PII: S0032-3861(97)00172-9

Polymer Vol. 38 No. 24, pp. 5905–5912, 1997

0032-3861/97/$17.00+0.00

polymer papers

Morphology, mechanical properties and interfacial behaviour of PA1010/PP/PP-g-GMA ternary blends

Zhang Xiaomin, Yin Zhihui, Na Tainhai and Yin Jinghua*
Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P.R. China
(Revised 27 January 1997)

Morphology, mechanical properties, and interfacial interaction of polyamide 1010/polypropylene (PA1010/PP) blends compatibilized with polypropylene grafted with glycidyl methacrylate (PP-g-GMA) were studied. It was found that the size of the PP domains, tensile and impact strength of ternary blends, and adhesion fracture energy between two layers of PA1010 and PP were all significantly dependent on the PP-g-GMA contents in the PP layer. Correlations between morphology and related properties were sought. The improvements in properties have been attributed to chemical and physical interaction occurring between PA1010 and PP-g-GMA. © 1997 Elsevier Science Ltd.

(Keywords: polypropylene; polyamide 1010; PP-g-GMA)

INTRODUCTION

Polyamide and polyolefins are two important classes of commercial polymers. Polyamides are frequently blended with lower modulus polyolefins[1–6] to prepare polymer alloys which have different properties. The addition of polyolefins lowers the water absorption, improves its dielectric properties and impact resistance and reduces the costs of polyamide. However, the direct mixing of polyamide with polyolefins usually leads to incompatible blends which exhibit poor properties. These blends require the addition of a compatibilizing agent to achieve satisfactory interfacial adhesion in order to develop an effective stress transfer between the two phases. Methods to synthesize compatibilizing agents and to improve phase adhesion between two immiscible components are the subjects of many research activities[7–11].

In a previous publication, we have reported the preparation and characterization of PP-g-GMA[12]. In the present work, PP-g-GMA was studied as a compatibilizer for polyamide 1010 and polypropylene blends. The aim of this study was to investigate the compatibilization mechanism and the effects of the amount of PP-g-GMA on morphology and related mechanical properties.

EXPERIMENTAL

Materials

The polyamide 1010 (PA1010) with relative viscosity of 2.1 was supplied by JiLin ShiJingGuo Union Chemical Plant (China). The melting temperature of PA1010 was 478 K, and its crystallization temperature and degree of crystallinity were 454 K and 38%, respectively. Polypropylene with melt index 1.0 was purchased from LiaoNing PanJin Natural Gas Co. (China). PP-g-GMA compatibilizer was prepared in this laboratory, using the preparation and characterization methods reported in the previous publication[12]. The contents of GMA in PP-g-GMA used in this work was 0.57 mol%. The materials were dried at 80°C in a vacuum oven for 12 h before blending.

Preparation of blends

The components were melt blended by using a Brabender type laboratory single-screw extruder. The temperature gradient was maintained in the barrel of the extruder, with the feed zone being kept at 185°C, the compression zone at 205°C, the melting zone at 205°C, and the die at 195°C. Blends of PA1010 and PP were mixed with different amounts of PP-g-GMA, using the same PA1010 fraction (75 wt%) and a total weight fraction of PP and PP-g-GMA of 25 wt%. In addition, the content of PP-g-GMA in the blends was varied from 0 to 25 wt%.

Determination of PP-g-GMA-graft-PA1010 copolymer formation

In order to determine the amount of PP-g-GMA-graft-PA1010 formed during blending, the following procedures were adopted. Ten grams of a ternary blend were extracted in 140 ml formic acid for 10 h. The formation of white, colloidal suspension was taken to be indicative of the occurrence of a grafting reaction[13,14]. The soluble and insoluble parts were separated by centrifugation, using a Sorvall Superspeed RC2-B. The PP residue was extracted again with formic acid. The same procedure was repeated three times to ensure complete extraction. At the end the solid residue was washed with water and dried overnight at 80°C in vacuum oven. The amount of PA1010 reacted with PP-g-GMA was determined using an ESCA CAB MK-2

---

* To whom correspondence should be addressed

electron spectrometer by measuring the weight percent of N element in the PP residue, from which the wt% PA1010 could be calculated.

A FTS-7 Fourier transform i.r. spectrophotometer was used to characterize the formation of PP-g-GMA-graft-PA1010, using the following specimen preparation method. Twenty grams of sample were first extracted in 140 ml xylene for 10 h, and then with 140 ml formic acid for another 10 h. The residue was washed with water, dried 10 h at 80°C in a vacuum oven and pressed into films for i.r. tests. The insoluble residue was considered to be the PP-graft-PA1010 copolymer[15], and the amount formed was determined by a gravimetric analysis.

Characterization of interfacial adhesion

The detailed analysis of fracture energy in a peel test have been reported by Wu[16]. If peeling test progresses at constant peel force F and peel angle θ, the work of peel test is given by[16]

$$W = F(\lambda - \cos\theta) \times c \tag{1}$$

where c is the peeled distance, λ is the extension ratio. The energy Γ expended in separating an interfacial area bc is given by

$$\Gamma = bcG \tag{2}$$

where G is the fracture energy per unit interfacial area. The energy is also expended in deforming the peeling strip in the straight region, that is

$$V = S_a bct_a + Sbct \tag{3}$$

where V is the deformation energy for peeling an interfacial area bc, S_a the deformation energy per unit volume of the adhesive, and S that of the flexible adherend. Conservation of energy requires that $W - \Gamma - V = 0$, using equations (1), (2) and (3) gives

$$F/b = (G + S_a t_a + St)/(\lambda - \cos\theta) \tag{4}$$

If the flexible adherend is inextensible, then $\lambda = 1$, $S_a = S = 0$. Equation (4) simplifies to

$$F/b = G/(1 - \cos\theta) \tag{5}$$

the adhesion fracture energy per unit interfacial area G is given by

$$G = (1 - \cos\theta)P \tag{6}$$

where P is the peel force per unit width.

