

Morphology and Properties of PET/PA-6/E-44 Blends

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ABSTRACT: Polymer blends incorporating poly(ethylene terephthalate) (PET), polyamide-6 (PA-6), and a reactive compatibilizer (low molecular weight bisphenol-A epoxy resin—E-44) were prepared with the following E-44 weight percent concentrations: 0, 0.3, 0.6, 1, 3, 5, and 10. The samples were studied by a scanning electron microscope (SEM), a polarizing microscope (PLM), dynamic mechanical thermal analysis (DMTA), wide-angle X-ray diffraction (WAXD), a differential scanning calorimeter (DSC), infrared spectroscopy (IR), and mechanical testing. SEM and PLM showed noticeable changes in both the amorphous region and the crystalline region of the blends. The changes indicated better compatibility between the dispersed phase (PA-6) and the matrix (PET), which was further confirmed by the DMTA test. The WAXD showed that PET and PA-6 crystallized separately and no cocrystallite was found. The melting and crystallization data, obtained by DSC, suggested that the crystallization of the blend was blocked, although the hindered mechanism for the effect of E-44 on PET was different from that on PA-6. The notched impact strength and flexural strength of the PET/PA-6 blends were significantly improved when the content of E-44 was 5 wt % (improved about 500 and 400%, respectively). IR was used to study the reaction among E-44, PET, and PA-6. The result indicated that the grafting reaction and the crosslinking reaction occurred during melt blending. The obvious increase of mechanical properties and the reinforcing and toughening effect were attributed to the formation of the crosslinking net in the blend. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1505–1515, 1998

Key words: PET; PA-6; E-44; blends; reactive compatibilization

INTRODUCTION

Poly(ethylene terephthalate) (PET) is widely used as a thermoplastic material for the fabrication of molded objects and films. As an engineering plastic, it is injection-molded for various automotive industries and other applications. PET has good comprehensive properties, such as thermal resistance, chemical resistance, and electronic properties. However, its poor impact strength limits the

extensive application of PET as an engineering plastic. One of the most effective modifications of its drawbacks is to blend it with other polymers, that is, by polymer–polymer alloying techniques.

The importance of the interface in multiphase polymer systems has been long recognized. Physical and chemical interactions across the phase boundaries are known to control the overall performance of immiscible polymer blends. Strong interactions result in good adhesion and efficient stress transferring from the continuous phase to the dispersed phase in the blends. As a result of the recent interest in the melt processing of reactive systems (reactive extrusion, reactive injection

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molding), emphasis will be placed on the compound used in conjunction with such processes.

The PET/PA-6 blend will be a promising blend if it combines the rigidity of PET with the toughness of PA-6. Since PET/PA-6 blends without adding any compatibilizer has worse properties than those of neat PET or PA-6, considerable efforts are directed to the improvement of the compatibility or to the suppression of incompatibility. One main interest has been focused on polyesteramides obtained by the polycondensation of monomeric hydroxyamido acids or amino alcohols with diacid chlorides.^{1,2} Searches^{3,4} have shown that the blending of PET and PA in the melt produces polyester-polyamide block copolymers, which could improve the compatibility of the blends. Unfortunately, most studies seldom improved the mechanical properties of the blends. It was reported^{5,6} that the microfibrillar-reinforced composites of PET and PA-6 had good mechanical properties. But they are difficult to use in industry because of their long annealing process.

In this article, we used E-44 as a reactive compatibilizer to improve the compatibility of PET/PA-6 blends and to study its effect on the morphology and properties of PET/PA-6 blends. Also, we discuss the mechanism that can greatly improve the mechanical properties of the blends.

EXPERIMENTAL

Materials and Preparation of Blends

The materials used in this study included PET, PA-6, and epoxy resin E-44. All were commercial grades of PET (S082C; intrinsic viscosity: 0.82 ± 0.02 dL/g; density: 1.40 ± 0.01 g/m³; melting point: 248 ± 3.0 °C; acetaldehyde: <1 ppm). PET was supplied by the POLYPET Factory (Indonesia); PA-6, by Ube Industries Ltd. (Japan); and epoxy resin E-44 (low molecular weight), by the Shanghai Chemical Reagent Plant (China).

Before compounding, PET was dried at 120°C for 8 h in a vacuum oven; PA-6, at 80°C for 12 h in a vacuum oven; and epoxy resin E-44, at 120°C for 5 h. All the melt compounding of the blends was carried out in a roller mixer of the Brabender plasticorder Model XSS-300 (temperature range of 295 ± 2.0 °C, roller speed at 32 rpm, time for 5 min).

Measurement of Mechanical Properties

The notched charpy impact strength tests were carried out on a VEB Werkstoffriifmchimer Leipzig Biegnoinent (made in Germany) pendulum impact tester. Samples for notched charpy strength testing were prepared by mold pressing at 295°C under 25 MPa for 5 min and then cooled to ambient temperature. A sample size of $(55 \pm 1) \times (6 \pm 0.2) \times (4 \pm 0.2)$ mm³ with a notch depth of one-third of the thickness and a notch width of 0.8 mm was made. Before measurement, the samples were equilibrated under ambient conditions for at least 24 h. The reported data were the average values of five to seven measurements. The flexural strength, measured on a Instron universal tester Model 1211 using three-point bending, was 7 cm. Five samples were tested in each case, and the average value was reported. All the tests were performed at ambient temperature.

