Morphology, Thermal Behavior, and Mechanical Properties of PA1010/PP and PA1010/PP-*g*-GMA Blends

XIAOMIN ZHANG, XING LIN LI, DONGMEI WANG, ZHIHUI YIN, JINGHUA YIN

Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

ABSTRACT: The modification of polypropylene (PP) was accomplished by melt grafting glycidyl methacrylate (GMA) on its molecular chains. The resulting PP-*g*-GMA was used to prepare binary blends of polyamide 1010 (PA1010) and PP-*g*-GMA. Different blend morphologies were observed by scanning electron microscopy (SEM) according to the nature and content of PA1010 used. Comparing the PA1010/PP-*g*-GMA and PA1010/PP binary blends, the size of the domains of PP-*g*-GMA were much smaller than that of PP at the same compositions. It was found that mechanical properties of PA1010/PP-*g*-GMA blends were obviously better than that of PA1010/PP blends, and the mechanical properties were significantly influenced by wetting conditions for uncompatibilized and compatibilized blends. A different dependence of the flexural modulus on water was found for PA1010/PP and PA1010/PP-*g*-GMA. These behaviors could be attributed to the chemical interactions between the two components and good dispersion in PA1010/PP-*g*-GMA blends. Thermal and rheological analyses were performed to confirm the possible chemical reactions taking place during the blending process. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1489–1498, 1997

Key words: polypropylene; glycidyl methacrylate; polyamide

INTRODUCTION

Multicomponent polymeric materials are frequently prepared by blending two or more polymers. It is very difficult to obtain good dispersion in polymer blends, particularly for combinations of polar and nonpolar polymers. Due to their difference of polarity, the system usually separates into two distinct phases. The major component forms a matrix and the minor component forms domains. The size and shape of the domains greatly depends upon several factors: melt viscosities of the components, interfacial tension and adhesion, processing condition, etc. Satisfactory physicomechanical properties critically depend upon the proper interfacial tension to generate a small phase size and strong interfacial adhesion to transmit force effectively between the two phases.[1] Methods to reduce interfacial tension and improve phase adhesion between immiscible components have been investigated and developed in the past two decades. Many articles[2–4] reported that the presence of a block or graft copolymer with appropriate chemical structure could provide lowering of the interfacial energy and improvement of the interfacial adhesion between two phases. Therefore, a small domain size and homogenous distribution of domains may be formed in these blending systems.

Polyolefins are often used to blend with polyamides (PAs) and polyesters to prepare blends and alloys with a combination of properties unattainable in any single polymer. Functionalized polyolefins are popular compatibilizers for these blending systems. Previous studies have shown
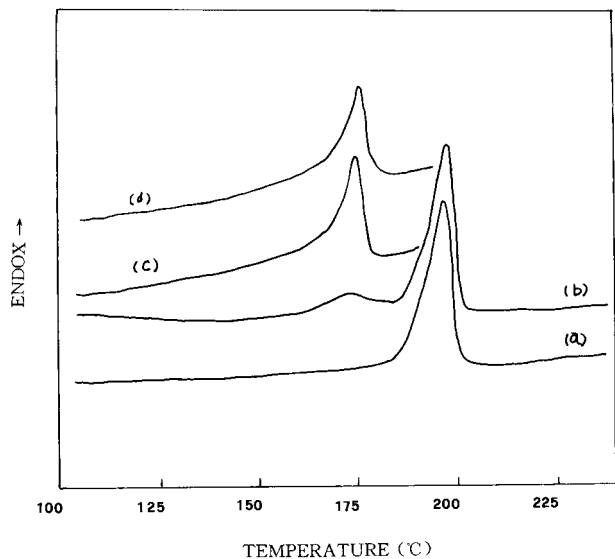
Figure 1 DSC thermograms of xylene extracted samples: (a) PA1010/PP (85/15), (b) PA1010/PP-*g*-GMA (85/15), (c) PP, (d) PP-*g*-GMA.

that ethylene–propylene grafted with maleic anhydride (EP-*g*-MAH) and polypropylene-*g*-MAH (PP-*g*-MAH) are effective compatibilizers for EP/PA6 and PP/PA6 blends.[5–10] Compatibilization is considered to occur through chemical linkage of the anhydride on the compatibilizer chain and end groups of PA6. The grafted copolymers preferentially reside at the interface and improve interfacial adhesion through chemical linkage across the interface. Some authors also modified PP with acrylic acid. This kind of grafted PP has been used to compatibilize PP/PA blends.[9]

As mentioned in the above paragraph, considerable research and development efforts have focused on polyolefin compatibilizers grafted with MAH.

