microscopy, Fourier transform infrared spectroscopy, differential scanning calorimetry, and thermogravimetric analysis were used to characterize the microstructure, melting and crystalline behavior, and thermal stability of the blends. The contact angles of the PP/PP-g-AA blends decreased monotonically with increasing PP-g-AA content. With the incorporation of EAA, the contact angles of the PP/PP-g-AA/EAA ternary blends decreased with increasing EAA content. When the

concentration of EAA was higher than 15 wt %, the contact angles of the ternary blends began to increase. Scanning electron microscopy observations confirmed that PP-g-AA acted as a compatibilizer and improved the compatibility between PP and EAA in the ternary blends. Differential scanning calorimetry analysis suggested that acrylic acid moieties could act as nucleating agents for PP in the polymer blends. Thermogravimetric analysis and differential thermogravimetry confirmed the optimal blend ratio for the PP/PP-g-AA/EAA ternary blends was 70/15/15. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 436–442, 2006

**Key words:** blends; hydrophilic polymers; poly(propylene) (PP)

## INTRODUCTION

Polypropylene (PP) is widely used for its low cost and versatile properties. However, a lack of reactive sites, difficulty in dyeing, and poor hydrophilicity limit its further application. To overcome these problems, it is necessary to introduce some polar groups into PP with a convenient modification method. Some techniques, such as chemical modification, additives, and physical treatment, have been developed.<sup>1–3</sup> On the basis of these techniques, blending PP in bulk with some polar polymers is one of the most frequently used modification methods.<sup>4–6</sup> Examples of blending PP to improve its properties include the following: PP blended with Novolak phenolic resin to raise the surface free energy of PP was studied by Son et al.,<sup>6</sup> PP/poly(ethylene glycol) blends were investigated by Mathiowitz et al.,<sup>7</sup> and PP/ethylene–acrylic acid copolymer (EAA) blends were studied by Novak and Florian.<sup>8</sup> The mod-

ification of the surface free energy of PP would lead to an improvement in the hydrophilicity of PP. An improvement in the hydrophilicity of PP was confirmed by investigations of PP/phenoxy blends<sup>9</sup> and PP/poly(ethylene-co-vinyl alcohol) blends.<sup>10</sup>

In this study, PP was blended with a polypropylene-grafted acrylic acid copolymer (PP-g-AA) and EAA. All the studied blends consisted of 70 wt % PP and a total of 30 wt % PP-g-AA and EAA in the ternary blends. The concentration of PP-g-AA was varied from 0 to 30 wt %, and that of EAA was varied from 30 to 0 wt %. The change in the surface properties was studied with the contact-angle test. The general properties of these blends, such as the chemical structure, morphology, and thermal properties, were also analyzed.

## EXPERIMENTAL

### Materials

The PPs used in this work were PP F401 particles and S700 powder (Yangzi Petrochemical Co., Nanjing, China) with melt flow rates of 2.3 and 14.2 g 10 min<sup>-1</sup>, respectively. The former was used as the matrix of the blends, and the latter was modified by acrylic acid (AA) via solid-phase grafting polymerization in the

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laboratory. The grafting degree of PP-g-AA was 0.85 wt %, as determined by acid–base titration. EAA Primacor 3002 (Dow Chemical Co., Midland, MI) contained 8 wt % AA and had a melt flow rate of 9.8 g 10 min<sup>-1</sup>. Distilled water and analytical-grade diiodomethane with surface tensions of 72.8 and 50.8 mN/m, respectively, were used as interface liquids for the contact-angle measurements.

### Melt blending and specimen preparation

The PP/PP-g-AA/EAA ternary blends were prepared via melt blending with a two-roll mixing mill operating at 170°C. PP particles were drawn into the gap of the two rollers, which made relative rotations at different velocities. PP-g-AA and EAA particles were added in turn when the PP particles were completely melted.

The film samples for contact-angle measurements and Fourier transform infrared (FTIR) spectra were prepared by compression molding at 180°C.

### Contact-angle test for polarity

The contact angles of distilled water and diiodomethane on the blends were measured with a Ramé-Hart goniometer (Ramé-Hart Instrument Co., Netcong, NJ). These samples were rinsed with acetone before the measurement of the contact angles. Each contact angle was an average of at least five droplets (2 μL) at different regions of the same piece of film taken at room temperature.