Scanning electron micrographs of freezing fracture surfaces, which were etched by 50°C formic acid to remove the PA-6 phase, and impact fracture surfaces were studied on a Hitachi S-570 scanning electron microscope. In preparation for the etched samples, a small rectangular strip of each sample was frozen in liquid nitrogen for 10 min. Prior to examination, all the fracture surfaces were made conductive by the deposition of a layer of gold in a vacuum chamber.

Polarizing micrographs were recorded by an Olympus BH-2-type polarizing microscope. The samples were isothermally crystallized at 150°C for 2 h.

Thermal analysis was done with a differential scanning calorimetry (DSC) instrument (Pekin-Elmer, DSC-7). All samples were melted at 295°C for 3 min and then quenched on an ice face. The samples were heated from 25 to 300°C at a rate of 10°C/min in a nitrogen atmosphere to obtain the heating curves and were held at 300°C for 2 min and subsequently cooled at the same rate to 25°C to obtain the cooling curves.

Dynamic mechanical thermal analysis was carried out using a Rheovibron-DDV-II-EA-type viscoelasticimeter with temperature ranging from -150 to 200°C at a frequency of 110 Hz and heating rate of 3°C/min. Wide-angle X-ray diffraction (WAXD) was recorded using a Rigaku D/max-3A-type X-ray diffractometer with nickel-filtered CuK α radiation. Prior to measurement, the samples were melted and crystallized isothermally at

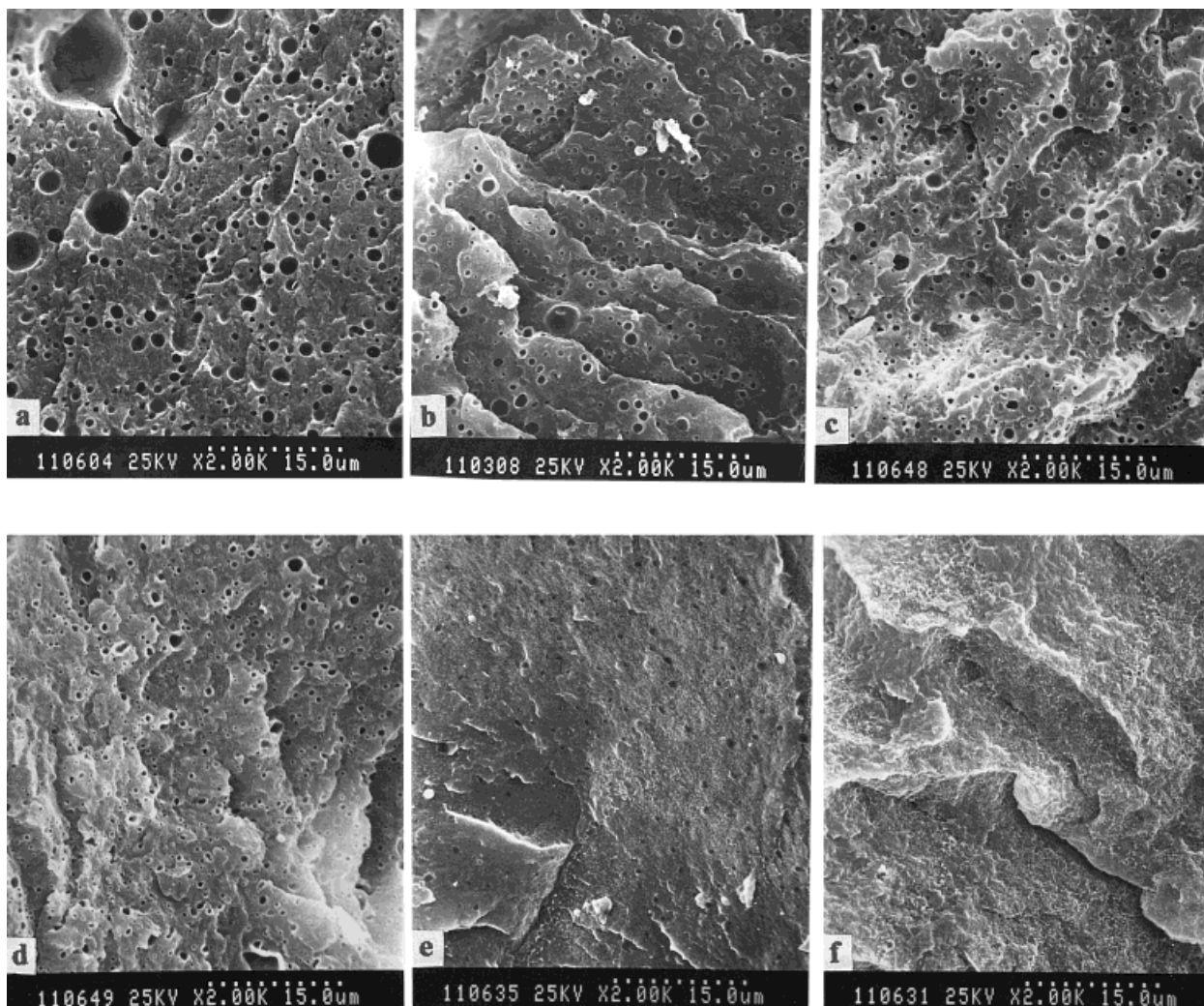


Figure 1 SEM micrographs of freezing fracture surfaces of PET/PA-6/E-44 blends. E-44 content (wt %): (a) 0; (b) 0.6; (c) 1; (d) 3; (e) 5; (f) 10.