In recent years, because of their versatile applications in many blending systems,[11–16] polyolefin compatibilizers with grafted glycidyl methacrylate (GMA) are becoming very important.
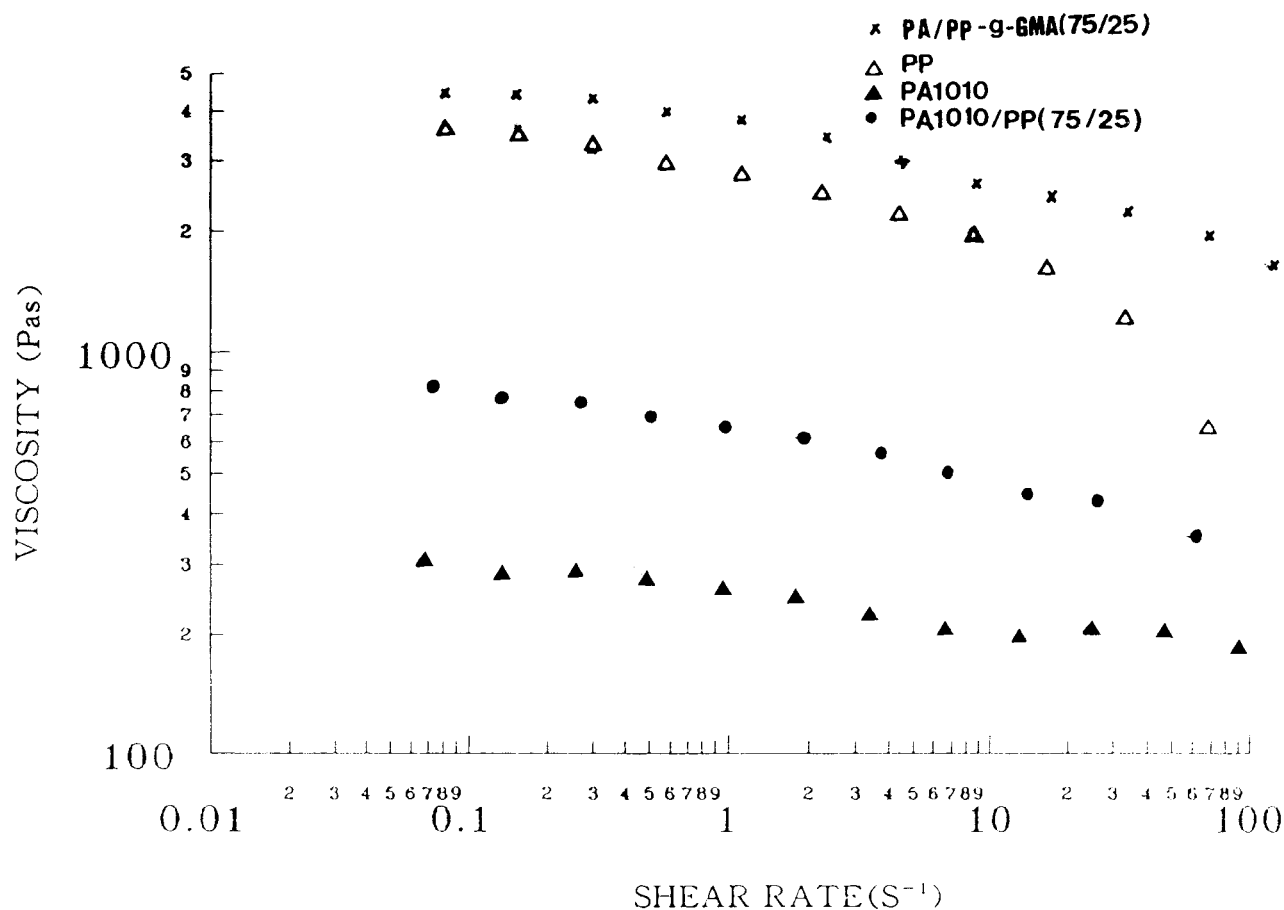
Figure 2 Apparent viscosities of PA1010/PP(PP-*g*-GMA) blends as a function of polymer contents and shear rate at 210°C.
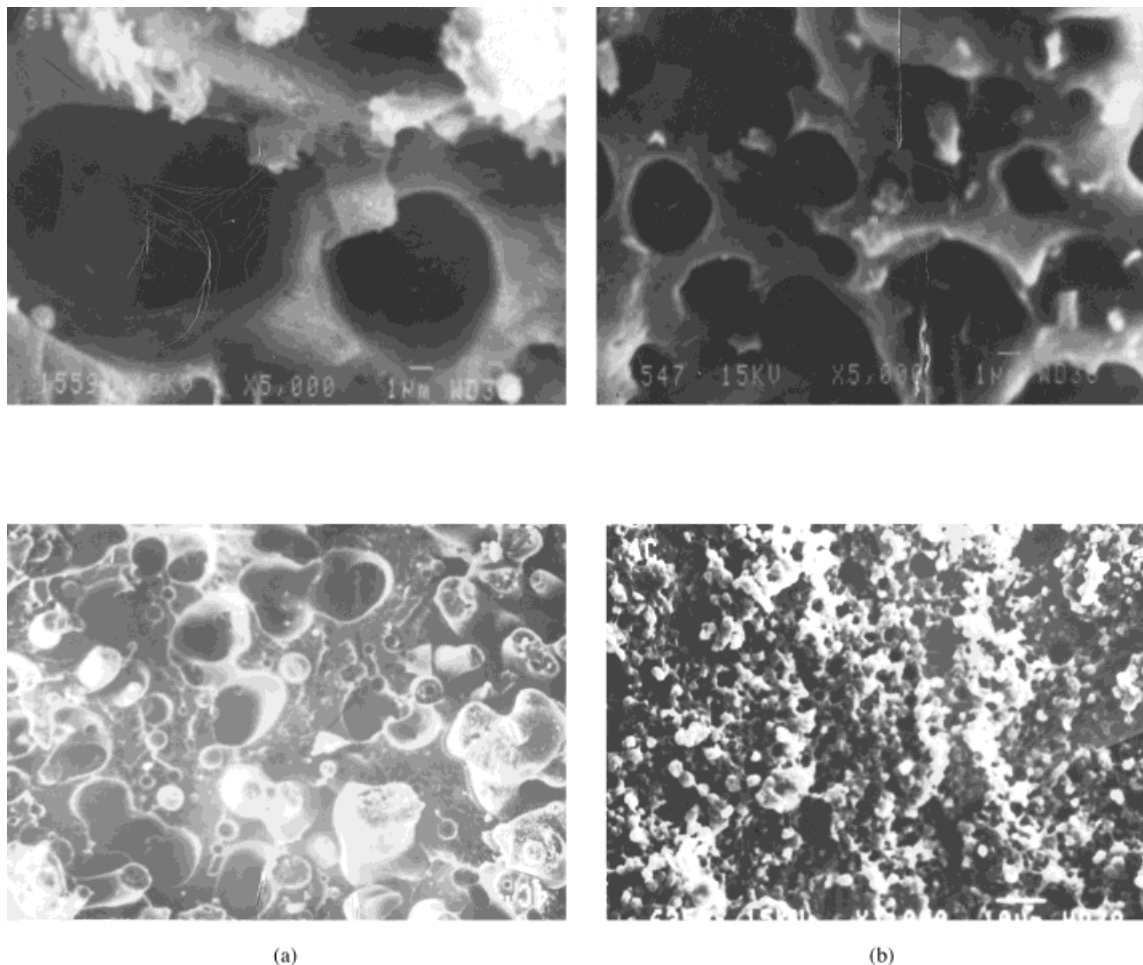
Figure 3 SEM micrographs of PA1010/PP and PA1010/PP-*g*-GMA blends with compositions of: (a) PA1010/PP (85/15 wt/wt), (b) PA1010/PP-*g*-GMA (85/15 wt/wt), (c) PA1010/PP (75/25 wt/wt), (d) PA1010/PP-*g*-GMA (75/25 wt/wt), (e) PA1010/PP (65/35 wt/wt), (f) PA1010/PP-*g*-GMA (65/35 wt/wt), (g) PA1010/PP (55/45 wt/wt), (h) PA1010/PP-*g*-GMA (55/45 wt/wt).