### Analysis of the chemical structure

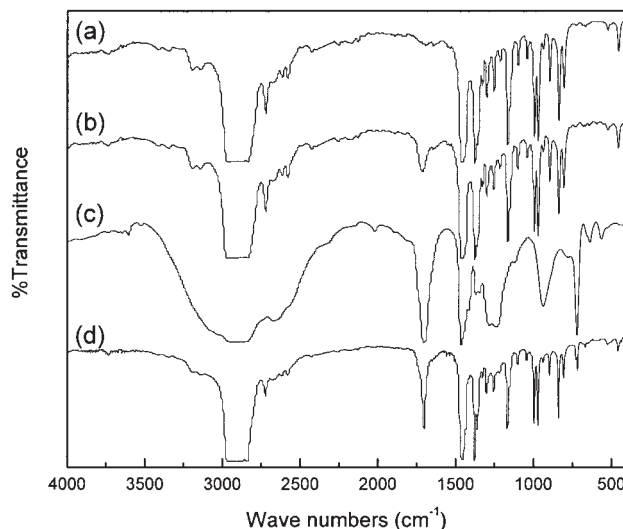
The chemical composition of the film surface was investigated by FTIR with a Nexus 670 spectrometer (ThermoElectron Corp., Waltham, MA).

### Morphological observation

The blend samples were fractured after cooling in liquid nitrogen. The cross sections were gold-coated and observed with an SX-40 scanning electron microscope (KASH, Japan).

### Thermal behavior

The melting and crystallization behavior of the samples was studied with differential scanning calorimetry (DSC) measurements taken with a PerkinElmer DSC-7C thermal analyzer (PerkinElmer Inc., Wellesley, MA) in a nitrogen atmosphere with 10°C/min heating and cooling rates. Samples of about 10 mg were heated from 30 to 220°C and then held for 3 min. The nonisothermal crystallization process was recorded from 220 to 50°C, and this was followed by



**Figure 1** FTIR spectra of (a) PP F401, (b) PP-g-AA (grafting degree = 0.85%), (c) EAA 3002, and (d) a PP/PP-g-AA/EAA (70/15/15) blend.

heating from 50 to 220°C for the second heating run. The crystallization and melting parameters were obtained from the cooling and reheating scans. The relative crystallinity ( $X_c$ ) of the samples was calculated with the following expression:

$$X_c = \frac{\Delta H_f}{\Delta H_f^*} \times 100\%$$

where  $\Delta H_f^*$  is the heat of fusion of the 100% crystalline polymer (PP or EAA) and  $\Delta H_f$  is the heat of fusion of the polymer in the blends. The values of  $\Delta H_f^*$  for PP and EAA were 209.0 and 293.0 J/g, respectively.<sup>11</sup>

Thermogravimetric analysis (TGA) was performed with an STA 449C/6/F (Netzsch, Germany) on samples of about 10 mg in a temperature range of 40–500°C at 10°C/min under a nitrogen flow of 30 mL/min.

## RESULTS AND DISCUSSION

### Chemical structure of the PP/PP-g-AA/EAA ternary blend

FTIR spectra of the PP/PP-g-AA/EAA (70/15/15) blend and its pure components are summarized in Figure 1. Peaks at 1713 cm<sup>-1</sup>, which were attributed to C=O stretching of AA,<sup>12</sup> appeared for PP-g-AA, EAA, and the blends. Although the spectra of the PP film showed almost no peak at 1713 cm<sup>-1</sup>, EAA showed a peak at 720 cm<sup>-1</sup>, which was related to the (CH<sub>2</sub>)<sub>n</sub> (*n* > 3) sway vibration. In comparison with the three pure components, PP, PP-g-AA, and EAA, there was no extraordinary peak from the blends. It was suggested that no chemical reaction occurred between PP,

TABLE I  
Contact Angles of Distilled Water and Diiodomethane  
on PP, PP-g-AA, and EAA

Sample	Contact angle (°)	
	Distilled water	Diiodomethane
PP F401	92.3	57.9
PP S700	90.0	—
PP-g-AA (GD = 0.85 wt %)	81.7	51.1
EAA 3002	76.5	49.7

GD, grafting degree.

EAA, and PP-g-AA during the process of melt blending.