The peel test were carried out on an Instron 1121 at a peel rate of 0.09 cm s^{-1}. The specimens were prepared by pressing together a plaque of the pure PA1010 (0.4 cm thick) and PP containing different content of PP-g-GMA at 170°C for 1 h. The bonded specimens were peeled at 180°C angle. Therefore, the fracture energy for 180°-peel test in our case is given by

$$G_a = [1 - (-1)]P = 2P \tag{7}$$

Measurement of mechanical properties

Dumbbell-shaped specimens, 3 mm thick, were prepared by using an injection moulding method. Tensile tests were carried out on an Instron 1121 machine at room temperature at cross-head speed of 50 mm min^{-1}. Measurements of Izod impact strength was performed with XJU-22 impact testing machine according to ISO/R180-1961 method. Before tests, all specimens were kept in a vacuum oven at 80°C for 12 h.

Morphological observation

The mechanical properties of the heterogeneous polymer blends were found to be related to their microstructure, especially size and shape of the dispersed phases. In order to determine the particle size and size distribution of the dispersed phase in the blends, the overall morphology of specimens broken in liquid nitrogen was examined. Sections were vacuum coated with gold and examined in a scanning electron microscope (JXA-840). Before observation, the samples were etched in xylene for 4 h to increase the contrast. The morphology of sections of specimens for tensile and impact tests were also examined by SEM.

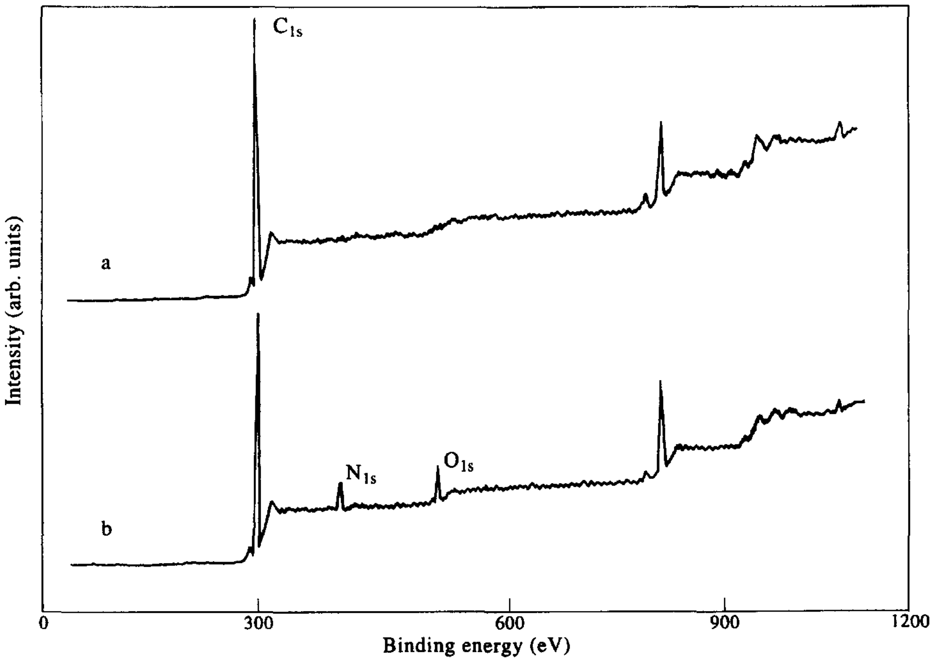


Figure 1 The e.s.c.a. spectrum of the samples extracted in formic acid for 10 h. (a) PA1010/PP (75/25) blend. (b) PA1010/PP-g-GMA (75/25) blend