In our previous publication[16] the preparation and characterization of EP-*g*-GMA was reported. The main purpose of this work was to study the morphologies and thermal, mechanical, and rheological properties of PA1010/PP and PA1010/PP-*g*-GMA blends. In particular PA1010 rich blends were investigated.

EXPERIMENTAL

Materials

PA1010 was purchased from JiLin ShiJingGou Union Chemical Co. (China). Its relative viscosity is 2.1 and melting index is 10 g/10 min. The PP was supplied by LiaoNing PanJin Gas Chemical Co. (China) with a melting index 1.0 g/10 min.

PP-*g*-GMA was prepared by reaction extruding initiated by dicumyl peroxide (DCP) as reported in a previous article.[16] The content of GMA in PP-*g*-GMA used in this work was 0.57% (in weight). The grafting degrees were determined by the chemical titration method.[16]

Preparation of PA1010/PP-*g*-GMA and PA1010/PP Blends

Binary PA1010/PP-*g*-GMA and PA/PP blends were prepared by melt mixing the polymers in a

(c)

(d)
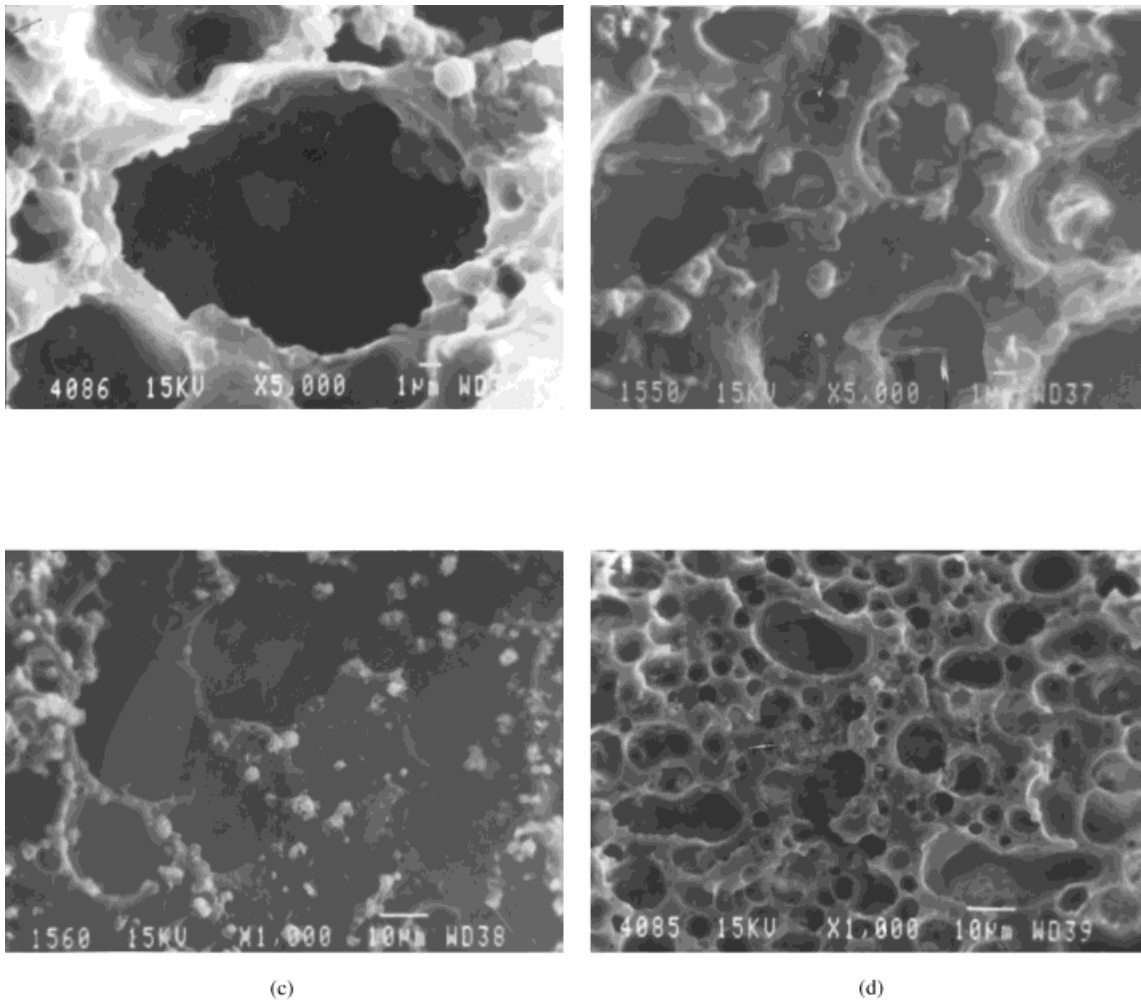
Figure 3   (*Continued from the previous page*)

