

Influence of Epoxy Resin on the Properties of Maleic Anhydride Functionalized Acrylonitrile–Butadiene–Styrene Copolymer Toughened Polyamide 6 Blends

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Received 8 July 2010; accepted 15 October 2010

DOI 10.1002/app.33648

Published online 25 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Maleic anhydride functionalized acrylonitrile–butadiene–styrene copolymer (ABS-g-MA) was used as an impact modifier of polyamide 6 (PA6). Epoxy resin was introduced into PA6/ABS-g-MA blends to further improve their properties. Notched Izod impact tests showed that the impact strength of PA6/ABS-g-MA could be improved from 253 to 800 J/m with the addition of epoxy resin when the ABS-g-MA content was set at 25 wt %. Differential scanning calorimetry results showed that the addition of epoxy resin made the crystallization temperature and melting temperature shift to lower temperatures; this indicated the decrease in the PA6 crystallization ability. Dynamic mechanical analysis testing showed that the addition of epoxy resin induced

the glass-transition temperature of PA6 and the styrene-co-acrylonitrile copolymer phase to shift to higher temperatures due to the chemical reactions between PA6, ABS-g-MA, and epoxy resin. The scanning electron microscopy results indicated that the ABS-g-MA copolymer dispersed into the PA6 matrix uniformly and that the phase morphology of the PA6/ABS-g-MA blends did not change with the addition of the epoxy resin. Transmission electron microscopy showed that the epoxy resin did not change the deformation mechanisms of the PA6/ABS-g-MA blends. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 909–915, 2011

Key words: core–shell polymers; polyamides; toughness

INTRODUCTION

New polymers can be obtained by copolymerization or polymer blending. Polymeric mixtures or polymer blends are more viable economically compared to copolymers and offer a diversity of possible routes for obtaining materials with desirable properties. Polymer blending has gained much interest in past decades because of the enhancement of polymer properties. The use of polymer blending to improve the impact strength of semicrystalline thermoplastics is especially interesting and is known as a *toughening process*.¹

Polyamide 6 (PA6), the semicrystalline thermoplastic, is an attractive polymer for engineering applications. It exhibits a high resistance to crack ini-

tiation, which imparts a high unnotched impact toughness. However, its low resistance to crack propagation leads to embrittlement in the presence of a notch.^{2,3} Core–shell polymers, such as acrylonitrile–butadiene–styrene copolymer (ABS), methyl methacrylate–butadiene–styrene copolymer, and acrylic impact modifiers, are one kind of important impact modifier for PA6.^{4–6} To modify the notch sensitivity and improve the notch impact strength of PA6, core–shell modifiers such as ABS have been used to successfully toughen PA6, and blends of PA6 and ABS materials are of significant commercial interest.^{7–23}

In a previous study,²⁴ reactive monomers, such as acrylic acid, maleic anhydride (MA), and glycidyl methacrylate (GMA) grafted ABS copolymers, were synthesized and used to successfully toughen PA6 in our laboratory, and maleic anhydride functionalized acrylonitrile–butadiene–styrene copolymers (ABS-g-MAs) showed a much superior toughening ability. However, the achievement of supertough properties by an increase in the disperse-phase content sacrificed the stiffness of PA6, so the question of how to obtain PA6 blends with supertough and stiffer mechanical properties has become very meaningful.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50803007.

Contract grant sponsor: Jilin Provincial Science and Technology Department; contract grant number: 20090142.