#### Determining the contact angles of the PP/PP-g-AA/EAA blends

The contact angles on distilled water and diiodomethane of PP F401, PP-g-AA, and EAA are listed in Table I. To investigate the influence of the graft comonomer on the contact angle of PP, the data for PP(S700) used for graft modification are also listed. The contact angles of PP-g-AA considerably decreased in comparison with those of pure PP, and this was attributed to the incorporation of AA. In the case of EAA, the high content of AA led to a further decrease in the contact angle. The decrease in the contact angles indicated an improvement in the hydrophilicity of the polymer.

The contact angles of water on the surfaces of the PP/PP-g-AA blends are shown in Figure 2. The contact angles of the PP/PP-g-AA blends decreased monotonically with increasing PP-g-AA content. This result suggested that the surface polarity of the PP/PP-g-AA blend was augmented by the increase in the

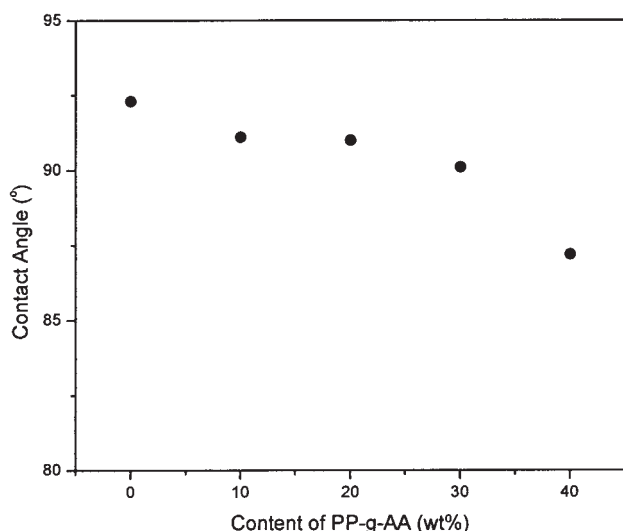


Figure 2 Contact angles of water on films of PP/PP-g-AA blends versus the contents of PP-g-AA.

