

# Studies on Polyamide-6/Polyolefin Blend System Compatibilized with Epoxidized Natural Rubber

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**ABSTRACT:** Infrared spectra of polyamide-6 (PA6) with and without epoxidized natural rubber (ENR) are presented. The influence of ENR used as a compatibilizer on the morphologies, crystallizability, mechanical properties, and thermal behavior of the polyamide-6/polyolefins (PO) blends are studied. The infrared spectra suggest that under normal processing conditions, the carboxyl end groups of PA6 could chemically react *in situ* with the epoxy groups of ENR, and ester groups are created. This means that the PA6-ENR grafting copolymer could be obtained during processing. All the morphological characterizations and thermal analyses

show that the compatibility of PA6/PO blends is obviously improved by ENR because the copolymer increases the interaction between PA6 and PO. It is also found that the toughness of PA6/PO blends increase significantly after using ENR, while the tensile strength and the softening temperature of PA6/PO blends have almost no change. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 398–403, 2003

**Key words:** epoxidized natural rubber; polyamide-6; polyolefin; blend; grafting copolymer; compatibility

## INTRODUCTION

The toughness of nylon, including the dry-state and low-temperature impact strength, can be greatly improved by blending polyamide-6 (PA6) with polyolefins (PO) such as polypropylene (PP) or polyethylene (PE). On the other hand, PP and PE have outstanding impact strength and good processability, while PA6 has high thermal resistance and mechanical properties. Hence, addition of certain amount of polyolefins to PA6 can generate a cheaper material to meet the engineering requirement. Therefore, the PA6/PO blend system has become an important field for study and has attracted great attention.<sup>1–10</sup> Because PA6 is incompatible with PO thermodynamically due to a great difference of molecular structure between them, the key to the study is to find suitable compatibilizers to modify the interfaces of the blend. Using small molecular compatibilizers, the tensile strength and heat resistance of materials usually decreased by a big margin. Recently, the grafting copolymers generated from free-radical reactions between polyolefins and

maleic anhydride or acrylic acid were mostly used as the compatibilizers.<sup>4–8,11,12</sup> However, the free-radical reactions were difficult to control and the crosslinking products that may impair the compatibilization were generally created during the reaction period.<sup>8,10,13,14</sup> In this study, the commercial epoxidized natural rubber (ENR) was chosen as a macromolecule improving agent for enhancing the compatibility of PA6/PO blends, and its effect on the crystallizability, mechanical properties, and thermal behavior of the PA6/PO blends was introduced.

## EXPERIMENTAL

### Materials

PA6 was obtained from Heilongjiang Nylon Factory (China). It is Type II and its relative viscosity is 3.0. Approximately, there is a carboxyl group per chain. Homopolypropylene (PP, F401) and commercial chips of ethylene-propylene-diene terpolymer (EPDM) were obtained from Lanzhou Chemical Industrial Co. (China). ENR was supplied by Institute of Tropical Farm Product in South China, with an extent of epoxidation of 50% of the double bonds in natural rubber.

### Blending

The bulk ENR was plasticated using a double-roll rubber-plasticating machine at room temperature for

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10 min, and then cut into granules with a hand cutter. Sequentially, PA6 previously dried at 90°C for 15 h, was compounded with the ENR granules in an internal mixing machine under 230°C for 10 min and cut into granules with a plastics chopper. Then the mixture of PP and the PA6/ENR granules was blended in a twin-screw extruder to obtain the PP/PA6/ENR blends in which polypropylene forms the matrix. The extruding conditions were as follows: temperature from hopper to die: 170, 220, 230, and 220°C, respectively; diameter of the screws: 25 mm; length to diameter (L/D) ratio: 33; rotation: 60 rpm. The blends were extruded through a rod die and pelletized, and finally injection molded into test specimens on a reciprocating screw injection molding machine. For getting the PA6/EPDM/ENR blends in which polyamide-6 forms the matrix, EPDM and ENR were first plasticated together on a double-roll rubber-plasticating machine at room temperature and cut into granules with a hand cutter; then the mixture of dried PA6 and the EPDM/ENR granules was blended in a twin-screw extruder, where conditions were the same as the preceding ones, and pelletized. Finally, the blends were injection molded into test specimens.