150°C for 2 h. The infrared (IR) spectra were recorded on a Nicolet Model 205 spectrophotometer.

RESULTS AND DISCUSSION

PET/PA-6 Blends Morphology and Compatibility

The morphology and compatibility of PET/PA-6 blends with or without epoxy resin E-44 were studied by scanning electron microscopy (SEM), polarizing microscopy (PLM), and dynamic mechanical thermal analysis (DMTA).

SEM

Figure 1 shows the SEM micrographs of the freezing fracture surfaces of PET/PA-6 blends, which

were etched by 50°C formic acid to remove the PA-6 phase. The addition of a small quantity of E-44 to the PET/PA-6 blends resulted in remarkable changes in the morphology of the blends. Two-phase morphology is observed on the etched surface of the PET/PA-6 blend without E-44. PA-6 disperses in a spherical shape in the continuous phase of PET. There is no evidence of adhesion between the minor phase and the matrix, since the cavities of the PA-6 particles are perfectly clear and smooth. This shows that PET and PA-6 are incompatible by simply blending. When 0.3 wt % E-44 was added, substantial morphological changes occurred. It can be seen that the dimensions of the dispersed PA-6 domains have decreased obviously and the PA-6 phase has a more uniform distribution.

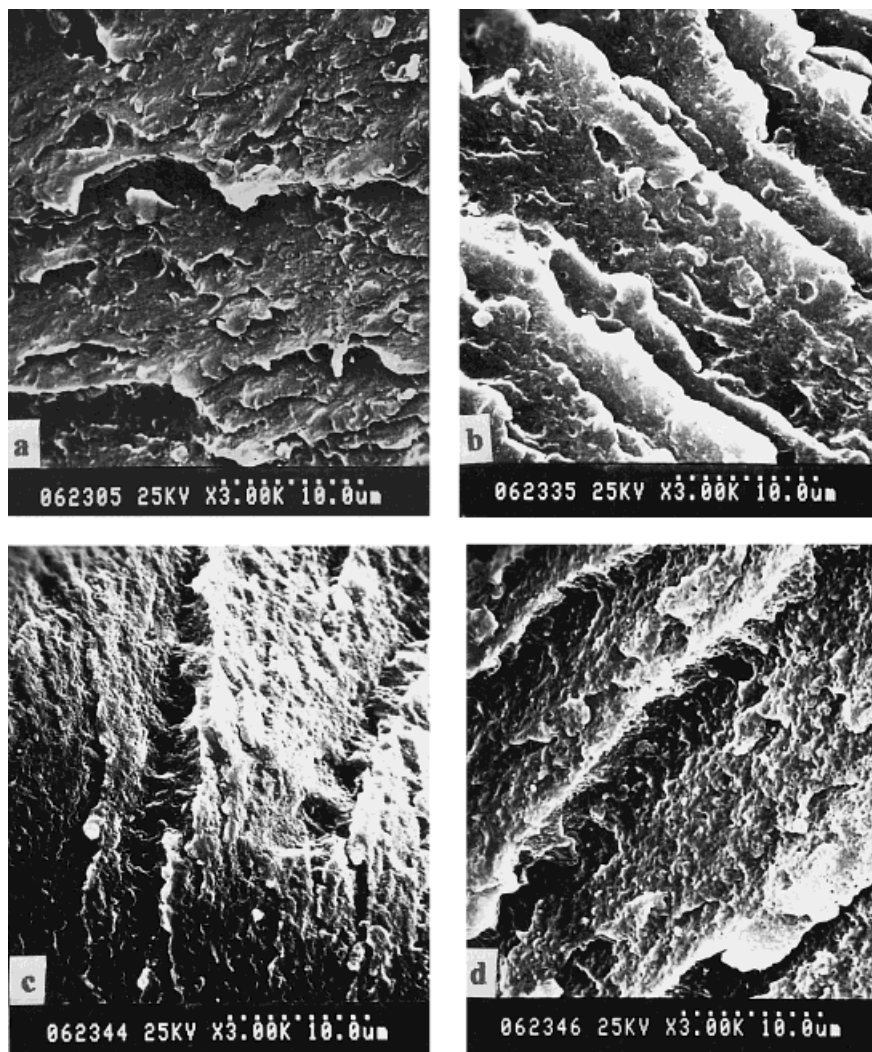


Figure 2 SEM micrographs of impact fracture surfaces of PET/PA-6/E-44 blends. E-44 content (wt %): (a) 0; (b) 1; (c) 5; (d) 10.

Figure 2 shows SEM micrographs of the impact fracture of the blends, which indicates the same change as above. When the content of E-44 reached 5 wt %, a ductile type of fracture is observed on the surface of the blends, which suggests a good interfacial adhesion and predicts a better impact strength.

PLM

Polarizing micrographs are used to study the morphology of the crystalline phase. PET and PA-6 are semicrystallizing polymers. Figure 3 shows that the morphology of the crystalline phase varied tremendously on adding even a small quantity of E-44. There is no obvious separ-

rating between the two crystalline phases when the content of E-44 reached 1 wt %. The size of the crystalline phase decreases and the distribution becomes more uniform. These phenomena show that the compatibility or interfacial adhesion between the crystalline phase of PET and that of PA-6 are enhanced on addition of E-44.