TABLE I
Properties of the ABS and ABS-g-MA Core-Shell Copolymers Used in This Study

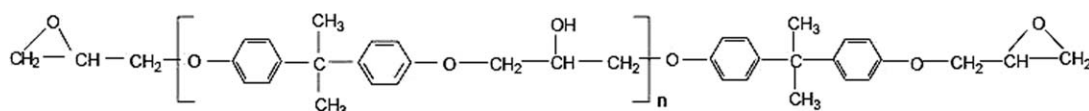
Designation	PB content (wt %)	Styrene/acrylonitrile (w/w)	MA content (wt %)	Torque (Nm)	Particle size (μm)
ABS	60	75/25	0	26	0.40
ABS-g-MA	60	75/25	1	26	0.42

In this study, ABS-g-MA copolymers were used as impact modifiers of PA6, and a middle-weight epoxy resin was introduced into the blends to modify their properties. Epoxy resin has been used as a chain-extension agent of polyesters and successful compatibilizer of polyester blends.^{25–27} However, the influence of epoxy resin on the mechanical properties of rubber-toughened PA6 blends has seldom been studied in detail. Similar to the blends of polyesters and epoxy resin, the amine and carboxyl groups of PA6 can react with the epoxy groups of epoxy resin, so the properties of the PA6 matrix can be modified by epoxy resin. In this study, the influence of epoxy resin on the mechanical properties, thermal characteristics, miscibility, and deformation properties of PA6/ABS-g-MA blends were investigated in detail.

EXPERIMENTAL

Materials

PA6 was purchased from Longjiang Plastics Plant (Heilongjiang, China). The concentrations of carboxyl and amine groups were 42.6 and 51.2 $\mu\text{equiv/g}$, respectively. Its intrinsic viscosity was 2.5 dL/g (0.01 g/mL, formic acid solution, 30°C), and its M_n was 2.4×10^4 g/mol. Before each processing step, PA6 was vacuum-dried in an oven for at least 24 h at 80°C to remove the absorbed water. The ABS and ABS-g-MA materials were synthesized by emulsion polymerization, as described in our previous article,²⁴ and the properties are listed in Table I. A middle-molecular-weight epoxy resin (trademark EPO 1691-410, E-03 609, diglycidyl ether of bisphenol A, epoxy equivalent weight = 2400–4000 g/eq) was supplied by Diandong Branch Plant of Shanghai Resin Plant (Shanghai, China). The chemical structure of the epoxy resin was as follows:



Diglycidyl ether of bisphenol A

Reactive blending and molding procedures

The PA6 blends were prepared in a corotating twin-screw extruder (SJSH-30 Nanjing Rubber & Plastics Machinery Factory, Nanjing, China). E0, E1, E3, E5, E7, and E10 in this article indicate the percentage content of epoxy resin in the PA6/ABS-g-MA blends. The temperatures along the extruder were set at 210, 220, 240, 240, 240, 240, and 240°C, and the rotation speed of the screw was 100 rpm.

The melt stripes of blends were cooled in a water bath and then pelletized. The blends were dried in a vacuum oven at 80°C for 24 h. Then injection molding was carried out to prepare Izod impact specimens and tensile specimens.

Differential scanning calorimetry (DSC) analysis

DSC measurements were conducted with a PerkinElmer DSC-7. The samples were taken from the injection-molded specimens and had a normal

weight of about 6 mg. The samples were heated from 20 to 240°C at 10°C/min under a nitrogen atmosphere, maintained for 3 min to remove their thermal history, and cooled at a rate of 10°C/min to 0°C to obtain the crystallization properties.

Dynamic mechanical analysis (DMA)

DMA was performed on a Netzsch DMA 242, which provided the $\tan \delta$ as a function of temperature. The scans were carried out in single-cantilever mode at a constant heating rate of 3°C/min and at a frequency of 10 Hz. The measurement was performed over the temperature range 20–160°C.

Mechanical properties

The notch of the Izod impact specimens was milled in a machine with a depth of 2.54 mm, an angle of 45°, and a notch radius of 0.25 mm. The notched