### Test

#### Fracture toughness

Chinese standard GB1843-80 was used for notched Izod impact strength testing at room temperature. The thickness of the specimens was 4 mm.

#### Tensile strength

Chinese standard GB1040-79 was used for tensile yield strength testing at room temperature. The crosshead speed was 50 mm/min and the thickness of the specimens was 4 mm.

#### Softening temperature

Chinese standard GB1633-79 was used for Vicat softening point testing. The size of the specimens was 4 × 20 × 20 mm. The testing conditions were as follows: load: 1000 g; heating rate: 2°C/min.

### Characterization of structure

#### Thermal analysis

The thermal properties and crystalline behavior of PA6/EPDM/ENR were determined by a Perkin-Elmer 7 differential scanning calorimeter (DSC). Samples were heated to 260°C at a 10°C/min scanning rate and held at that temperature for 5 min, followed by cooling to 30°C at 5°C/min scanning rate. The melting point and the melting enthalpy of PA6 in the blends

were recorded. The crystallinity of PA6 in the blends could be calculated by following equation:

$$X_c = (\Delta H_x / \Delta H_0) \times 100\%$$

where  $\Delta H_x$  was the melting enthalpy of PA6 in the blends.  $\Delta H_0$  was the melting enthalpy of PA6 of 100% crystallization, using 182.9 J/g.<sup>15</sup>

#### Infrared spectrum analysis

The PA6/ENR blends were obtained by mixing ENR and PA6 with a 1:1 weight ratio in the internal mixing machine under 230°C for 5 and 20 min, respectively. Some samples were treated for 5 days by immersing and steeping their granules in a large volume of saturated CaCl<sub>2</sub> methanol solution, in which the solubility of PA6 molecule in methanol was increased by CaCl<sub>2</sub>. Then the remains were washed and steeped with sufficient distilled water repeatedly. Finally, the FTIR spectra of all the samples after drying were measured on a Perkin-Elmer Paragon 1000 spectrometer at a resolution of 4 cm<sup>-1</sup>.

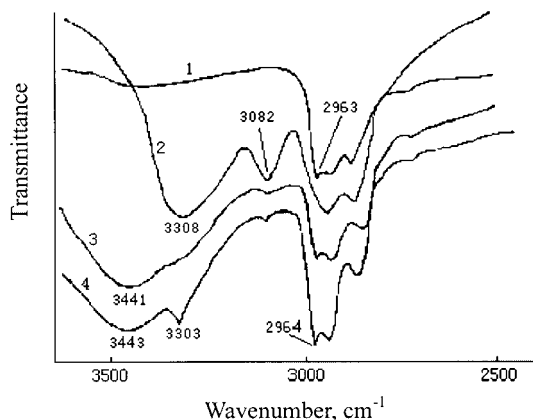
#### Morphological characterization

The samples were directly fractured after being frozen in liquid nitrogen for 40 min. The fracture surfaces for observation were made conductive by the deposition of a layer of gold in a vacuum chamber. A JSE-5900LV scanning electron microscope (SEM) was used to examine the differences in morphologies of the surfaces.

## RESULTS AND DISCUSSION

### The molecular structures and the morphologies of the blends

Generally, one material that has a strong interaction with both PA6 and PO can improve the compatibility of PA6/PO blends. The main chains of natural rubber have many nonpolar hydrocarbon segments, which have partial structural similarity with the molecules of PO, and thus have strong interaction with PO molecular chains but very weak interaction with PA6 composed of strong polarity chains. For this reason, it should first be considered how to improve the interaction between natural rubber and PA6 molecular chains if using nature rubber as the compatibilizer of PA6/PO blends. Natural rubber can be partially epoxidized to become ENR. It has been noted that the epoxy groups introduced in the ENR chains have a certain polarity and can improve the adhesion between rubber and PA6. Furthermore, the epoxy groups have the possibility to chemically react with the carboxyl groups and amine groups of PA6. The products generated from this reaction will greatly en-



**Figure 1** FTIR spectra of PA6/ENR blends and their components in the high frequency zone. (1) ENR treated by saturated  $\text{CaCl}_2$  methanol solution. (2) Nontreated PA6. (3) Nontreated PA6/ENR. (4) PA6/ENR treated by saturated  $\text{CaCl}_2$  methanol solution.