DMTA

DMTA is used to determine the miscibility of the blends by investigating the variation of the glass transition temperature (T_g) of the blend components. Figure 4 shows the dynamic modulus–temperature curves of the PET/PA-6 blend and the PET/PA-6 blends containing epoxy resin E-44. All

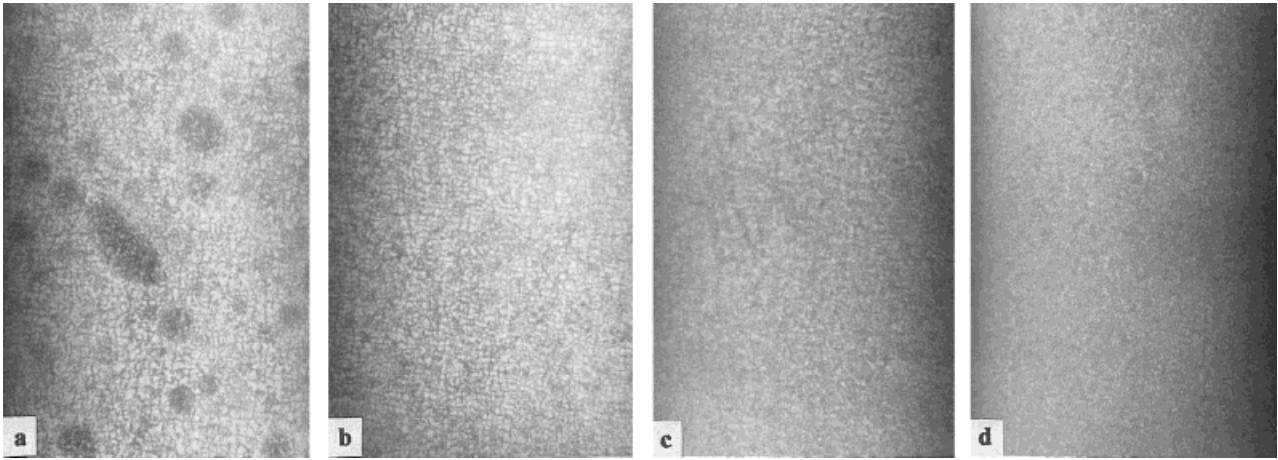


Figure 3 PLM micrographs of PET/PA-6/E-44 blends. E-44 content (wt %): (a) 0; (b) 0.3; (c) 0.6; (d) 1.0.

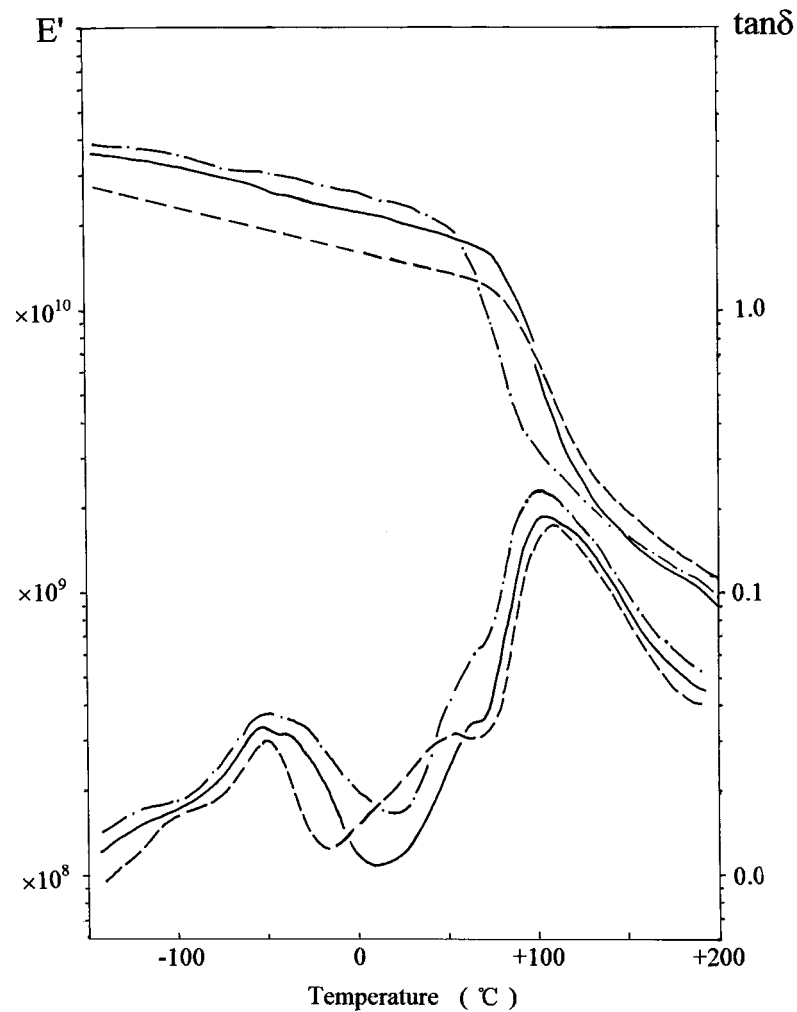


Figure 4 Dynamic modulus-temperature curves of PET/PA-6/E-44 blends: (-----) PET/PA-6; (—) PET/PA-6/E-44 (1 wt %); (-·-·-) PET/PA-6/E-44 (5 wt %).