RESULTS AND DISCUSSION

Characterization of formation of PP-g-GMA-graft-PA1010 copolymer

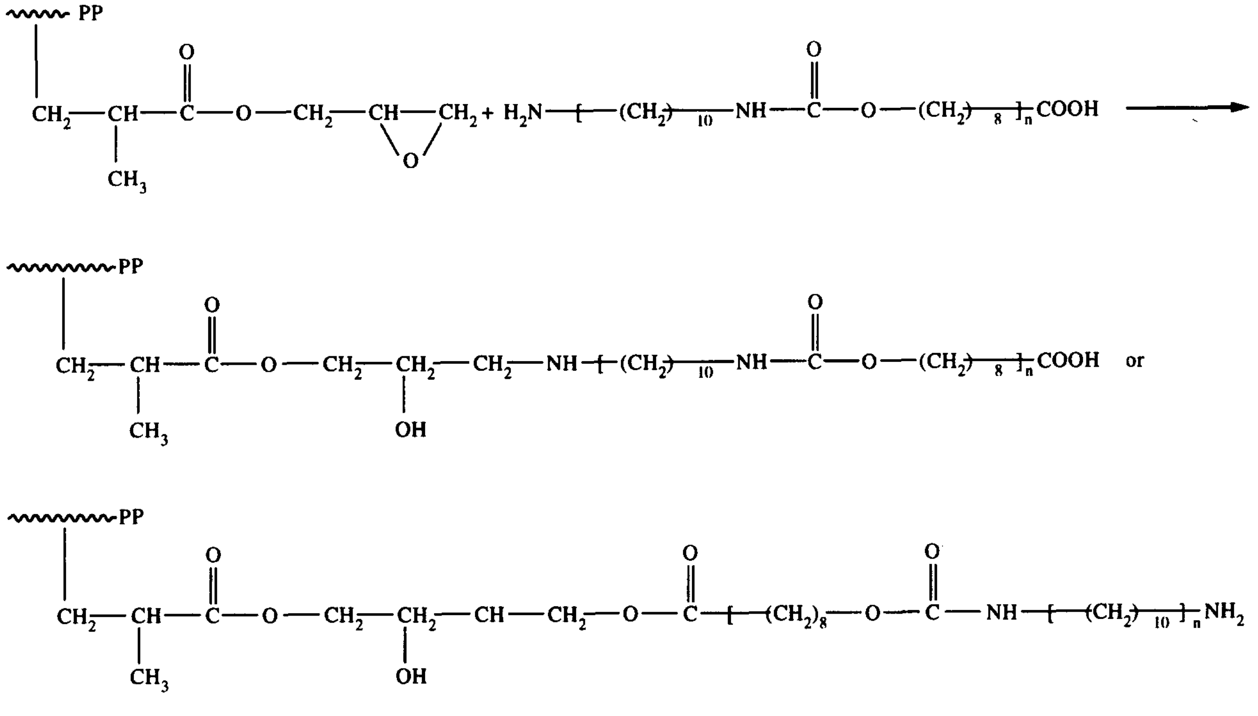
E.s.c.a. spectra obtained in residues of PA1010/PP(75/25) and PA1010/PP-g-GMA(75/25) samples extracted with formic acid are shown in *Figure 1*. If the PA1010 component in PA1010/PP completely dissolves in formic acid, the extracted residue should only contain the PP component. This assumption is supported by the data in *Figure 1a*, which gives evidence for the absence of PA1010. On the other hand, N_{1s} and O_{1s} peaks which correspond to the nitrogen and oxygen elements are apparent in the spectra of *Figure 1b*, suggesting that some PA1010 component is left in the residue of the PA1010/PP/PP-g-GMA sample extracted with formic acid. As shown in *Figure 1a*, uncombined PA1010 is very easy to extract out from the PA1010/PP blends with formic acid. It can be concluded therefore that PA1010 left in the extracted residue of PA1010/PP-g-GMA has reacted with PP-g-GMA.

The amount of PA1010 combined with PP-g-GMA was determined by an elemental analysis on the basis of the N element content obtained from e.s.c.a. measurements. The extent of grafting (G) of PA1010 combined with PP-g-GMA can be expressed as

$$G = \frac{\text{weight of PA1010 combined with PP-g-GMA}}{\text{total weight of PP}}$$

As shown in *Figure 2*, values of G increases with the content of PP-g-GMA. The higher the content of PP-g-GMA, the greater the available reaction sites. Dividing $G\rho_{\text{PP}}$ by the interfacial area per unit PP volume ($V = 6/d$, where d is the average PP particle diameter) gives β, a parameter that may be considered as a measure of the potential interfacial adhesion[15]. The calculated values are reported in *Figure 3*, showing that β, the amount of PA1010 coupled to the PP-g-GMA per unit interfacial area, increases with increasing the content of PP-g-GMA in the blends.

The type of coupling reactions between PA1010 and PP-g-GMA are shown as



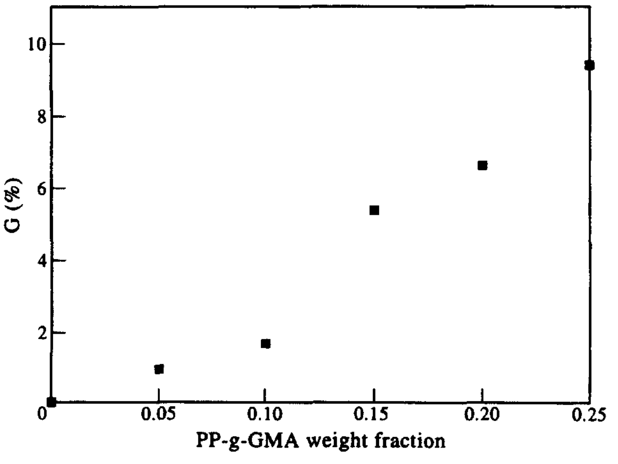


Figure 2 The dependence of PA1010 reacted with PP-g-GMA on the content of PP-g-GMA in the blends

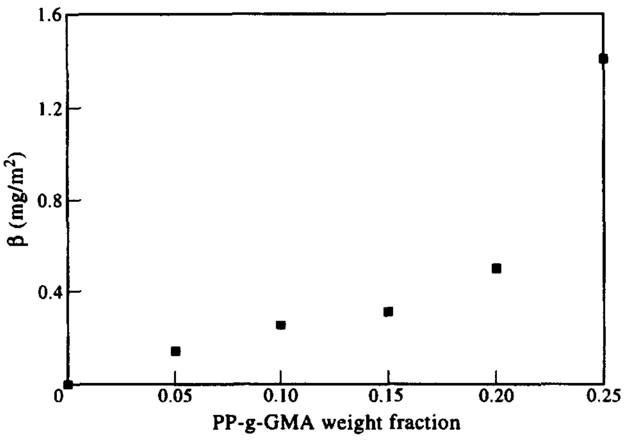


Figure 3 The relationship of the amout of PA1010 coupled to the PP per unit interfacial area (β) with the content PP-g-GMA in the blends