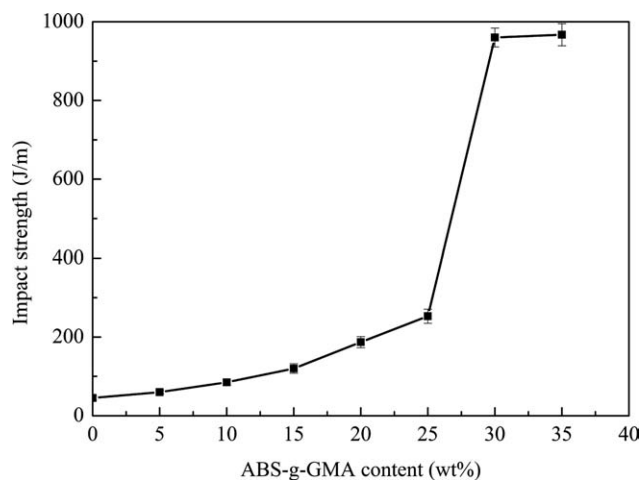


Figure 1 Effect of the ABS-g-MA content on the impact properties of the PA6 blends.

Izod impact strength of the PA6 blends was measured by a XJU-22 Izod impact tester (Chengde Tester Machinery Factory, Chengde, China) at 23°C according to the ASTM D 256. The tensile properties were measured with a universal tensile machine (Shimadzu AGS-H, Kyoto, Japan) with a crosshead velocity of 50 mm/min at room temperature according to ASTM D 638.

Morphological analysis

The dispersed phase morphology of the PA6 blends was characterized by scanning electron microscopy (SEM; model Japan JSM-5600, JEOL Ltd., Tokyo, Japan). The sample surface was cut at low temperature with a glass knife until a smooth surface was obtained. Then, the samples were etched with tetrahydrofuran for 5 h at room temperature to remove the dispersed phase and were coated with a gold layer for SEM observation.

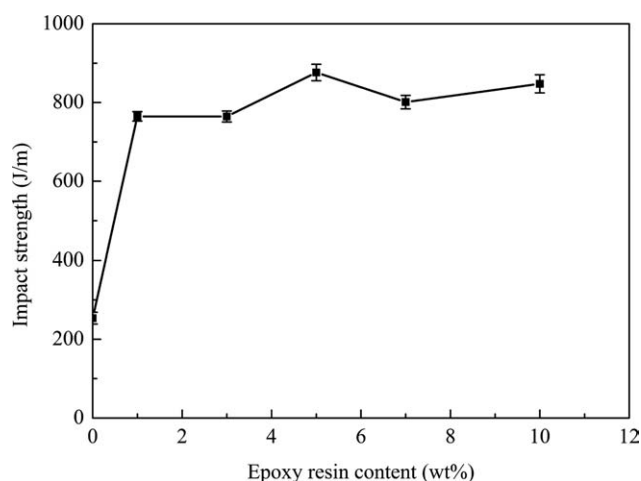


Figure 2 Effect of the epoxy resin on the impact strength of the PA6/ABS-g-MA blends.

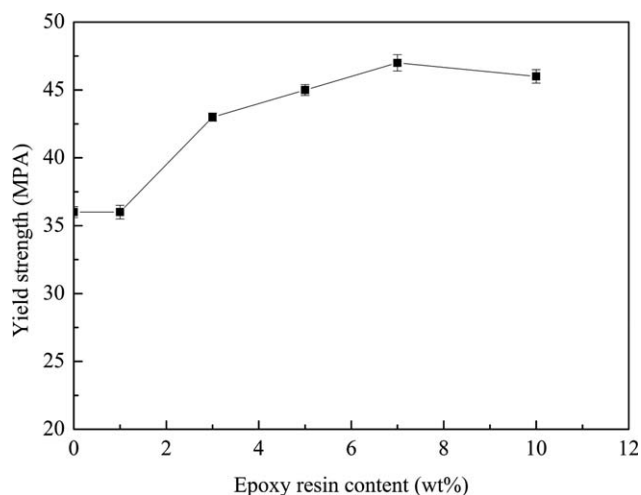


Figure 3 Effect of the epoxy resin on the yield strength of the PA6/ABS-g-MA blends.

The deformation morphology of the PA6 blends was observed by transmission electron microscopy (TEM; model Japan JEM-2000EX, JEOL Ltd., Tokyo, Japan). Ultramicrotomed sections were obtained with a Leica ultramicrotome (Wetzlar, Germany) at -100°C and stained with an OsO_4 solution for 8 h before observation.