Table I Angular Positions of the Reflections for PET and PA-6 (Refs. 8 and 9)

Sample	2θ (°)							
PET	16.2	17.2		21.7	22.7		26.0	32.4
PA-6			19.8			23.5		

three $\tan \delta$ - T curves show two obvious glass transition peaks, which confirm the presence of two phases. The peak at about 110°C is the glass transition peak of PET, while the glass transition peak of PA-6 is at 50–60°C. It is evident that the α -peak of PA-6 moves toward high temperature while the α -peak of PET moves to low temperature with increasing content of E-44. It indicates that the compatibility of the two phases (PET and PA-6) is improved. On the other hand, the broadening on the high-temperature side of the α -peak of the PET reflects that the PET amorphous region is more bound due to the presence of epoxy resin E-44. This phenomenon suggests that there is a stronger interfacial adhesion in the system containing E-44. Also, the E' - T curves exhibit that the storage modulus E' has a relatively high value in the blends with E-44, which indicates that the rigidity of the blends increases. The result is attributed to the decrease in the segmental mobility of the chains or increase in the intermolecular friction, which would result from the fine dispersion and some chemical, rather than physical, changes that we will discuss below.⁷

Crystallizing Properties of PET/PA-6 Blends

WAXD

Table I gives WAXD characteristic peaks of PET and PA-6. Figure 5 displays the WAXD crystalline peaks for PET, PA-6, and the PET/PA-6 blend without and with E-44. No new peak can be found, which proves that PET and PA-6 crystallize separately and there is no cocrystallite in the blends under our experimental condition. The observed drop in the intensities of the PET and PA-6 could be attributed to the decrease in the perfection and crystallinity.

DSC

To understand the effect of E-44 on the crystallization in immiscible PET/PA-6 blends, the interface between the polymer components must

be considered. The interface will affect the overall crystallization growth by affecting two basic factors: the nucleation rate and crystal growth rate. The DSC data of the PET/PA-6 system are summarized in Table II. The results are discussed in terms of the following quantities: (1) The higher the T_c (crystallization temperature), the easier is the polymer component crystallized; (2) the smaller the ΔT_c (the degree of supercooling, defined as the difference between the melting peak temperature and the crystallization temperature), the easier is the polymer component crystallized; (3) according to the degree of crystallinity, $X_c = \Delta H_m / (F \times \Delta H^0)$ (where ΔH_m is the heat of the melting peak; F , the weight fraction of each component in the blend; ΔH^0 , the ideal heat of melting of the poly-

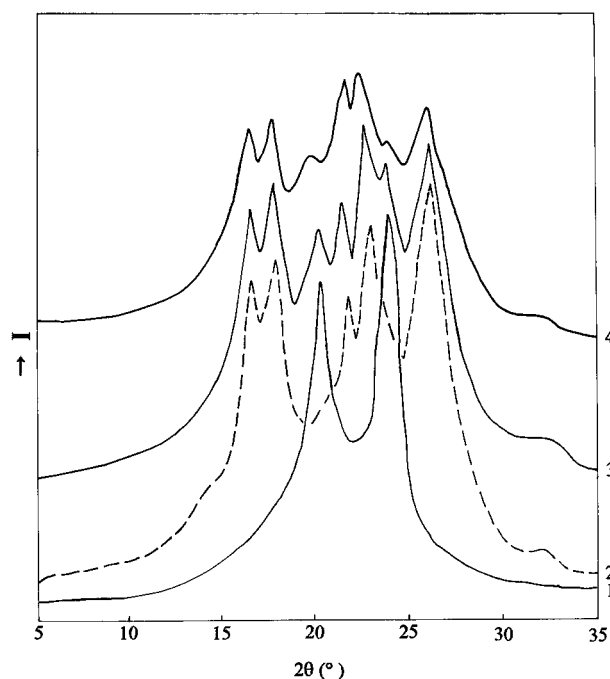
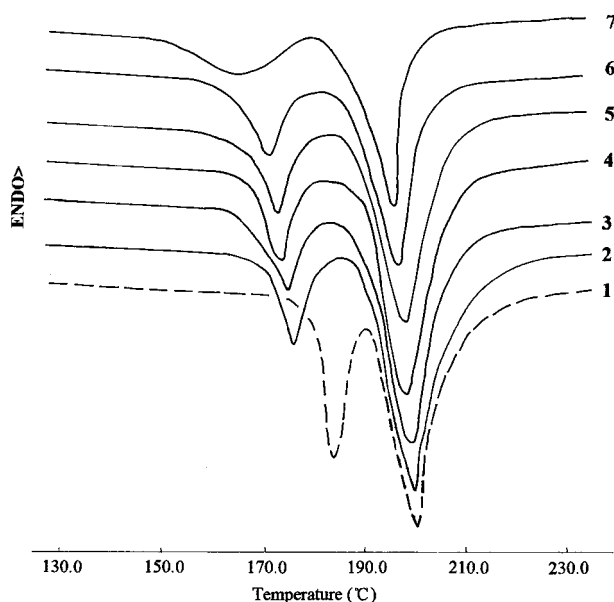


Figure 5 WAXD crystalline peaks for PET/PA-6/E-44 blends: (1) PET; (2) PA-6; (3) PET/PA-6; (4) PET/PA-6/E-44 (10 wt %).