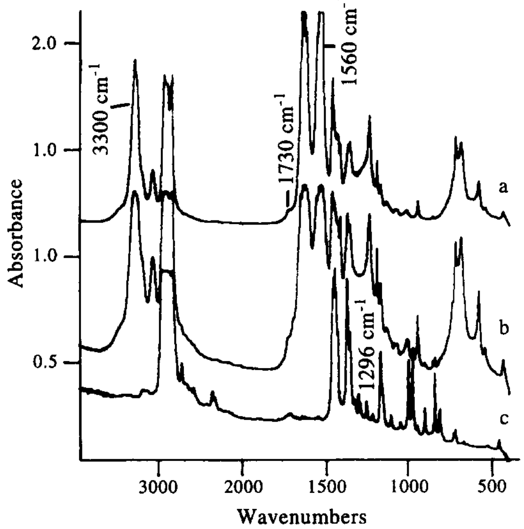


Figure 4 *FT*i.r. spectrum of the samples extracted in xylene and formic acid for 10 h, respectively. (a) PA1010. (b) PA1010/PP-g-GMA (75/25) blend. (c) PP-g-GMA

Table 1 The gravimetric analysis of the investigated blends extracted with xylene and formic acid for 10 h, respectively

Blend composition (PA1010/PP/PP-g-GMA in weight)	Insoluble weight fraction (%)
75/25/0	0.0
75/15/10	0.2
75/5/20	2.3
75/0/25	3.2

In both cases, epoxy group of PP-g-GMA can react with PA1010 through either carboxylic or amino end groups of PA1010. The occurrence of these reactions was partially confirmed by *FT*i.r. analysis (*Figure 4*) of PA1010, PP-g-GMA and the residue of PA1010/PP-g-GMA blend extracted with formic acid and xylene. As shown in *Figure 4*, the absorbing peak at 1296 cm^{-1} which is attributed to epoxy group of PP-g-GMA do not appear in the residue of the extracted blending sample. It suggested that the epoxy groups of PP-g-GMA have reacted with the end group of PA1010 in the blending process. Compared with the spectrum of PP-g-GMA, that of PP-g-GMA/PA1010 blend shows the presence of amide groups as evidenced from carbonyl 1730 cm^{-1} and N–H bending at 3300 cm^{-1} and N–H bending at 1560 cm^{-1}.

The amount of PP-g-GMA-graft-PA1010 in ternary blends is strongly dependent upon the content of PP-g-GMA. As shown in *Table 1*, when the content of PA1010 is fixed at 75%, the wt% of PP-g-GMA-graft-PA1010 increases with the addition of PP-g-GMA and could reach 3.2% when PP is replaced completely by PP-g-GMA.

There is no satisfactory method for measuring directly the adhesion between the two phases in a blend. Here, the peel test method was used to measure indirectly the adhesion between PA1010 and PP. Due to the formation of PP-g-GMA-graft-PA1010 copolymer, the interfacial adhesion fracture energy should depend on the amount of PP-g-GMA in the blend. As shown in *Figure 5*, the adhesion fracture energy of PA1010 and PP is less than 80 J m^{-2}. With addition of PP-g-GMA, the adhesion fracture energy increases to amount of 400 J m^{-2} when PP is replaced completely with PP-g-GMA.

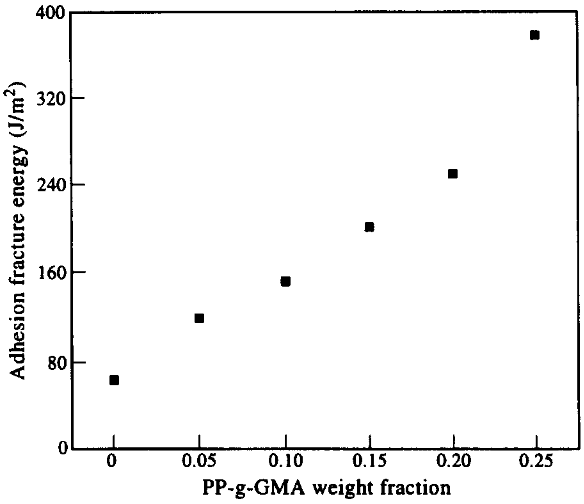


Figure 5 The dependence of the adhesion fracture energy Ga on the added amount of PP-g-GMA in the PP

Overall morphology

Figure 6 shows SEM micrographs of PA1010/PP and PA1010/PP/PP-g-GMA blends. The effect of the compatibilizer (PP-g-GMA) on the morphology of the ternary blend can be demonstrated in these micrographs. The white continuous phase is PA1010 and the dark hole is left by the etched PP domains. The uncompatibilized blend of PA1010/PP (75/25) has a coarse morphology with domain size as large as 10–15 μm. For the compatibilized blends, the PP domains are dispersed in the PA1010 matrix as spherical particles. The presence of 5 phr PP-g-GMA clearly results in smaller domain size, with an even larger reduction in the dimensions of the dispersed phase being observed at higher concentration of compatibilizer. Better dispersion and improved interfacial adhesion are attributed to formation of PP-g-GMA-graft-PA1010 from the reaction of epoxy groups of PP-g-GMA with terminal groups of PA1010 during melt mixing. A narrowing of the size distribution for compatibilized ternary blends is also observed.