RESULTS AND DISCUSSION

Mechanical properties

The relationship between the ABS-g-MA content and the notched impact strength of the PA6/ABS-g-MA blends is shown in Figure 1. Pure PA6 was a notch-sensitive polymer, and its notched Izod impact strength was only 30 J/m. The impact strength of PA6 was improved significantly by the ABS-g-MA copolymer. The brittle-ductile transition took place

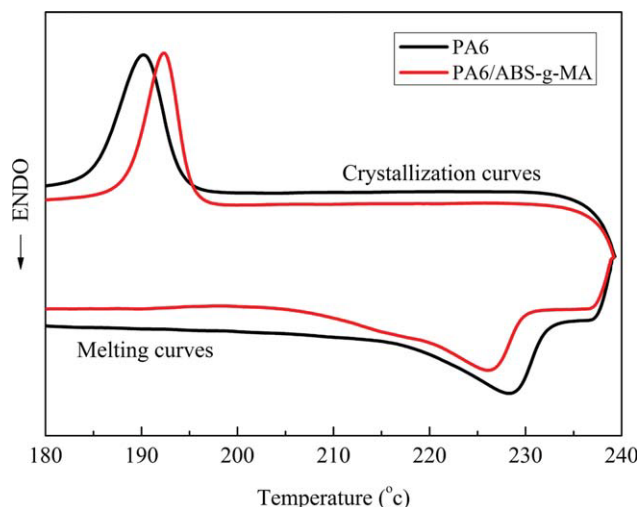


Figure 4 Thermal properties of the PA6 and PA6/ABS-g-MA blends. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

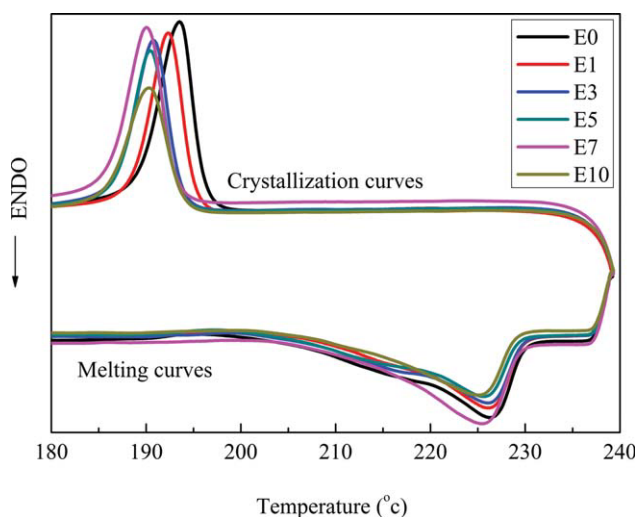


Figure 5 Effect of the epoxy resin on the thermal properties of the PA6/ABS-g-MA blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

when the ABS-g-MA content was between 25 and 30 wt %, and an impact strength of 960 J/m was achieved with the addition of 30 wt % ABS-g-MA. Shear yielding of the PA6 matrix and the cavitation of the rubber phase in ABS-g-MA were the major energy absorption modes. The ABS-g-MA particles in the PA6 matrix significantly relaxed the strong stresses developed in front of the notches and imparted ductility, so the toughness of PA6 was improved evidently.

As shown in Figure 1, the PA6/ABS-g-MA blends still fractured in brittle mode when the content of ABS-g-MA was lower than 25 wt %. Therefore, in the following part of the study, the content of ABS-g-MA was set at 25 wt % in the PA6/ABS-g-MA/epoxy resin blends, and the effects of the epoxy resin content on the properties of the blends were investigated in detail. The influence of epoxy resin on the toughness of the PA6/ABS-g-MA blends is shown in Figure 2. The addition of epoxy resin induced PA6/ABS-g-MA blend fracture from brittle way to ductile