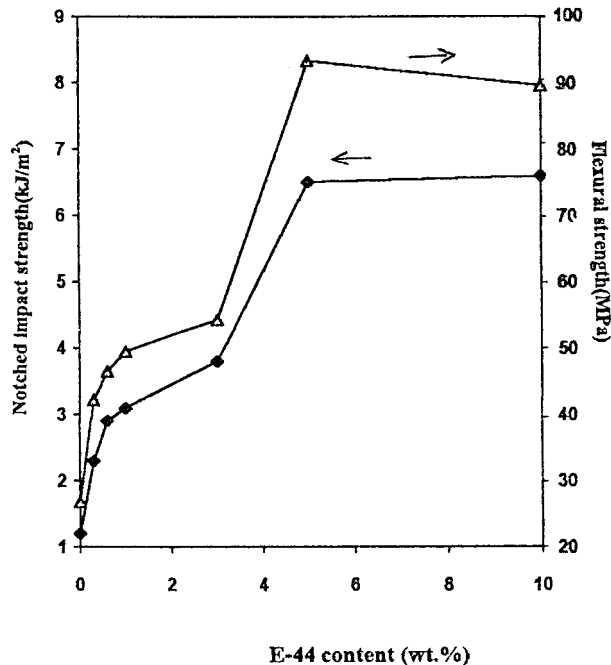
Table II DSC Data of PET/PA-6-E-44 Blends

Material		Sample						
		1	2	3	4	5	6	7
E-44 (wt %)		0	0.3	0.6	1.0	3.0	5.0	10.0
PET	T_m (°C)	250.6	250.3	249.8	248.5	248.5	248.1	248.2
	T_c (°C)	199.5	199.0	198.6	197.5	196.8	196.2	195.6
	ΔT_c (°C)	51.1	51.4	51.2	51.0	54.5	54.8	54.9
	ΔH_m (J/g)	29.0	28.4	26.9	25.5	24.9	24.3	21.5
	t_{\max} (s)	43.3	43.0	42.5	42.1	40.1	43.5	48.6
PA-6	T_m (°C)	219.8	218.0	216.2	215.9	212.3	213.2	213.0
	T_c (°C)	183.7	178.3	175.2	172.1	169.7	169.1	168.3
	ΔT_c (°C)	36.1	39.8	41.0	43.8	47.6	48.0	48.7
	ΔH_m (J/g)	10.5	8.3	7.8	7.3	7.1	6.8	6.3
	t_{\max} (s)	21.6	21.7	22.2	24.2	25.1	27.2	29.3

mer component; in present case, $F \times \Delta H^0$ is constant), the smaller the ΔH_m , the smaller is the X_c ; and (4) the smaller the value of t_{\max} (fastest crystallization time, $t_{\max} = [T_{\text{onset}} - T_c]/c$, where T_{onset} is the temperature at which the thermogram initially departed from the baseline, and c , the cooling rate), the faster is the nucleation rate of the polymer component. As shown in Table II, the T_c and ΔH_m of PET and PA-6 decrease and the ΔT_c of both increase.

**Figure 6** DSC cooling curves of PET/PA-6/E-44 blends. E-44 content (wt %): shown in Table II.

Such variations indicate that the crystallization of PET and PA-6 are inhibited by the presence of E-44, attributed to them having many small and imperfect crystallites. Also, Figure 6 clearly demonstrates the broadening of the crystallization temperature range. However, there is a little difference between the effect of E-44 on PET and on PA-6.

**Figure 7** Mechanical properties of PET/PA-6/E-44 blends.

First, as shown in Table II, the $T_{c_{PA-6}}$ and $\Delta T_{c_{PA-6}}$ change more than do those of PET, which indicates that the reaction force between PA-6 and E-44 is greater than is the force between PET and E-44. It is well known that PA-6 is a high melting polymer because of the hydrogen bonding between the molecular chains. Since the reaction between E-44 and PA-6 can decrease the amount of hydrogen bonding between the molecular chains of PA-6 and the crystallinity of PA-6, $T_{m_{PA-6}}$ decreases obviously, although the reaction can improve the chain stiffness. Second, the high-temperature side of the melting crystalline peaks of PET narrowed but the low-temperature side widened. However, both sides of the PA-6 melting crystalline peaks broadened. In nonisothermal crystallization kinetics, the nucleation rate controls the shape of the high-temperature side and the crystal growth rate controls the low-temperature side. Moreover, the t_{max} of PET becomes smaller, but the t_{max} of PA-6 becomes larger. So, with the increasing content of E-44, the nucleation rate of PET increased but the crystal growth rate

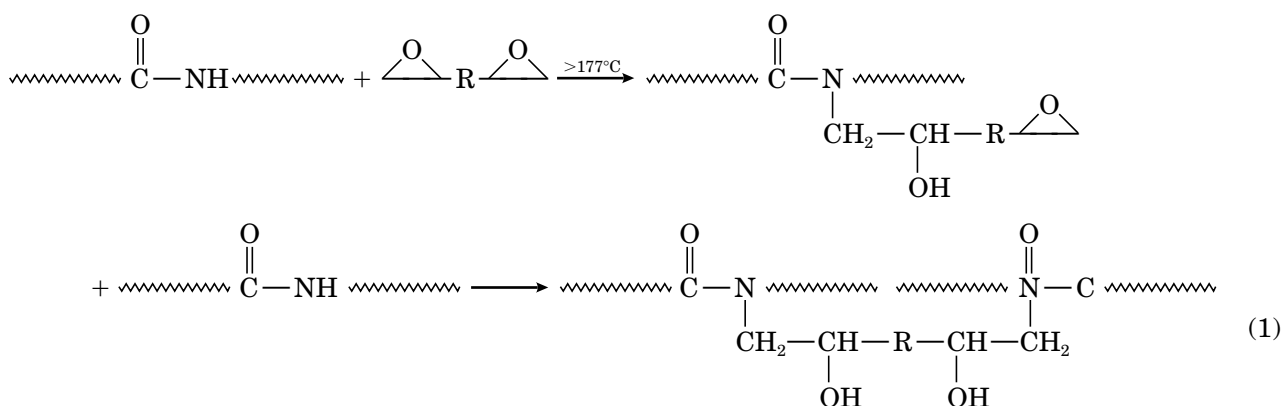
decreased. However, both rates of PA-6 decreased.