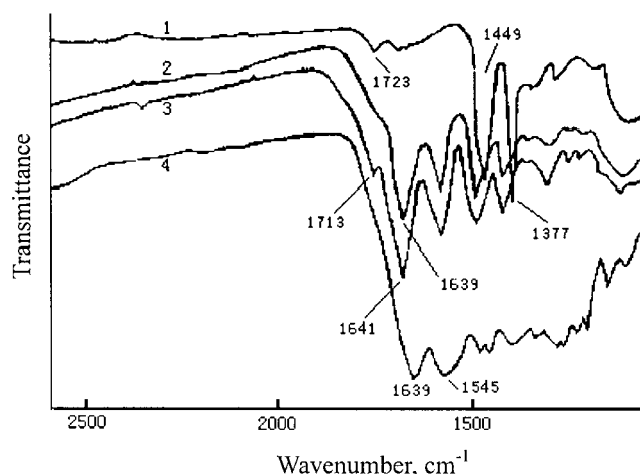
hance the interaction between PO and PA6 if this reaction is controlled effectively under suitable conditions, especially the conditions suitable for the processing of the polymer materials. For this purpose, PA6, ENR, and the PA6/ENR blends (mixed under  $230^\circ\text{C}$ ) have been investigated by infrared spectrum analysis here. To characterize the products reacted between PA6 and ENR clearly, some samples were digested in saturated  $\text{CaCl}_2$  methanol solution at room temperature for a period of time to remove an amount of nonreacted PA6 molecules from the samples and to increase the ratio of reacted products in the samples.

The infrared spectra of PA6/PO blends and their neat component in the high wavenumber zone above  $2500\text{ cm}^{-1}$  are shown in Figure 1. It can be seen clearly that both the neat PA6 (curve 2) and ENR (digested and used as the reference for the digested blend for eliminating the influence of the solution, curve 1) have no obvious absorption band at  $3450\text{ cm}^{-1}$ ; but the PA6/ENR blends are quite different from their neat component. The nondigested PA6/ENR blend has a strong absorption band at about  $3440\text{ cm}^{-1}$  in Fourier transform infrared (FTIR) spectrum (curve 3) and the digested PA6/ENR blend also has similar strong absorption band at about  $3440\text{ cm}^{-1}$  (curve 4), which presumably resulted from the fact that there are new groups inside the PA6/ENR blend, and a chemical reaction could have taken place between PA6 and ENR or between the epoxy group and  $\text{H}_2\text{O}$ .

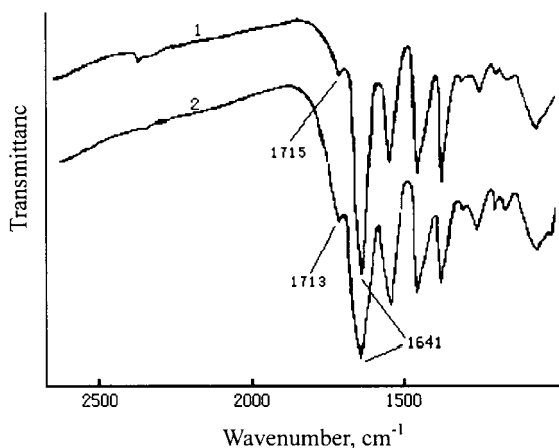
The infrared spectra of the samples of the PA6/ENR blend and its neat components below  $2500\text{ cm}^{-1}$  are shown in Figure 2. It was found that the bending vibration band of the  $-\text{C}-\text{H}$  bond in natural rubber at  $1449\text{ cm}^{-1}$  is the major absorption band of digested ENR (curve 1), the strongest absorption bands of PA6 are the flexible vibration band of the  $-\text{C}=\text{O}$  bond in the acyl amine group at  $1639\text{ cm}^{-1}$  and the bending