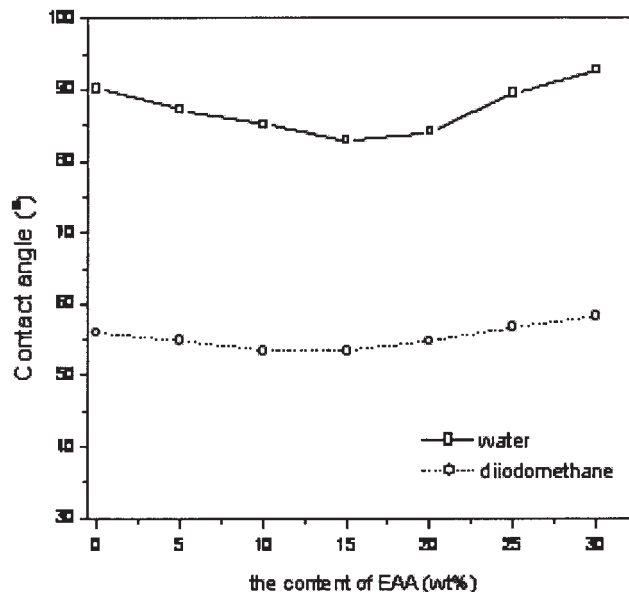


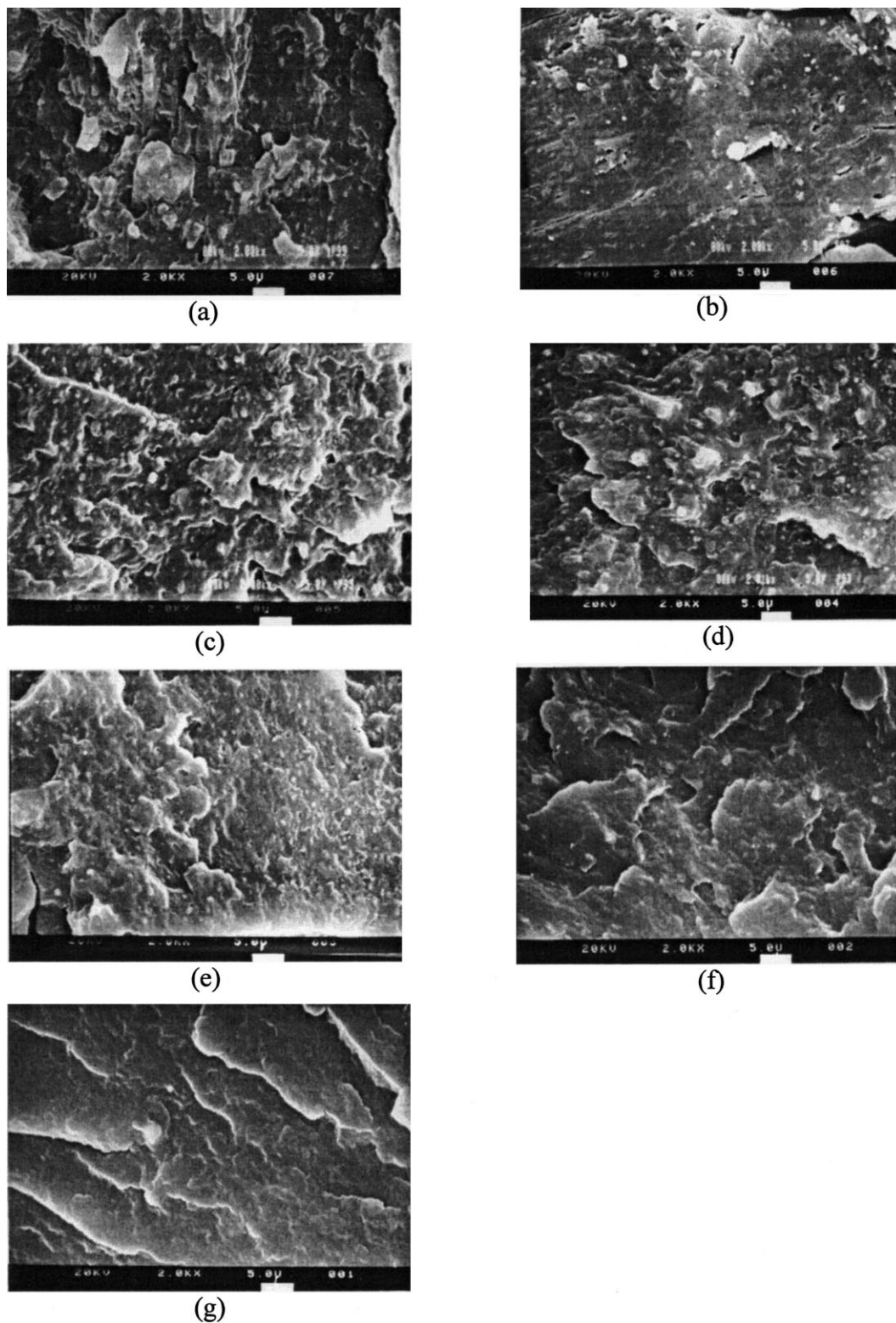
Figure 3 Contact angles of water and diiodomethane on films of PP/PP-g-AA/EAA blends versus the contents of EAA.

proportion of AA. Moreover, when the concentration of PP-g-AA reached 40%, the lowest contact degree was obtained, 87.0°, which was only 5° lower than that of pure PP. This might be attributed to the low grafting degree of PP-g-AA.

To make a further improvement in the hydrophilicity of the PP/PP-g-AA blends, PP-g-AA was partially replaced with EAA. The dependence of the contact angles of PP/PP-g-AA/EAA ternary blends on the concentration of EAA is shown in Figure 3. When the concentration of EAA was lower than 15 wt %, the contact angles of the ternary blends decreased with increasing EAA content. However, when the concentration of EAA was higher than 15 wt %, a further increase in the EAA concentration led to an increase in the contact angles of the ternary blends. The contact angles of the ternary blends on water and diiodomethane possessed a similar tendency, and the influence of EAA on the contact angles of the ternary blends was more obvious in the case of diiodomethane.