Brabender single-screw extruder ($L/D = 20$) at 195–210°C and a residence time of 2.5 min. Compositions of PA/PP (or PP-*g*-GMA) had weight ratios of 95/5, 85/15, 75/25, 65/35, and 55/45. Testing specimens for mechanical properties were prepared by using a JSWF17SA injector with a barrel temperature of 195–210°C and injection pressure of 60 MPa.

Measurements of Mechanical Properties

Measurements of tensile properties of specimens were performed by means of an Instron 1121 on the basis of ISO/R527-1966E. Measurements of flexural modulus and strength were also performed with an Instron 1121 on the basis of ISO178-1975E. Izod impact strength tests were carried out with an XJU-22 impact testing machine (ISO/R180-1961). Dried specimens were prepared in a vacuum oven at 80°C for 12 h, and the wet specimens were obtained by keeping them in water for 12 h at room temperature.

Morphological Observation

A scanning electron microscope (JXA-840) was used to observe the morphologies of the blends. Before observation the samples were etched with xylene for 6 h to increase the contrast.

Thermal Analysis

The thermal behavior of blending samples was determined on a Perkin–Elmer DSC II. The fusion thermogram was obtained from 50 to 250°C at a heating rate of 10°C/min. All measurements

(e)

(f)
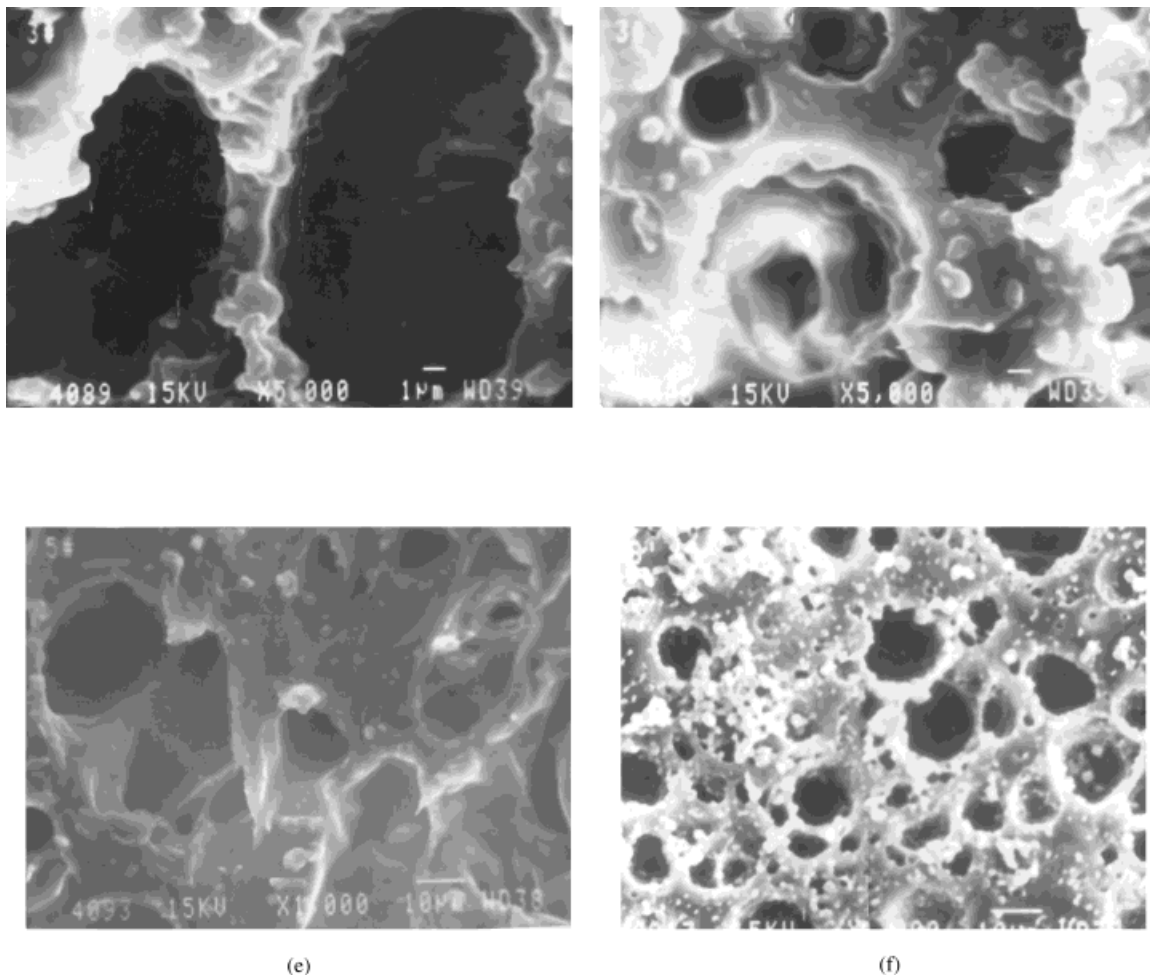
Figure 3   (*Continued from the previous page*)

were performed under a nitrogen atmosphere. Samples used for DSC experiments were extracted with xylene to remove the PP component from related binary blends.