The total area fraction of dispersed phase can be measured on the micrograph sampling surface. This area fraction can be used to express the volume fraction of the dispersed phase in the blends[17,18]. As the particle size of PP decreases with increasing PP-g-GMA content in the blends, the number of the dispersed particles should increase, and the total area fraction of the dispersed phase must increase. Since the SEM samples in this work have been extracted in xylene (good solvent for PP), PP in the blends would be removed by the solvent. For the compatibilized blends, it was impossible to dissolve all the dispersed phase because of the copolymer formation between PA1010 and PP-g-GMA. The more content PP-g-GMA was added to the blends, the more the amount cannot be removed by the solvent. Therefore, it is meaningful to measure the total area fraction of dispersed phase for conforming the formation of PA1010-graft-PP copolymer. The measured area fraction of dispersed phase as a function of compatibilizer concentration are given in *Figure 7*. This shows that the measured area fractions of PP decreases with increasing the content of PP-g-GMA in the blends. The reduction of the measured area fraction of the dispersed phase could be caused by the chemical reaction in the reactive extrusion. The copolymer PA1010-graft-PP formed by

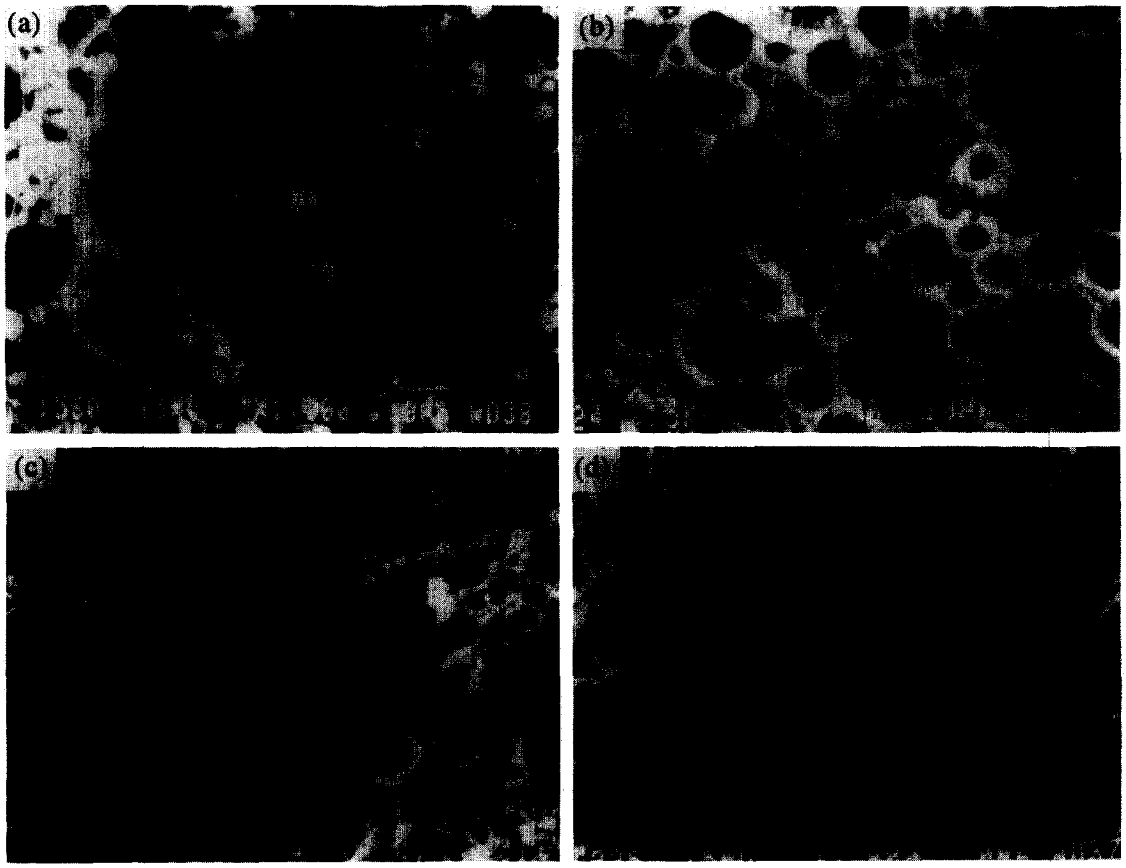


Figure 6 The SEM pictures of the ternary blends containing PP-g-GMA. (a) 0%, (b) 10%, (c) 15%, (d) 20%

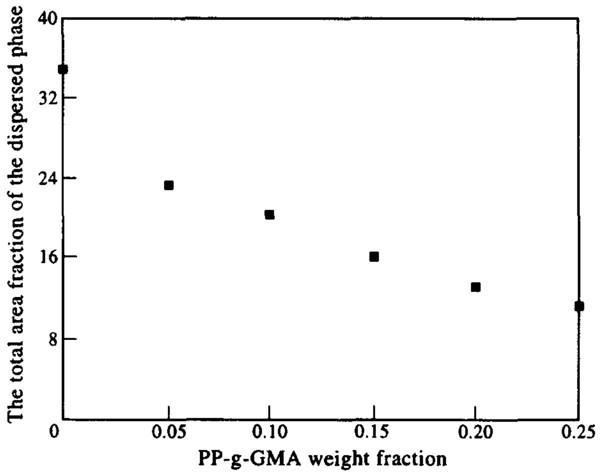


Figure 7 The total area fraction of the dispersed phase as a function of PP-g-GMA concentration

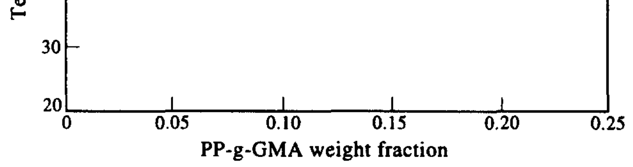


Figure 8 The dependence of the tensile strength on the PP-g-GMA concentration

the chemical reaction at the interface is not soluble under the extraction condition used here. This would explain the reduction in the measured area fraction of the dispersed phase.