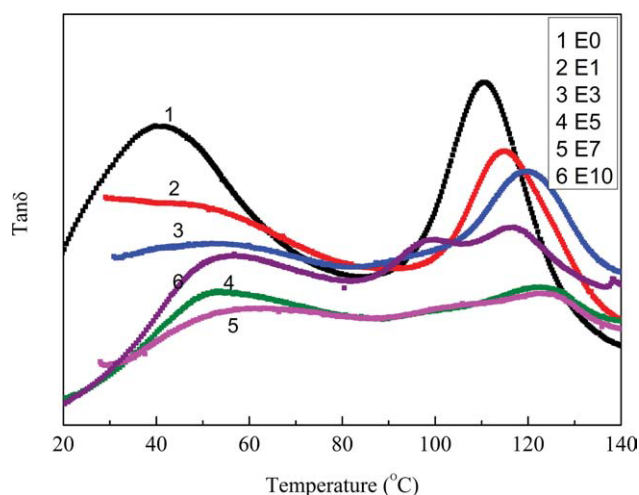


Figure 6 Effect of the epoxy resin on the dynamic mechanical properties of the PA6/ABS-g-MA blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mode, and a 1 wt % epoxy resin was sufficient to modify the fracture properties of the PA6 blends. The impact strength of PA6/ABS-g-MA was improved from 253 to 800 J/m. So from the impact test, we found that the epoxy resin had a positive effect on the mechanical properties improvement of the PA6/ABS-g-MA blends. Some reasons induced the toughness improvement of the PA6/ABS-g-MA blends with the addition of epoxy resin. First, the molecular weight of PA6 increased because of the chain-extension effect of the epoxy resin. In general, the inherent ductility, or the ability to be toughened, of the polymers increased with molecular weight. Second, for semicrystalline matrices such as PA6, the crystallization restraint increased the toughness because of the reactions in the PA6/ABS-g-MA/epoxy resin blends, as discussed in the thermal analysis part.

Figure 3 shows the influence of the epoxy resin on the yield strength of the PA6/ABS-g-MA blends. The yield strength of the PA6/ABS-g-MA blends was affected by the epoxy resin and increased with

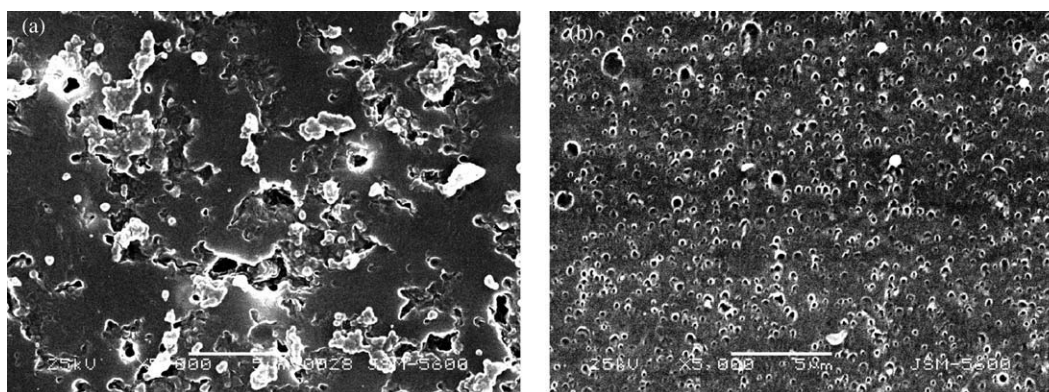


Figure 7 SEM phase morphology of (a) PA6/ABS and (b) the PA6/ABS-g-MA blends.

increasing epoxy resin content. The increasing yield strength was due to the chemical reactions between PA6, ABS-g-MA, and epoxy resin, as discussed in the following part. The addition of epoxy resin not only induced the improvement of toughness but also the stiffness of the PA6/ABS-g-MA blends.