Rheological Properties

Melt viscosities of the blends were measured at 210°C with a cone–plate viscometer (Contraves Rheomat 120). The diameter of the cone–plate was 20 mm and the cone angle was 0.5°. The thickness of testing specimens obtained by using a molding method was about 0.2 mm. Experiments were carried out under nitrogen atmosphere.

Experiments of Water Absorption

The samples were added to a vacuum oven at 80°C for 12 h. After weighing the same samples were put into water at room temperature for 12 h. The rate of water absorption was obtained by dividing the weight of the dried samples with the difference of the wet and dried samples.

RESULTS AND DISCUSSION

Thermal and Rheological Properties

Thermograms of PA1010/PP and PA1010/PP-*g*-GMA blends after extraction with xylene are shown in Figure 1. In the thermogram (a) that corresponds to the extracted residue of PA1010/PP, only one peak of fusion at nearly 199.7°C appeared. This peak can be attributed to PA1010, because PP was extracted by xylene from the PA1010/PP blend. However, two peaks can be observed in the thermogram (b) of the extracted residue of PA1010/PP-*g*-GMA. The peak at 199.7°C is attributed to PA1010. The other peak at 169°C
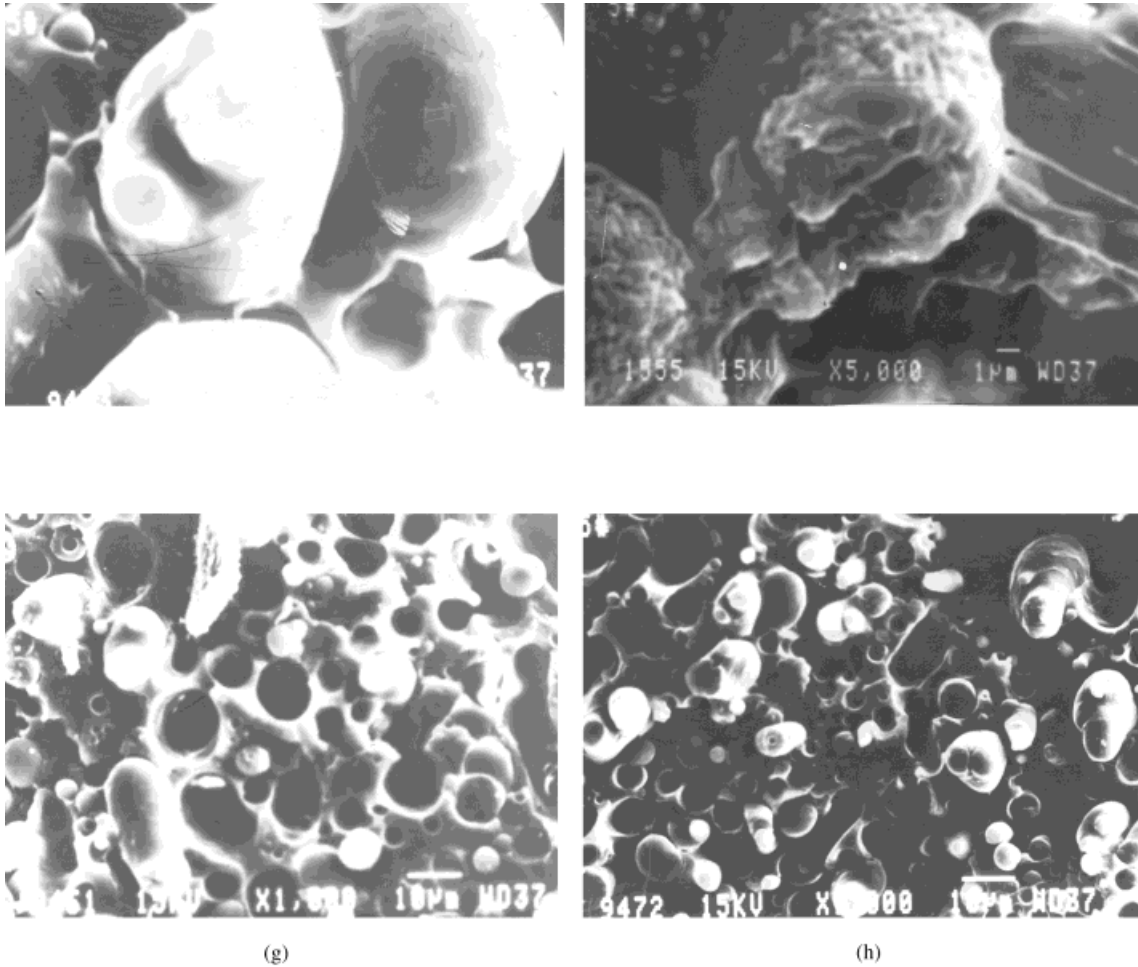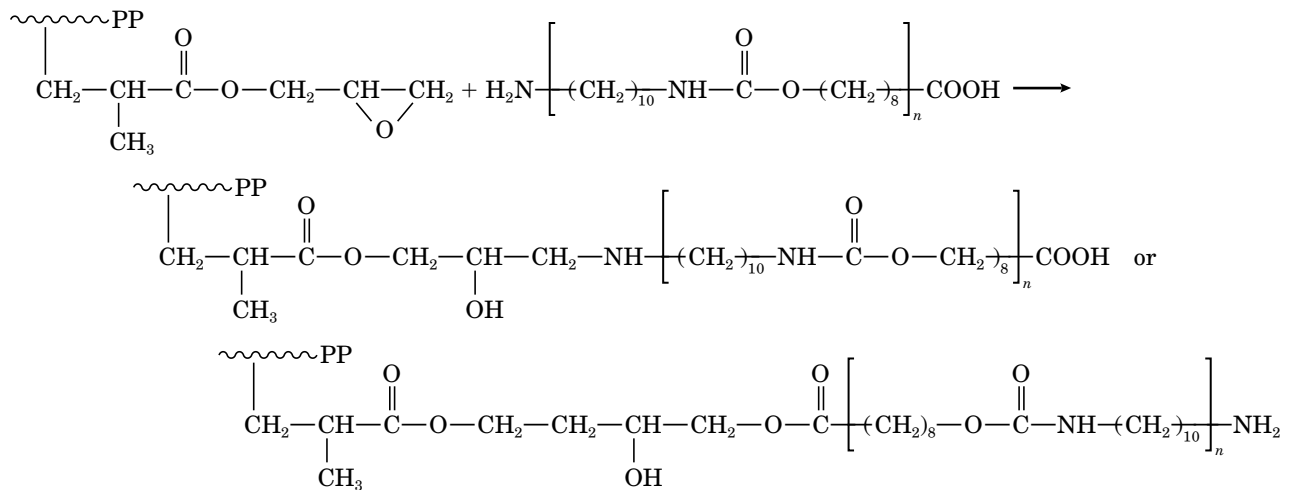
(g)