Mechanical Properties

The mechanical properties of polymer blends are greatly influenced by their miscibility. Table III shows the notched charpy impact strengths and flexural strengths at various epoxy resin E-44 contents for the PET/PA-6 blends. Because of poor compatibility of the two components, the mechanical properties of the blends are less desirable. After adding a small amount of the epoxy resin E-44, the mechanical properties of the blends increased obviously, especially when the E-44 content reaches 5 wt %, as shown in Figure 7. The maximum flexural strength and notched impact strength are 400 and 500% of the simple blends, respectively.

Reaction in PET/PA-6/E-44 System

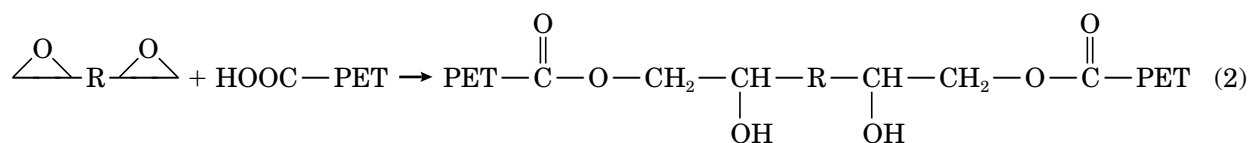
It was reported¹⁰ that the epoxy groups could react with polyamide without any catalyst at 177°C as follows:



This reaction was proved by the gelatin phenomenon that resulted from blending of PET, PA-6

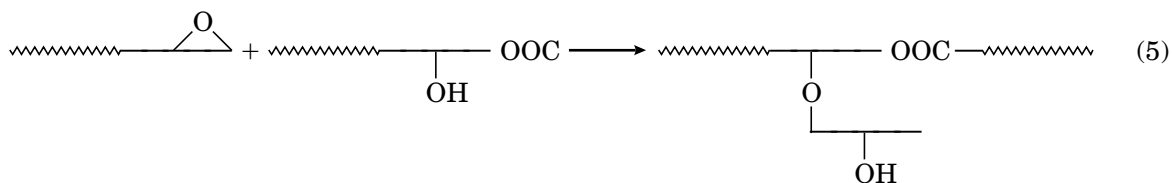
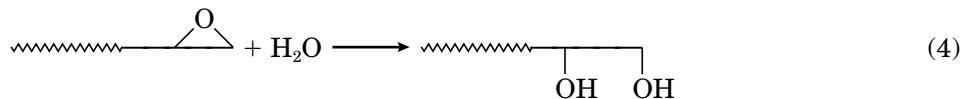
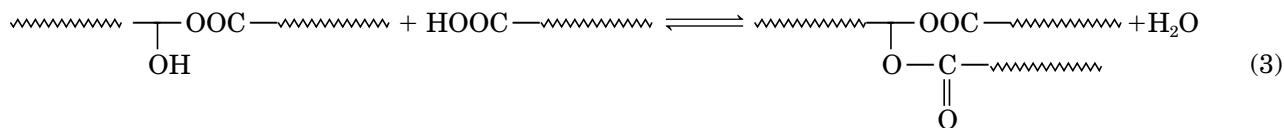
(≥ 30 wt %), and E-44 (≥ 20 wt %).

The epoxy-carboxyl reaction,



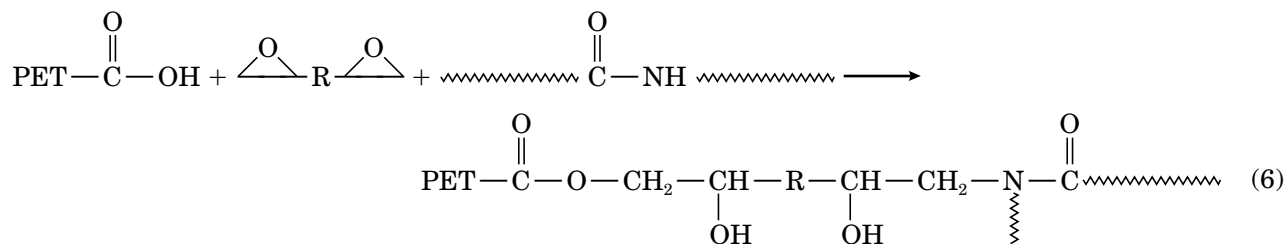
has been used not only to build the polymer chain, but also to modify the side or end groups of chains

to prepare monomers and as a curing agent. In principle, at least three side reactions are possible¹¹:



The probability of reactions (3) and (4) were small in that no bubble could be found in the samples even after blending 20 min. Since E-44 is selective, there is an equilibrium between the re-

action of epoxy groups with PA-6 and the reaction of epoxy groups with PET. The probable reaction on the interface between PET and PA-6 during melt mixing is



It was reported¹² that the grafting of carboxyl-terminated polybutadiene to nylon was accom-

plished by using an epoxy resin as follows (usually in the temperature range of 190–230°C):