Mechanical properties and related morphology

The tensile strength of PA1010/PP/PP-g-GMA blends with 75% PA1010 and various composition ratio of PP/PP-g-GMA is shown in *Figure 8*. This shows that the tensile strength increases gradually with increasing the content of PP-g-GMA in the blends. When PP is completely replaced by PP-g-GMA, the tensile strength of the blend reaches the value of 64 MPa, which is about 1.5 times that for the binary PA1010/PP blend (43 MPa).

The improvement in tensile strength can be attributed to the change of their morphology and the improved interfacial adhesion. The interfacial adhesion between PA1010 and PP-g-GMA can be further confirmed by SEM photographs of fracture sections of specimens for tensile tests. Because the tensile yield strength of the PP particles is lower than that of PA1010, an indication of the interfacial strength can be derived from the extent by which the PP particles were deformed when the blend fractured. As shown in *Figure 9a*, the fracture surface of the uncompatibilized specimen is smooth. The holes left by pulled out PP domains are very round as these have suffered no deformation, and indicates that the

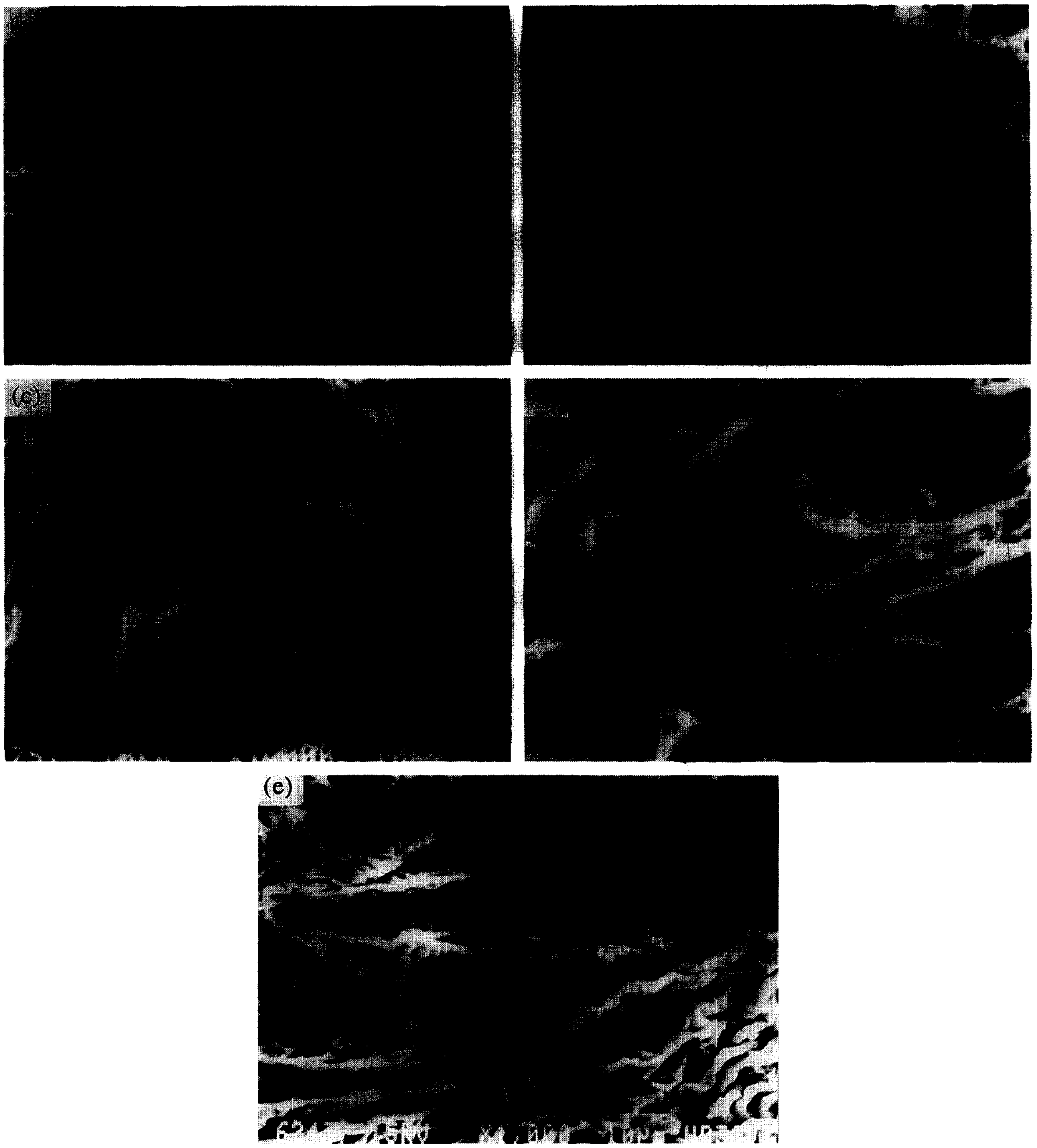


Figure 9 The morphologies of the tensile fracture surfaces containing PP-g-GMA. (a) 0%, (b) 10%, (c) 15%, (d) 20%, (e) 25%

interfacial strength is very low. In contrast to this feature, fracture surfaces of compatibilized specimens (*Figures 9b–e*) are much rougher. Deformed holes, which are left by the pulled-out PP domains, can be found in *Figure 8b*. Even fibrous structure can be observed in the ternary blends.The higher content of PP-g-GMA in the blends, the higher extent of the particle draw-out. These results indicate that the interfacial strength is significantly improved.