The decrease in the contact angles of the ternary blends with increasing EAA content could be attributed to the higher concentration of AA in EAA. This was consistent with the influence of PP-g-AA on the contact angles. The influence of EAA on the contact angles of the ternary blends was more effective than that of PP-g-AA because of the difference in the AA concentrations between EAA and PP-g-AA. Therefore, the incorporation of EAA into the ternary blends resulted in a considerable improvement in the surface polarity and hydrophilicity of PP. However, a further increase in the EAA concentration did not lead to a further decrease in the contact angles. This might be

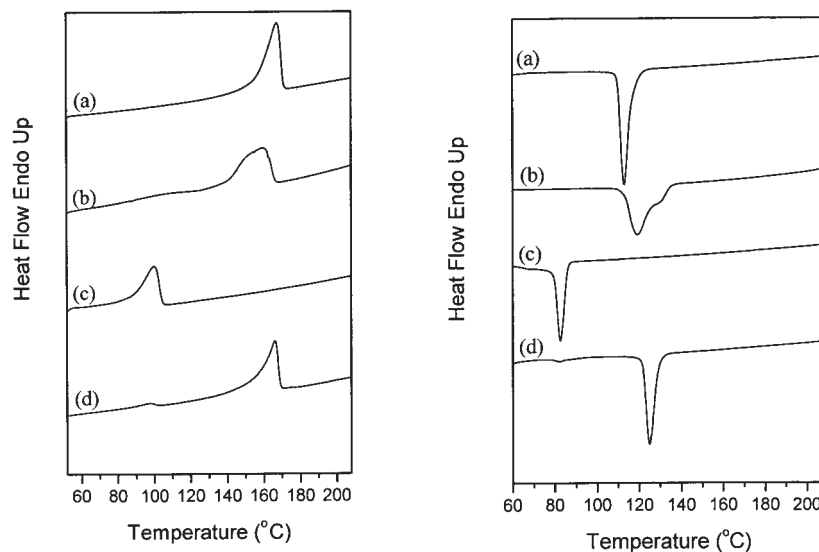




**Figure 4** SEM photographs of fracture surfaces of PP/PP-g-AA/EAA blends of different proportions (2000 $\times$ ): (a) 70/0/30, (b) 70/5/25, (c) 70/10/20, (d) 70/15/15, (e) 70/20/10, (f) 70/25/5, and (g) 70/30/0.

attributed to the influence of poor compatibility between EAA and PP. Because PP and EAA were immiscible, PP-g-AA acted as a compatibilizer for PP and EAA in the ternary blends. The increase in the EAA

concentration meant a decrease in the PP-g-AA concentration, which resulted in a weakened effect on the compatibility of the ternary blends. The poor compatibility between PP and EAA blocked the migration of



**Figure 5** DSC melting and crystallization behavior of (a) PP F401, (b) PP-g-AA (GD = 0.85%), (c) EAA 3002, and (d) 70/15/15 PP/PP-g-AA/EAA.

EAA chains to the surface during the preparation of the films and consequently weakened the surface polarity of the films.<sup>13</sup> When the concentration of EAA reached 30 wt %, the contact angle of the PP/EAA blends was even higher than that of PP/PP-g-AA blends. The result suggested the strong influence of the compatibility on the hydrophilicity of the polymer blends.

### Morphological observation

Figure 4 shows the morphology of the fracture surfaces of PP/PP-g-AA/EAA ternary blends with 70 wt % PP. Scanning electron microscopy (SEM) analysis revealed a two-phase morphology with the polydispersity of a binary PP/EAA (70/30) blend [Fig. 4(a)] with spherical EAA particles in the PP matrix as a result of high interfacial tension and coalescence, and

the interface boundary was sharp. With the addition of PP-g-AA to replace the EAA in the blend, the phase morphology changed, and the surface boundary disappeared gradually. A more uniform particle size distribution was obtained when the PP-g-AA concentration was more than 20 wt %. As shown in Figure 4(g), PP and PP-g-AA were perfectly compatible. It was confirmed that PP-g-AA acted as a compatibilizer and improved the compatibility between PP and EAA in the ternary blends.