vibration band of the  $-\text{N}-\text{H}$  bond in the amide group at  $1545\text{ cm}^{-1}$  (curve 4). As PA6 can absorb the infrared spectrum strongly, it is difficult to clearly observe the tiny change of the spectrum of the nondigested PA6/ENR blend near its strong absorption band (curve 2), but observing the infrared spectrum of digested PA6/ENR blend, near the strongest absorption band of PA6 at  $1641\text{ cm}^{-1}$ , an absorption band of  $1713\text{ cm}^{-1}$  occurs clearly (curve 3). Once again, by observing the spectrum of the single component of the blend, PA6 and ENR, it can be seen that there is no absorption band with such strength in this wavenumber zone. In addition, the reaction products of epoxy groups and  $\text{H}_2\text{O}$  (similar to polyvinyl alcohol) had no marked absorption band about the zone. It is shown that a most probable chemical reaction happened between the carboxyl groups of PA6 and the epoxy groups of ENR in the blend to produce ester groups since the position of this absorption band is just fit with the flexible vibration band of the  $-\text{C}=\text{O}$  bond in ester group.

In general, the quantity of chemical reaction products is directly related to the reaction time under other similar reacting conditions. Figure 3 shows the infrared spectra of the PA6/ENR blends mixed at  $230^\circ\text{C}$  for different times. By comparing the sample mixed for 20 min (curve 2) with the one mixed for 5 min (curve 1), it is obvious that the former has a much stronger absorption band at about  $1713\text{ cm}^{-1}$  than the latter, although they both had the same components and composition, and both underwent the same treatment. This means that, during this mixing period, the quantity of the products generated from the chemical reaction was increased as long as the increase of mixing time and more ester groups could be formed. This fact additionally supports the existence of a chemical reaction between PA6 and ENR during mixing process.



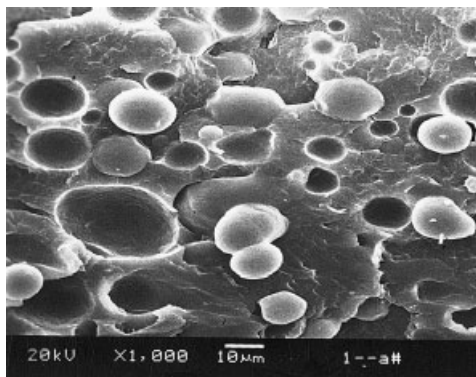
**Figure 2** FTIR spectra of the PA6/ENR blend and its components. (1) ENR treated by saturated  $\text{CaCl}_2$  methanol solution. (2) Nontreated PA6/ENR. (3) PA6/ENR treated by saturated  $\text{CaCl}_2$  methanol solution. (4) Nontreated PA6.



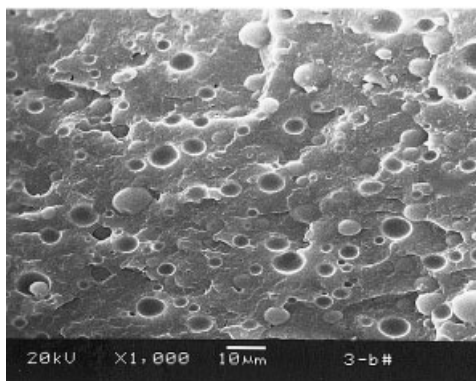
**Figure 3** FTIR spectra of the PA6/ENR blends mixed for different times. (1) PA6/ENR treated by saturated CaCl<sub>2</sub> methanol solution (mixed for 5 min). (2) PA6/ENR treated by saturated CaCl<sub>2</sub> methanol solution (mixed for 20 min).