DSC analysis

Figure 4 shows the thermal properties of PA6 and the PA6/ABS-g-MA blends. From the crystallization curves, we observed that compared with pure PA6, the crystallization temperature of PA6/ABS-g-MA shifted to higher temperature; this indicated that the crystallization ability of PA6 increased with the addition of ABS-g-MA because of the nucleation effect. As for the melting behavior, the melting temperature (T_m) of the PA6 phase in the PA6/ABS-g-MA blend shifted to a lower temperature compared with pure PA6; this indicated the improved compatibility between PA6 and ABS-g-MA according to the T_m depression criterion.^{28,29} The improvement of the compatibility between PA6 and ABS-g-MA was due to the chemical reactions between the amine groups of PA6 and the MA groups of ABS-g-MA; this has been used widely in other studies.

The influence of epoxy resin on the thermal properties of the PA6/ABS-g-MA blends is shown in Figure 5. From the crystallization curves, we found that the crystallization temperature shifted to a lower temperature with increasing epoxy resin content; this indicated that the addition of epoxy resin inhibited the crystallization process and was not beneficial to the crystallization of PA6. The reason was the chemical reactions between PA6, ABS-g-MA, and the epoxy resin. Chemical reactions between the carboxyl groups and amine groups of PA6 and epoxy groups of epoxy resins were used in some studies.^{4,30} The epoxy resin can act as a chain-extension agent; this induces an increase in the PA6 viscosity. On the other hand, some hydroxyl groups existed in the ABS-g-MA copolymer. The hydroxyl groups came from the preparation progress of ABS, as pointed out in a previous article.³¹ The epoxy resin could react with the hydroxyl groups of the ABS-g-MA and amine and carboxyl groups of PA6 to form the PA6-co-epoxy resin-co-ABS copolymer, which induced the increase in the viscosity of the PA6 blends and hindered the process of crystallization and crystal growth. As for the melting property, T_m shifted to a lower temperature with increasing epoxy resin content. This further proved that the compatibility between PA6 and ABS-g-MA was improved because of the chemical reactions.

DMA

The influence of the epoxy resin on the dynamic mechanical properties of the PA6/ABS-g-MA blends is