(h)

Figure 3 (*Continued from the previous page*)

can be considered as contributions of crystals of PP. This feature suggested that some chemical reactions occurred between GMA in PP-*g*-GMA and the terminal amino or carboxylic groups of PA1010 in the PA1010/PP-*g*-GMA blend as shown in the following:

$$\text{\textasciitilde PP}$$

$$\underset{\substack{| \\ CH_3}}{CH_2-CH-}\overset{\substack{O \\ \|}}{C}-O-CH_2-\underset{\diagdown O \diagup}{CH-CH_2} + H_2N\left[(CH_2)_{\overline{10}}NH-\overset{\substack{O \\ \|}}{C}-O\text{--}(CH_2)_{\overline{8}}\right]_n COOH \longrightarrow$$

$$\text{\textasciitilde PP}$$

$$\underset{\substack{| \\ CH_3}}{CH_2-CH-}\overset{\substack{O \\ \|}}{C}-O-CH_2-\underset{\substack{| \\ OH}}{CH-CH_2}-NH\left[(CH_2)_{\overline{10}}NH-\overset{\substack{O \\ \|}}{C}-O-CH_2\text{--}_{\overline{8}}\right]_n COOH \quad \text{or}$$

$$\text{\textasciitilde PP}$$

$$\underset{\substack{| \\ CH_3}}{CH_2-CH-}\overset{\substack{O \\ \|}}{C}-O-CH_2-CH_2-\underset{\substack{| \\ OH}}{CH-CH_2}-O-\overset{\substack{O \\ \|}}{C}\left[(CH_2)_8-O-\overset{\substack{O \\ \|}}{C}-NH\text{--}(CH_2)_{\overline{10}}\right]_n NH_2$$

Table I Tensile Strength (σ_b), Young's Modulus (E_y), Flexural Strength (σ_f), and Flexural Modulus (E_f) of Dried Samples of PA/PP and PA/PP-*g*-GMA Blends

Sample	Composition (wt %)	σ_b (MPa)	E_y (MPa)	σ_f (MPa)	E_f (MPa)
PA1010	100/0	51	—	70	1278
PA/PP	85/15	33	820	58	998
PA/PP-*g*-GMA	85/15	48	827	69	1250
PA/PP	75/25	40	784	33	612
PA/PP-*g*-GMA	75/25	46	816	64	1203
PA/PP	65/35	36	620	30	554
PA/PP-*g*-GMA	65/35	42	712	61	1181
PA/PP	55/45	34	711	26	506
PA/EP-*g*-GMA	55/45	40	733	60	1157

The coupling reaction between the two components made it impossible to extract all the PP component from the PA1010/PP-*g*-GMA blends by using xylene.

The possible coupling interaction between PA1010 and PP-*g*-GMA was confirmed again by comparing the apparent viscosities of PA1010/PP and PA1010/PP-*g*-GMA blends. As shown in Figure 2, an increase of apparent viscosity of PA/PP-*g*-GMA could be attributed to the enhancement of the molecular weight of the blending components.[17] An obvious increase of viscosities at the same compositions and shear rate was observed for PA1010/PP-*g*-GMA blends. This result indicated that the molecular weight of the blending components of PA/PP-*g*-GMA is higher than that of PA/PP, which is induced by coupling reactions between the epoxy groups of PP-*g*-GMA and amino or carboxylic groups of PA1010.