Strong adhesion is needed for increasing impact strength of the blends because interfacial adhesion between two phases must be high to ensure effective stress transfer. The minimum adhesion required for touching should be that the dispersed particles are not detached from the matrix during fracture. The enhancement of interfacial adhesion also results in the improvement of impact resistance of ternary blends. As reported

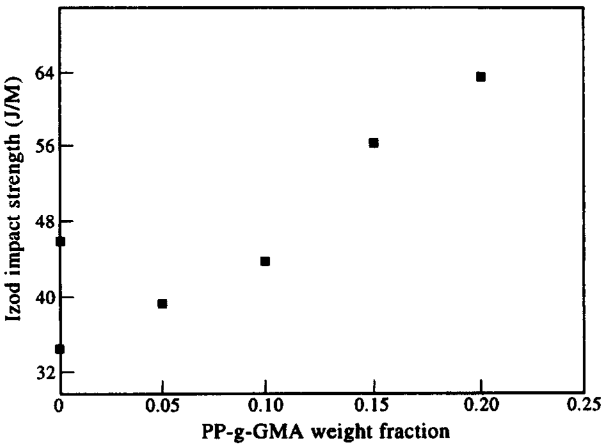


Figure 10 The Izod impact strength vs the PP-g-GMA content in the blends

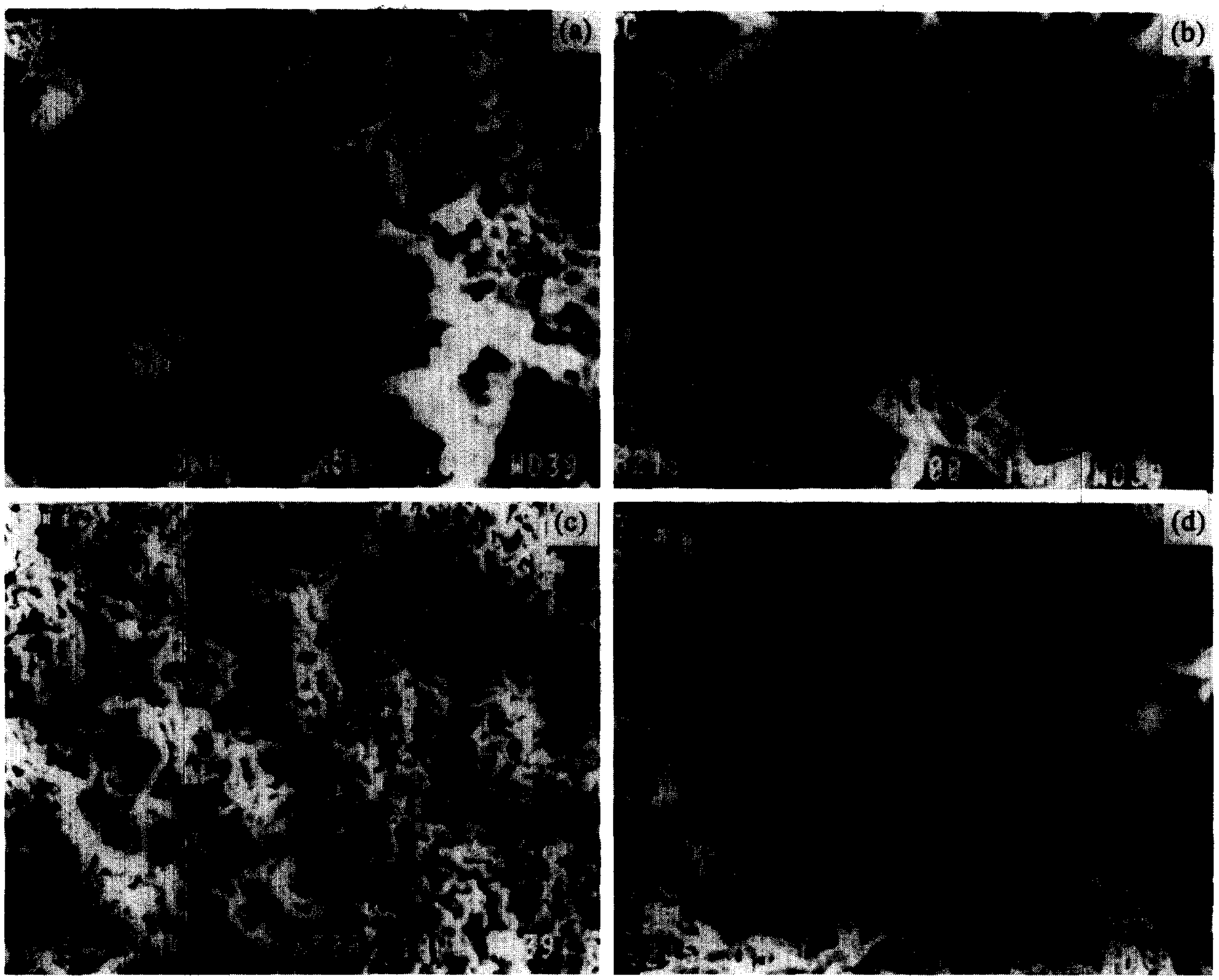


Figure 11 The SEM pictures of the impact fracture surfaces. (a) PA1010/PP (75/25) blend. (b) PA1010/PP (75/25) blend etched with xylene for 30 min. (c) PA1010/PP-g-GMA/PP (75/20/5) blend. (d) PA1010/PP-g-GMA/PP (75/20/5) blend etched with xylene for 30 min

in *Figure 10*, the Izod impact strength values of ternary PA1010/PP/PP-g-GMA blends are higher than for the binary PA1010/PP blend. When PP is completely replaced by PP-g-GMA, the Izod impact strength is double that of the PA1010/PP(75/25) blend. This behaviour should be attributed to the augmentation of adhesion between PA1010 and PP-g-GMA components and good dispersion of PP phases. The difference is also reflected in their morphologies.

SEM micrographs of Izod fracture surfaces of PA1010/PP binary and PA1010/PP/PP-g-GMA ternary blends are reported in *Figure 11*. SEM photomicrographs of fracture surfaces for compatibilized blend shows extensive matrix yielding, and that for noncompatibilized shows very little matrix yielding. It is observed that the fracture surface of the noncompatibilized blend is relatively smooth and has many spherical holes, which correspond to exposed PP particles. When PP-g-GMA is added to the blend, on the other hand, there are no PP particles visible on the fracture surface. To confirm this, the fracture surfaces were etched with xylene for 0.5 h and reexamined by SEM. The etched surfaces remained almost the same as the unetched ones. If the PP particle had been exposed on fracture surfaces, they would have been dissolved away by xylene, leaving spherical holes. These features suggest that PP domains were firmly attached to the PA1010 matrix by means of interfacial interactions.

CONCLUSIONS

(1) E.s.c.a. and *FT*i.r. experiments have confirmed that PP-g-GMA-graft-PA1010 copolymer is formed during reactive extrusion of PA1010, PP, and PP-g-GMA as a result of the reaction between the end group of PA1010 and epoxy groups of PP-g-GMA.