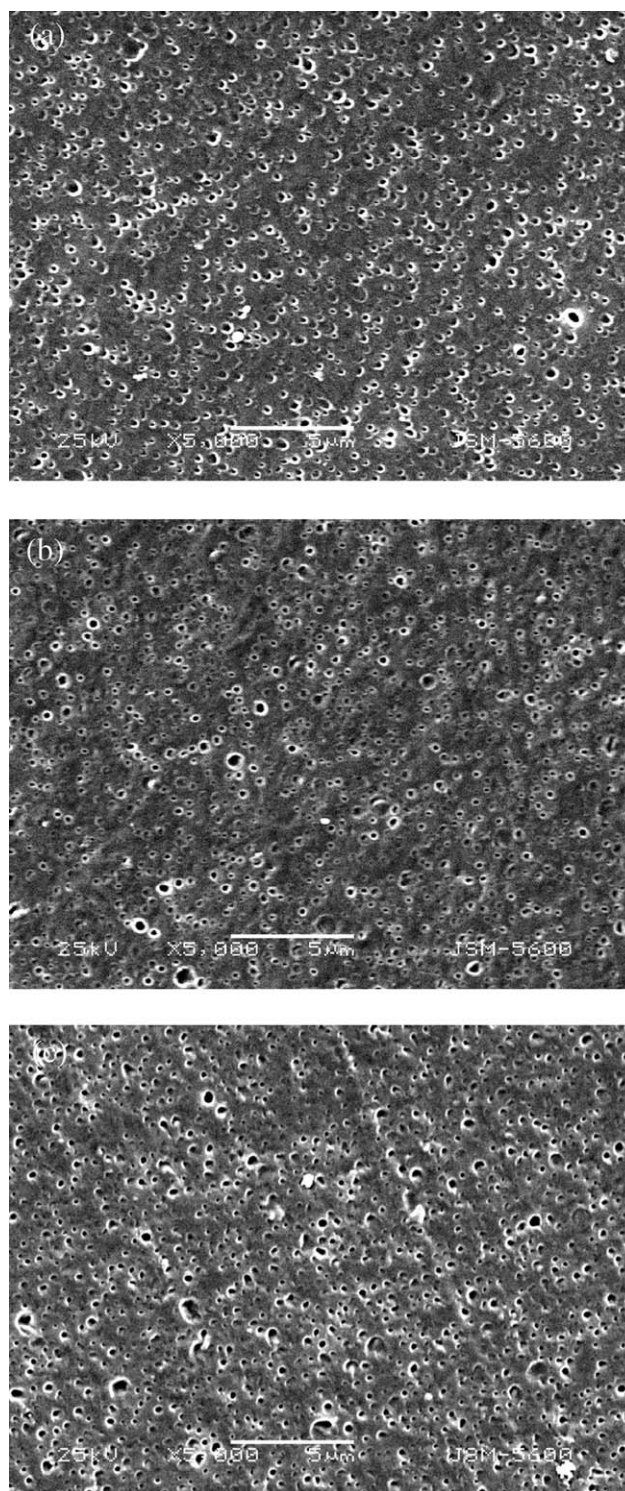


Figure 8 Effect of the epoxy resin on the SEM morphology of the PA6/ABS-g-MA blends: (a) PA6/ABS-g-MA/E1, (b) PA6/ABS-g-MA/E5, and (c) PA6/ABS-g-MA/E10.

shown in Figure 6. The glass-transition temperature (T_g) of the PA6 phase shifted to a higher temperature with the addition of the epoxy resin. The greater the content of the epoxy resin was, the higher the T_g was. There may have been two reasons that increased T_g of the PA6 phase. One was the improvement in the

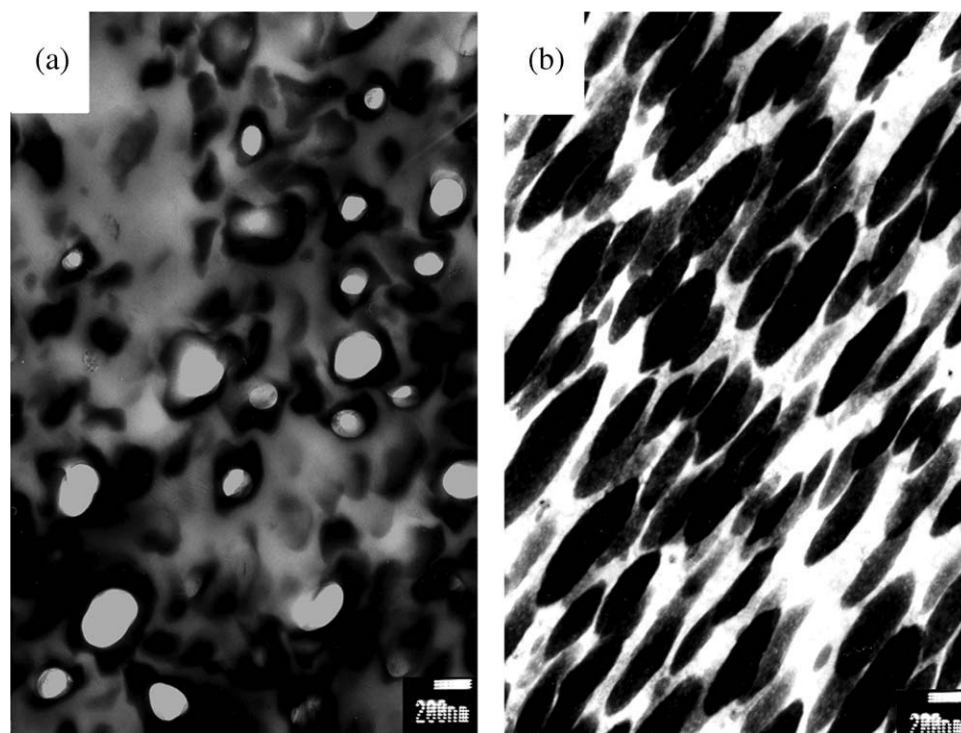


Figure 9 Deformation morphology in the stress-whitening zone of the PA6/ABS-g-MA/epoxy resin blend (a) parallel and (b) perpendicular to the fracture surface.