Morphology

Figure 3 shows the SEM micrographs of samples of PA1010/PP and PA1010/PP-*g*-GMA blends etched with xylene. White matrix is PA1010 and black holes were left by the removed PP domains. Several features can be observed from these pictures. Sizes of PP-*g*-GMA domains of PA1010/PP-*g*-GMA blends are much smaller than that of PP of PA1010/PP. As shown in Figure 3(a,c,e,g), the diameters of holes left by PP domains are about 7–20 μm, and the corresponding values of PP-*g*-GMA shown in Figure 3(b,d, f ,h) are 3–10 μm. Homogeneous dispersion of PP-*g*-GMA domains can be observed in Figure 3(b,d, f ,h). Interfaces between PA1010 matrix and PP domains are much clearer and smoother for PA1010/PP blends. This indicated that PP domains were completely removed during the extraction with xy-

Table II Tensile Strength (σ_b), Young's Modulus (E_y), Flexural Strength (σ_f), and Flexural Modulus (E_f) of Wet Samples of PA/PP and PA/PP-*g*-GMA Blends

Sample	Composition (wt %)	σ_b (MPa)	E_y (MPa)	σ_f (MPa)	E_f (MPa)
PA1010	100/0	49	—	38	617
PA/PP	85/15	36	768	39	736
PA/PP-*g*-GMA	85/15	41	813	65	1122
PA/PP	75/25	35	621	25	420
PA/PP-*g*-GMA	75/25	38	801	62	1139
PA/PP	65/35	31	599	23	398
PA/PP-*g*-GMA	65/35	37	756	59	1123
PA/PP	55/45	31	576	21	354
PA/PP-*g*-GMA	55/45	35	697	55	1124
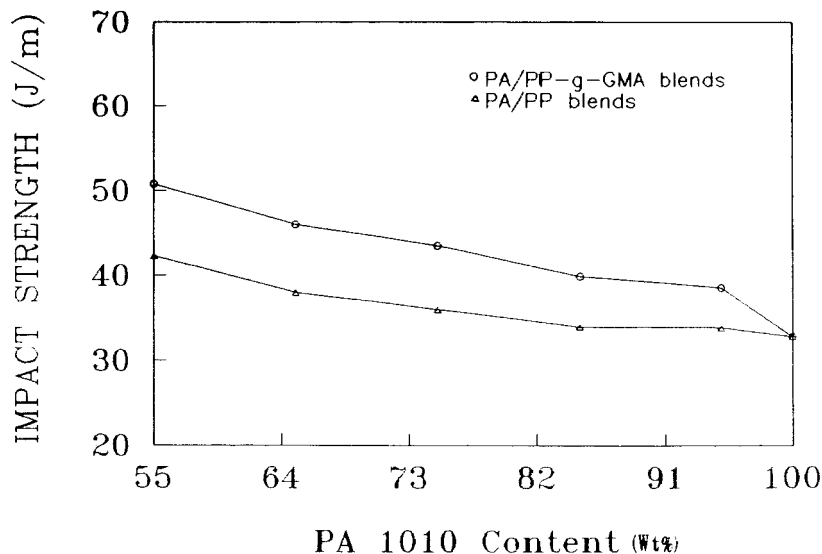
Figure 4 Dependence of Izod impact strength of dried samples as a function of the PA1010 content.

lene. However, interfaces between PA1010 and PP-*g*-GMA are rough and not so smooth. As shown in Figure 3(b,d,f), "protruding objects" could be found in the holes formed by unremoved PP-*g*-GMA. Fibrous structures connecting the matrix and domains were formed [Fig. 3(h)]. The above results strongly suggested that the miscibility of PA1010 and PP-*g*-GMA phases was improved by possible coupling reactions between ep-

oxy groups of PP-*g*-GMA and amino or carboxylic end groups of PA1010. As pointed out by Illing,[2] a graft copolymer stays preferentially on the surfaces of dispersed domains, acting as an "interfacial agent." The presence of such an interfacial agent would require less energy for breaking large dispersed particles during melt blending, and thus make it possible for domains to adhere to the continuous phase.
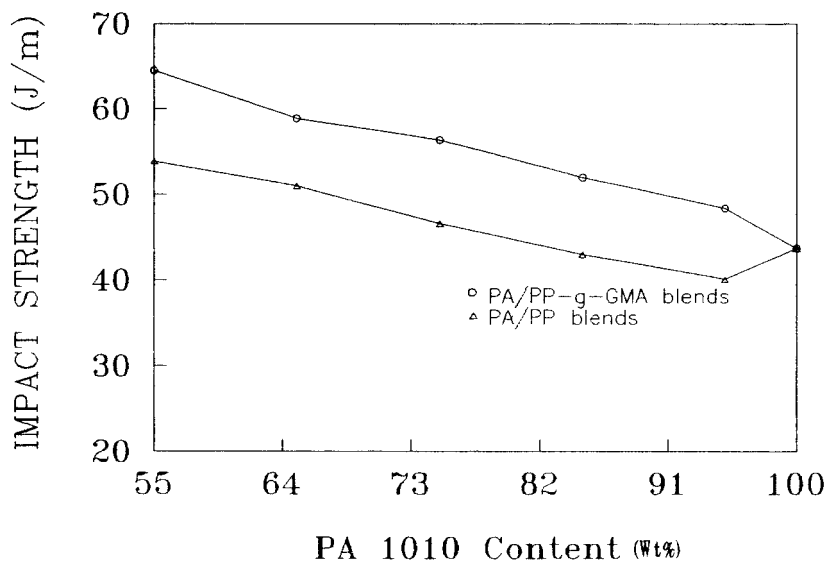
Figure 5 Dependence of Izod impact strength of wet samples as a function of the PA1010 content.

Mechanical Properties

The mechanical properties of dried and wet samples of PA1010/PP and PA1010/PP-*g*-GMA blends, such as tensile strength (σ_b), Young's modulus (E_y), flexural strength (σ_f), and flexural modulus (E_f), are reported in Tables I and II, respectively. It can be noted that when the contents of PA1010 are the same, σ_b values of PA1010/PP-*g*-GMA were 10–50% higher than that of PA1010/PP. Similar results are also observed for parameters σ_f, E_y, and E_f. These features could be attributed to the improvement of interfacial adhesion and homogeneous dispersion of PP-*g*-GMA domains, which is due to interfacial reactions between PP-*g*-GMA and PA1010 components.