### Analysis of the thermal behavior in the PP/PP-g-AA/EAA ternary blend

The thermal behaviors of the blends at heating and at cooling are shown in Figure 5, and the data from DSC analysis are summarized in Tables II and III. The melting temperatures of PP, PP-g-AA, and EAA were

**TABLE II**  
DSC Melting Results of PP, PP-g-AA, EAA, and Their Binary and Ternary Blends with 70 wt % PP

Sample	$T_{m,EAA}^{on}$ (°C)	$T_{m,EAA}^p$ (°C)	$\Delta H_{m,EAA}$ (J/g)	$X_{c,EAA}$ (%)	$T_{m,PP}^{on}$ (°C)	$T_{m,PP}^p$ (°C)	$\Delta H_{m,PP}$ (J/g)	$X_{c,PP}$ (%)
PP F401	—	—	—	—	156.0	167.4	88.1	42.1
PP-g-AA (GD = 0.85 wt %)	—	—	—	—	139.6	159.4	66.1	31.6
EAA 3002	87.2	100.1	55.1	18.8	—	—	—	—
PP/PP-g-AA/EAA								
70/0/30	87.4	98.2	11.1	12.6	154.5	167.0	74.2	50.7
70/5/25	86.1	98.2	8.4	11.4	154.3	167.2	77.5	49.4
70/10/20	82.9	97.8	5.7	9.7	157.0	167.2	75.9	45.4
70/15/15	85.9	97.2	4.4	10.0	156.9	166.2	78.4	44.1
70/20/10	—	—	—	—	157.5	166.0	77.6	41.2
70/25/5	—	—	—	—	152.5	166.2	88.9	44.8
70/30/0	—	—	—	—	153.8	166.0	92.2	44.1

$T$ , temperature;  $\Delta H$ , specific enthalpy;  $m$ , melting;  $on$ , onset;  $p$ , peak;

TABLE III  
DSC Crystallization Results of PP, PP-g-AA, EAA, and Their Binary and Ternary Blends with 70 wt % PP

Sample	$T_{c,PP}^{on}$ (°C)	$T_{c,PP}^p$ (°C)	$\Delta T_{PP}$ (°C)	$\Delta H_{c,PP}$ (J/g)	$T_{c,EAA}^{on}$ (°C)	$T_{c,EAA}^p$ (°C)	$\Delta T_{EAA}$ (°C)	$\Delta H_{c,EAA}$ (J/g)
PP	116.9	113.0	54.4	-95.7	—	—	—	—
PP-g-AA (GD = 0.85 wt %)	128.2	119.3	40.1	-83.0	—	—	—	—
EAA	—	—	—	—	85.9	82.6	17.5	-49.6
PP/PP-g-AA/EAA								
70/0/30	122.7	118.9	48.1	-68.7	86.7	83.4	14.8	-9.3
70/5/25	128.6	123.9	43.3	-76.4	85.6	82.0	16.2	-7.1
70/10/20	128.5	123.9	43.3	-78.8	85.6	81.5	16.3	-5.7
70/15/15	128.9	125.0	41.2	-82.4	86.5	82.2	15.0	-3.6
70/20/10	129.9	126.3	39.7	-88.7	—	—	—	—
70/25/5	130.9	126.6	39.6	-91.9	—	—	—	—
70/30/0	131.1	127.2	38.8	-95.1	—	—	—	—

$T$ , temperature;  $\Delta T$ ,  $T_m - T_c$ ;  $\Delta H$ , specific enthalpy;  $c$ , cooling;  $on$ , onset,  $p$ , peak.

167.4, 159.4, and 100.1°C, respectively. When PP and EAA were blended at a weight ratio of 70/30, two peaks were observed in the melting curve. The lower peak obviously corresponded to the melting of EAA, whereas the higher one corresponded to the melting of PP. Because the melting temperatures of EAA and PP in PP/EAA blends showed little difference in comparison with those in the pure state, the two polymers could in general be considered immiscible. The change in the PP-g-AA content and EAA content had little influence on the melting temperature of PP in the ternary blends with respect to that of pure PP. When the concentration of EAA decreased less than 20% and that of PP-g-AA increased more than 10%, the melting peak of the EAA moiety of the blend was hard to observe.

The results of the crystallinity assessed from the DSC profiles are listed in Table III. The crystallinity of PP in the ternary blends was higher than that of the neat polymer. The result indicated that AA moieties

acted as nucleating agents for PP in the polymer blends.<sup>13</sup> With an increase in the PP-g-AA concentration and a decrease in the EAA concentration, the onset and peak temperatures of PP increased.