Therefore, it can be concluded that under certain conditions (such as the high temperature for processing of polymers) the carboxyl groups at the end of PA6 macromolecules could react *in situ* with the epoxy groups of ENR and open the epoxy rings to form the PA6/ENR grafting copolymer (see Scheme 1). Such a PA6-ENR grafting copolymer has not only a very strong interaction with PA6 phase through the pendant polar polyamide chains but also good adhesion with polyolefin through the nonpolar hydrocarbon chain segments of ENR. This copolymer can enhance the adhesion between PA6 and PO, thus improving the compatibility of PA6/PO blends.<sup>4,11,16,17</sup>

Figure 4 shows the morphologies of the PA6/EPDM (80/20) blend and the PA6/EPDM/ENR (80/15/5) blend. It can be seen from scanning electron micrographs of the fracture surfaces of the blends that there was a remarkable rubber-particle size reduction in the



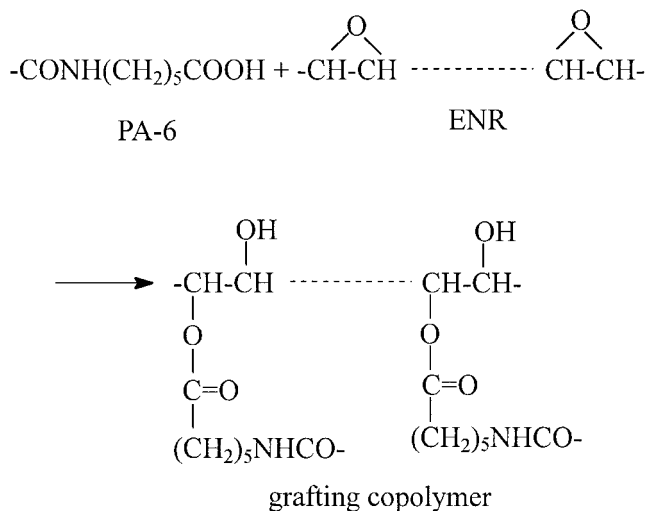
(a)



(b)

**Figure 4** Scanning electron micrographs of the frozen fracture surfaces. (a) PA6/EPDM (80/20); (b) PA6/EPDM/ENR (80/15/5).

PA6/EPDM/ENR blend. With the same rubber content (20 wt %) in the blends, the particles of the blend only with the EPDM had diameters of 3 ~ 20 μm (most of them were bigger than 10 μm), while the ones of the blend with the mixed rubber of ENR and EPDM had diameters of 1 ~ 10 μm (most of them were less than 3.5 μm). This shows ENR improved the compatibility of PA6/EPDM and supports the arguments that the ENR reacted with PA6. The interest of the reaction is also that it provides a simple way of compatibilization without using free-radical initiators and inhibits the crosslinking reaction.



**Scheme 1** Esterification of PA-6 with ENR.

**The influence of ENR on the crystallization of the blends**

Table I shows the DSC test results for the PA6/EPDM (80/20) blend and the PA6/EPDM/ENR (80/15/5) blend. It can be seen that when a small quantity of EPDM is replaced by ENR, the melting temperature (melting point) during rising temperature, and the crystalline temperature during reducing temperature of PA6 in the PA6/EPDM/ENR blend were somewhat low in comparison with those of the PA6/EPDM

**TABLE I**  
Data Obtained from DSC Analysis of the Blends

Specimen	Melting point (°C)	Temperature of crystal peak (°C)	Converted crystal enthalpy (J/g)	Crystal enthalpy (J/g)	Crystallinity (%)
PA6/EPDM (80/20)	228.3	194.9	64.4	62.6	35.2
PA6/EPDM/ENR (80/15/5)	227.2	193.6	62.5	58.6	34.0

blend; at the same time, its converted crystal enthalpy (melting enthalpy) and crystal enthalpy were reduced obviously too. This shows that addition of ENR in the mixing process can surely improve the compatibility of the PA6/EPDM blend, i.e., strengthen the adhesion between PA6 and rubber phase, impede the movement and arrangement of PA6 molecule chains during crystal process, and decrease the crystallinity of PA6. These results have the reasonable relationship with the effect of the PA6/ENR grafting copolymer generated from the chemical reaction between ENR and PA6.<sup>13,17</sup>

#### The influence of ENR on the properties of the blends

For determining whether the ENR with its copolymer has a compatible effect on PA6/PO blends, the ENR was added separately into the blends in which the PA6 and PO were the matrix, respectively, to explore the changes of the mechanical properties and the thermal behavior.