compatibility between PA6 and ABS-g-MA. The chemical reactions between the epoxy resin, PA6, and ABS-g-MA induced the formation of the PA6-co-epoxy resin-co-ABS; this resulted in the higher T_g of the PA6 phase and higher compatibility. The second reason may have been in the branching or crosslinking reactions between PA6 and the epoxy resin. The branching or crosslinking structure may have limited the movement PA6 chains and induced the shift of T_g to a higher temperature. As for the styrene-co-acrylonitrile copolymer (SAN) phase, the shell of the ABS-g-MA copolymer, T_g also shifted to a higher temperature with increasing epoxy resin content. The reason may have been the chemical reactions between the epoxy resin and the hydroxyl groups of ABS-g-MA. A high epoxy resin content could have induced the crosslinking reactions; this has been discussed in other articles.^{31,32} The crosslinking reactions limited the movement of the SAN chain and induced the increase in T_g .

Morphology

Figure 7(a) presents the morphology of the PA6/ABS blend. When ABS was mixed with PA6, a very poor dispersion of ABS particles was obtained. In this blend, most of the ABS particles clustered together, which indicated the poor compatibility of PA6 and ABS. Figure 7(b) displays the SEM micrograph of the PA6/ABS-g-MA blend. In this blend,

the coalescence of ABS particles was depressed, and ABS particles dispersed in the PA6 matrix uniformly. The better spatial distribution of ABS-g-MA identified the compatibilization effect of the PA6-co-ABS copolymer.

Figure 8 shows the SEM morphology of the PA6/ABS-g-MA blends with the addition of epoxy resin. As shown in Figure 8, the ABS-g-MA copolymers dispersed in PA6 matrix uniformly, and no agglomeration took place. The change in the epoxy resin content had almost no effect on the SEM morphology of the PA6/ABS-g-MA blends; this was consistent with the mechanical properties of the PA6 blends, as shown in Figure 2.

Deformation mechanism

The shear yielding of the PA6 matrix and the cavitation of rubber particles were the major toughening mechanisms of the PA6/ABS blends, as examined in a previous study.⁴ In this study, TEM was used to examine whether the addition of epoxy resin affect the deformation mechanisms of the PA6 blends. Figure 9(a) shows the deformed morphology in the stress-whitening zone parallel to the fracture surface. The polybutadiene (PB) phase of ABS-g-MA was stained black. Some white cavities existed in the PB particles, which indicated that the cavitation of the PB phase took place. Figure 9(b) shows the deformed morphology in the stress-whitening zone

perpendicular to the fracture surface. The black PB particles were remarkably elongated, and obvious deformation of the PB particles was observed; this indicated that the shear yielding of the PA6 matrix took place. The shear yielding was initiated by the stress concentration associated with rubber particles; consequently, the cavitation of the rubber particles released the hydrostatic tensile stress and encouraged the shear yielding to proceed. The TEM results showed that the deformation mechanisms of the PA6 blends were not influenced by the addition of the epoxy resin.

CONCLUSIONS

Epoxy resin improved the toughness and stiffness of the PA6/ABS-g-MA blends. The DSC results indicated that the crystallization ability of PA6 decreased and the compatibility between PA6 and ABS-g-MA improved because of the chemical reactions between PA6, ABS-g-MA, and the epoxy resin. DMA tests showed that the chemical reactions between the epoxy resin, PA6, and ABS-g-MA induced the formation of PA6-co-epoxy resin-co-ABS, which achieved a higher T_g of PA6 and a higher compatibility. The crosslinking reaction between the epoxy resin and the hydroxyl groups of ABS-g-MA induced the T_g of SAN phase to shift to a higher temperature. SEM and TEM indicated that the addition of the epoxy resin did not change the phase morphology or the deformation mechanisms of the PA6/ABS-g-MA blends.

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