(2) Due to the formation of PP-g-GMA-graft-PA1010 copolymer, the adhesion fracture energy for the interface of PA1010 and PP containing PP-g-GMA is increased several times over that of PA1010 and pure PP binary system.

(3) The addition of PP-g-GMA in the blend of PA1010 and PP gives a significant reduction in the domain size and improvement in interfacial interaction between PA1010 matrix and PP domains. These features are strongly dependent on the amount of PP-g-GMA used in the blends.

(4) Tensile strength and Izod impact strength of PA1010/PP/PP-g-GMA ternary blends are much higher than those of PA1010/PP binary blend. The improvement in mechanical properties of ternary blends is attributed to morphological effect and enhancement of interfacial adhesion between PA1010 and PP.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support of the Chinese National Nature Science Foundation Committee, Project No. 59433010.

REFERENCES

1. Wu, S., *Polymer*, 1985, **26**, 1855.
2. Margolina, A. and Wu, S., *Polymer*, 1988, **29**, 2170.
3. Fukui, T., Kikuchi, Y. and Inoue, T., *Polymer*, 1991, **32**, 2367.
4. Hobbs, S. Y., Bopp, R. C. and Paul, D. R., *Polymer*, 1992, **23**, 3173.
5. Hobbs, S. Y., Bopp, R. C. and Watkins, V. H., *Polym. Eng. Sci.*, 1983, **23**, 380.
6. Padwa, A. R., *Polym. Eng. Sci.*, 1992, **32**, 1703.
7. Ide, F. and Hasegawa, A., *J. Appl. Polym. Sci.*, 1974, **18**, 963.
8. Park, S. J., Kim, B. K. and Jeong, H. M., *Eur. Polym. J.*, 1990, **26**, 131.
9. Willis, J. M., Caldas, V. and Favis, B. D., *J. Mater. Sci.*, 1991, **26**, 4742.
10. Hosoda, S., Kojima, K., Kanda, Y. and Aoyagt, M., *Polym. Networks Blends*, 1991, **1**, 51.
11. Holsti-Miettinen, R. and Seppaia, J., *Polym. Eng. Sci.*, 1992, **32**, 868.
12. Zhang, X. M., Yin, Z. H. and Yin, J. H., *J. Appl. Polym. Sci.*, 1996, **61**, 2253.
13. Molau, G. E., *Kolloid Z. Z. Polymer*, 1970, **238**, 493.
14. Illing, G., *Angew, Makromol. Chem.*, 1981, **95**, 83.
15. Borggreve, R. J. M. and Gaymans, R. J., *Polymer*, 1989, **30**, 63.
16. Wu, S., *Polymer Interface and Adhesion*. Marcel Dekker, New York, 1982, pp. 534–545.
17. Russ, J. C., *Practical Stereology*. Plenum Press, New York, 1986.
18. Underwood, E. E., in *Quantitative Microscopy*, ed. R. T. Dohoff and F. F. N. Rhines. McGraw-Hill, New York, 1968, pp. 151–200.