Table II shows the mechanical properties and heat resistance of PA6/EPDM/ENR blends with different components and compositions. It is clear that the tensile yield strength and Vicat softening point of materials had been reduced after the EPDM was added into PA6, and the more the EPDM was used, the larger the range of reduction would be, whereas the notched Izod impact strength was increased accordingly. When keeping the rubber (EPDM plus ENR) content in the blends constant (20 wt %), by comparing with the blend only with the EPDM, the properties of the blends had been improved obviously when using the mixed rubber of ENR and EPDM. In particular besides their tensile yield strength and Vicat softening point rising back notably, the notched Izod impact strength

had also been increased by a wide margin based on the 20% EPDM enhancing the impact strength of PA6. It was twice as high as the impact strength of PA6, up to 14 kJ/m<sup>2</sup>. This indicates that ENR has a significant toughening effect. Furthermore, it should be noted that the ENR not only replaced partial EPDM but also played the role of the compatibilizer for PA6/EPDM blends. It distributed itself between PA6 and PO, and adhered to each of the blend components. Using the ENR as the compatibilizer had the advantage of reducing the loss of the tensile strength and Vicat softening point of the blends even, probably, improving these properties especially when compared to the small molecule compatibilizer, which could cause the tensile strength and heat resistance of blends to drop down notably.

In addition, the changes of the mechanical properties of PP/PA6/ENR blends that took polyolefin as the matrix are shown in Table III. It was found that after adding PA6 into PP, the tensile strength and notched Izod impact strength had been reduced greatly. The reason is that the compatibility between polar PA6 and nonpolar PP becomes worse, their blends belong to the extremely incompatible system, the adhesion between the two blend components is very weak, and serious phase-separation occurs.<sup>16</sup> By adding ENR into PP/PA6 blends again, the properties of the blend had a slight increase. The effect of ENR on the improvement of the notched Izod impact strength for PP/PA6 blends was not as effective as that on PA6/EPDM blends. It was probably involved with its molecular structure features. The ENR chosen here had high extent of epoxidation in order to increase the active points with PA6. This caused the nonpolar hydrocarbon chain segments in ENR becoming shorter and less; therefore, the interaction to PP became con-

**TABLE II**  
Influence of ENR on the Properties of PA6/EPDM Blends

PA6/EPDM/ENR (by weight ratio)	Notched Izod impact strength (kJ/m <sup>2</sup> )	Tensile strength (MPa)	Vicat softening point (°C)
100/0/0	6.1	63	217
90/10/0	8.8	49	215
80/20/0	9.9	37	211
80/18/2	11.6	41	212
80/15/5	13.8	43	215

**TABLE III**  
**Influence of ENR on the Properties of PP/PA6 Blend**

PP/PA6/ENR (by weight ratio)	Notched Izod impact strength (kJ/m <sup>2</sup> )	Tensile strength (MPa)
100/0/0	17.5	27
80/20/0	6.3	19
80/20/2.5	7.1	20
80/20/5	7.8	20

strained. This shortcoming can be remedied by balancing and adjusting the ENR molecule structure and by improving the efficiency of the chemical reaction. Even so, the influence of ENR on the tensile strength of PP/PA6 blends was quite different from the obvious dropping of the rigid polymer material's strength caused by general elastomers. In this case, when adding elastic ENR into rigid PP/PA6 blends, the tensile yield strength of materials had no change or even a little improvement. This means that the ENR had taken the role of linking the two major components, increasing the adhesion between each other and improving the compatibility of PP/PA6 blends. The increase of tensile strength by this effect was good enough to remedy the loss of material tensile strength caused by the introduced elastomer.

### CONCLUSIONS

PA6/PO blends had poor compatibility. The PA6/ENR grafting copolymer without using free-radical initiators could be formed *in situ* by adding ENR in PA6/PO blends during the mixing process to improve the compatibility of the blends obviously. Adding ENR in the experimental range could increase the impact fracture toughness without any harmful effect

on the tensile strength and heat resistance of PA6/PO blends.

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