Izod impact strength of dried and wet specimens of PA1010/PP and PA1010/PP-*g*-GMA blends with different compositions are shown in Figures 4 and 5. They increased significantly with the addition of PP or PP-*g*-GMA. This suggested that both PP and PP-*g*-GMA materials are good toughening agents for PA1010. The higher the content of PP or PP-*g*-GMA is, the higher the Izod impact strength. However, the toughening effect of PP-*g*-GMA is much better than PP. For example, values of dried samples of PA1010/PP blends are about 10 J/m higher than PA/PP blends at the same compositions. This result can also be attributed to the homogeneous morphological dispersion and improved interfacial adhesion of PA1010/PP-*g*-GMA blends.

Comparing the mechanical properties of wet and dried samples it is seen that properties of PA1010/PP-*g*-GMA and PA1010/PP blends are affected by water. Except for the impact strength, other mechanical properties of the dried samples are all superior to wet samples. Among all the properties of PA1010, the dependence of flexural properties on water is significant. What should be noted is that the flexural strength was more influenced by wetting conditions for noncompatibilized blends than for PA1010/PP-*g*-GMA blends. It is well known that the amino and amide groups in PA may form a hydrogen bond with water and result in water absorption of PA. The rates of water absorption of the investigated materials are given in Table III. Water absorption decreased after PP or PP-*g*-GMA was added in the blends, and the rate of water absorption for PA1010/PP-*g*-GMA blends was less than that for PA1010/PP blends. The reaction and good dispersion in the compatibilized blends should be responsible for the above behavior.

Table III   Rate of Water Absorption for Investigated Materials

Sample	Water Absorption (%)
PA1010	1.57
PA1010/PP (85/15)	1.21
PA1010/PP-*g*-GMA (85/15)	1.16
PA1010/PP (75/25)	0.82
PA1010/PP-*g*-GMA (75/25)	0.56
PA1010/PP (65/35)	0.50
PA1010/PP-*g*-GMA (65/35)	0.45
PA1010/PP (55/45)	0.27
PA1010/PP-*g*-GMA (55/45)	0.21

CONCLUSIONS

The thermal and rheological evidence suggested that the modified PP (PP-*g*-GMA) undergoes chemical reactions during the melt blending with PA1010, leading to the formation of PP-*g*-PA1010 graft copolymer. The PA1010 side chains are likely linked to PP backbone by means of an imidie or carboxylic bond.

The morphological studies show that the PP-*g*-GMA behaves as an interfacial agent by improving the adhesion between PP particles and PA1010 matrix, significantly reducing the average dimensions of the PP dispersed phase. Interfaces between PA1010 and PP-*g*-GMA phases were rough. In addition, protruding objects and fibrous structure were observed.

Mechanical properties of PA1010/PP-*g*-GMA blends are superior to PA1010/PP blends. Dependence of flexural properties on water is different for PA1010/PP and PA1010/PP-*g*-GMA. These behaviors can be attributed to the homogeneous morphological dispersion of PP-*g*-GMA and the improved interfacial adhesion between PA1010 and PP-*g*-GMA phases.

REFERENCES

1. J. W. Barlow and D. R. Paul, *Polym. Eng. Sci.,* **24,** 525 (1984).
2. G. Illing, in *Polymer Blends, Processing, Morphology and Properties,* E. Martuscelli, R. Palumbo, and M. Kryszewski, Eds., Plenum, 1980, p. 167.
3. M. Avella, R. Greco, N. Lanzetta, G. Maglio, R.

Palumbo, E. Martuscell, G. Ragosia, and M. Malinconico, in *Polymer Blends, Processing, Morphology and Properties,* E. Martuscelli, R. Palumbo, and M. Kryszewski, Eds., Plenum, 1980, p. 191.

4. F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.,* **18,** 963 (1974).

5. P. Scholz, D. Froelich, and R. Muller, *J. Rheol.,* **33,** 481 (1989).

6. S. Hosoda, K. Kojima, Y. Kanda, and M. Aoyagi, *Polym. Networks Blends,* **1,** 51 (1991).

7. S. J. Park, B. K. Kim, and H. M. Jeong, *Eur. Polym. J.,* **26,** 131 (1990).

8. Z. Mang and H. L. Willams, *J. Appl. Polym. Sci.,* **44,** 699 (1992).

9. C. D. Han, Y. J. Kim, and H. B. Chin, *Polym. Eng. Rev.,* **4,** 177 (1984).

10. J. Y. J. Chung and R. P. Carter, Jr., U.S. Pat. 4,554,315 (1985).

11. F. C. Chang and Y. C. Hwu, *Polym. Eng. Sci.,* **31,** 1509 (1991).

12. S. H. Chen and F. C. Chang, in *Proceedings of the 15th ROC Polymer Symposium 1992,* Taiwan, 1992, p. 445.

13. B. X. Chang and F. C. Chang, in *Proceedings of the 15th ROC Polymer Symposium 1992,* Taiwan, 1992, p. 425.

14. H. H. Chang, J. S. Wu, and F. C. Chang, in *Proceedings of the 4th Asian Chemistry Congress,* Beijing, August 1991, p. 699.

15. S. Suzuki and T. Yamamoto, *Plastics (Jpn),* **4**(6), 116 (1990).

16. X. M. Zhang, Z. H. Yin, and J. H. Yin, *J. Appl. Polym. Sci.,* **61,** 2253 (1996).

17. R. D. Favis and D. Therrien, *COMPALLOY'90,* 1990, p. 59.