The curves of TGA and differential thermogravimetry (DTG) of the PP/PP-g-AA/EAA (70/15/15) ternary blend and the three pure components are shown in Figure 6. The TGA curves of other blends (not shown in Fig. 6) presented a profile so similar to that of the 70/15/15 PP/PP-g-AA/EAA blend that it was hard to differentiate one curve from another. The thermal stability of the blends was characterized in terms of the temperatures of 5, 10, and 50% degradation. From the data summarized in Table IV, it could be concluded that there were few difference between PP-g-AA and EAA, especially when the temperature was higher than 440°C. The thermal stability of PP-g-AA was better than that of PP. The grafting of AA onto the PP chain resulted in the improvement of the thermal stability of PP. The results indicated that the weight proportions of EAA and PP-g-AA had little influence

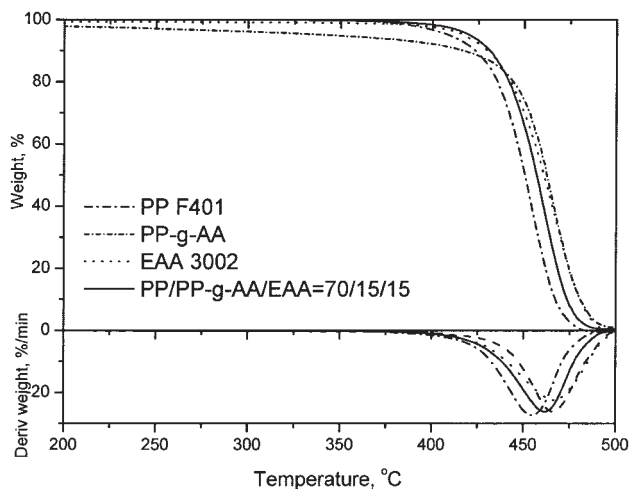


Figure 6 TGA and DTG curves of a 70/15/15 PP/PP-g-AA/EAA ternary blend and three pure components.

TABLE IV  
TGA and DTG Data of PP, PP-g-AA, EAA, and Their Binary and Ternary Blends with 70 wt % PP

Sample	TGA (°C)			DTG (°C)
	$T_{5\%}$	$T_{10\%}$	$T_{50\%}$	
PP	408.8	423.2	450.4	453.1
PP-g-AA (GD = 0.85 wt %)	345.0	417.3	462.3	464.1
EAA	417.2	430.0	460.7	465.1
PP/PP-g-AA/EAA				
70/0/30	414.2	425.5	452.1	456.7
70/5/25	417.1	427.6	454.1	456.6
70/10/20	417.0	428.9	456.1	460.1
70/15/15	420.3	431.2	456.8	462.0
70/20/10	412.4	427.9	457.0	461.1
70/25/5	368.0	417.9	455.1	462.2
70/30/0	391.0	416.9	451.5	458.0

$T_{5\%}$ , temperature of 5% degradation;  $T_{10\%}$ , temperature of 10% degradation;  $T_{50\%}$ , temperature of 50% degradation.

on the thermal stability of the ternary blends. Even then, this inappreciable variation could be more clearly understood from the differential thermograms, shown in Figure 5, and the DTG peak temperatures, listed in Table IV. On the basis of the DTG temperatures, the optimal blend ratio for the ternary blends was 70/15/15 PP/PP-g-AA/EAA.

### CONCLUSIONS

To improve the hydrophilicity of PP, PP-g-AA and EAA were melt-blended with PP. FTIR results confirmed that no chemical reaction occurred between PP, EAA, and PP-g-AA during the process of melt blending. The contact angles of the PP/PP-g-AA blends decreased monotonically with increasing PP-g-AA content. However, because of the low grafting degree, the influence of PP-g-AA on the hydrophilicity of PP was quite limited. With the incorporation of EAA, the contact angles of the PP/PP-g-AA/EAA ternary blends decreased with increasing EAA content. When the concentration of EAA was higher than 15 wt %, the contact angles of the ternary blends began to increase. The SEM observations confirmed that PP-g-AA acted as a compatibilizer and improved the compatibility between PP and EAA in the ternary blends. The DSC analysis suggested that the change in the PP-g-AA content and EAA content had little influence on the

melting temperature of PP in the ternary blends. It was also found that AA moieties could act as nucleating agents for PP in the polymer blends. The TGA and DTG analysis confirmed that the optimal blend ratio for the PP/PP-g-AA/EAA ternary blends was 70/15/15.

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