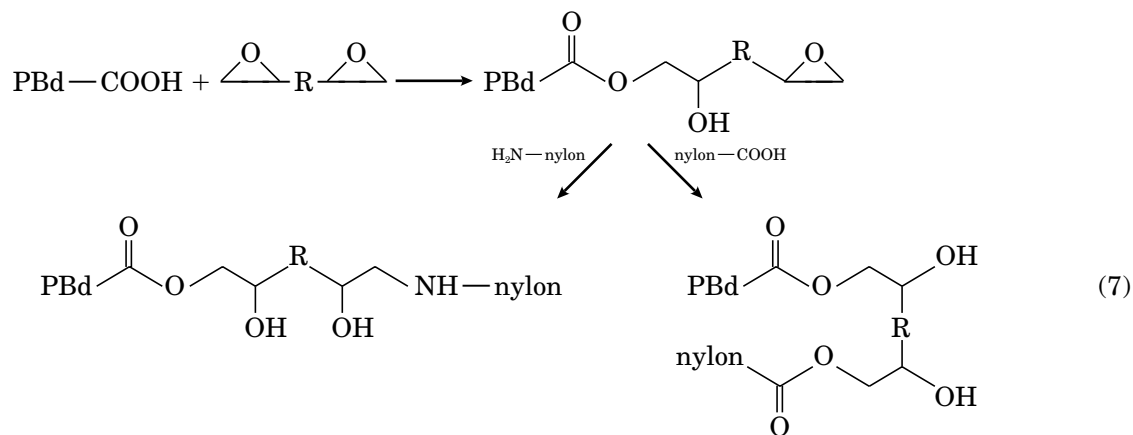


Table III Mechanical Properties of PET/PA-6/E-44 Blends at Varying Epoxy Resin E-44 Content

Mechanical Properties	Sample						
	1	2	3	4	5	6	7
E-44 content (wt %)	0	0.3	0.6	1.0	3.0	5.0	10.0
Flexural strength (MPa)	26.8	42.2	46.5	49.5	54.2	93.4	89.6
Notched impact strength (kJ/m ²)	1.2	2.3	2.9	3.1	3.8	6.5	6.6

Since our experimental temperature was about 295°C, all the reactions except (3) and (4) probably occurred.

IR

IR spectroscopy was used to detect the PA-6 component which was extracted by formic acid. Figure 8 shows that the samples with E-44 have particularly strong peaks at 830, 1020, and 1510 cm⁻¹, which are the characteristic absorption frequencies for the epoxy group. On the other hand, the band of C=O stretching of PA-6 shifts from 1662 to 1642 cm⁻¹ and the band of N—H bending of

PA-6 shifts from 1560 to 1544 cm⁻¹. These results indicate that there is a reaction between PA-6 and E-44. Moreover, the specific peak of PET at 1730, 1104, and 730 cm⁻¹ shows up in the IR spectra, which indicates the formation of a grafting copolymer. This copolymer acts as an interfacial agent, leading to improving the compatibility of the blends. All these indicate that the chemical reaction during the melt blending involved a grafting reaction and a crosslinking reaction. When the content of E-44 was low, the grafting reaction was the main reaction in favor of improving the compatibility of the blends. The properties of the blends were improved greatly when the crosslinking net was formed in the blends.

CONCLUSION

1. There are noticeable morphological changes in both the amorphous region and the crystalline region of the blends. The dimension of the dispersed PA-6 domains decreases greatly and the PA-6 phase has a more uniform distribution.
2. PET and PA-6 separately crystallize in the blends. E-44 blocks the crystallization of PET and PA-6. When the E-44 weight percent is over 5%, the hindered effect was dramatized.
3. The grafting reaction in the blends results in good compatibility between PET and PA-6; the crosslinking reaction results in a great increase of the mechanical properties of the blends.
4. The mechanical properties of PET/PA-6 blends can be substantially improved on adding epoxy resin E-44. When the E-44 weight percent reaches 5%, the notched impact strength and the flexural strength of the blends were improved about 500 and 400%, respectively.

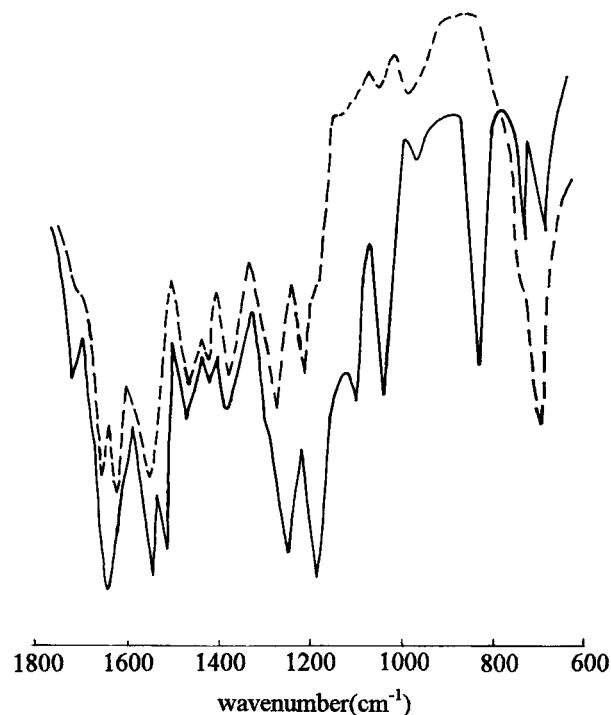


Figure 8 IR spectra of PA-6 component in the blends: (----) PET/PA-6; (—) PET/PA-6/E-44.

5. Since the rigidity and toughness of the blends are both improved, the reactive compatibilization of E-44 shows specific toughness and reinforcing effects.

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