

Special Effect of Epoxy Resin E-44 on Compatibility and Mechanical Properties of Poly(butylene terephthalate)/Polyamide-6 Blends

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SYNOPSIS

An attempt was made to modify the properties of poly(butylene terephthalate) (PBT) by blending it with polyamide-6 (PA-6). Since PBT and PA-6 are incompatible, epoxy resin was used as a compatibilizer to form an alloy. Alloys of PBT and PA-6 with varying amounts (0–12%) of epoxy resin E-44 were prepared by melt blending. The notched Izod impact strength and flexural strength as a function of epoxy resin E-44 content were studied. Ultimate mechanical properties showed significant improvement on addition of epoxy resin E-44. The maximum increase of the notched Izod impact strength ($\approx 600\%$) of PBT/PA-6 blends is obtained at 3% (weight) epoxy resin E-44 content. The impact fracture surfaces were studied using scanning electron microscopy (SEM): The SEM micrographs showed a noticeable change in the type of surface structure on adding epoxy resin E-44. DMTA also showed improved compatibility between PBT and PA-6 on adding epoxy resin E-44. DSC studies showed that the presence of epoxy resin E-44 hindered the crystallization of both PBT and PA-6 in the alloys. Wide-angle X-ray diffraction (WAXD) showed no obvious difference on crystallinity of PBT and PA-6 in the alloys with the presence of a small amount of epoxy resin E-44. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Thermoplastic polyesters represent a new class of engineering plastics; they are extensively used for injection-molded articles, synthetic fibers, films, and blow-molded containers. The most commonly used thermoplastic polyester is poly(butylene terephthalate) (PBT). PBT has excellent electronic properties, chemical resistance, thermal resistance, and low water absorption. But PBT is relatively weak on notched impact strength. Reinforcing PBT with glass fiber is a common modification of PBT. However, glass fiber-reinforced products distort easily after being molded, resulting in anisotropism. These drawbacks limit the extensive application of PBT as an engineering

plastic. The most effective modification of PBT is to blend PBT with other polymers, such as PBT/PET, PBT/PC, and PBT/PA, i.e., polymer-polymer alloying techniques.

In this article, we focus on the blends of PBT/PA-6. The nonmodified samples of PBT/PA-6 blends had poor interphase adhesion, which was responsible for low notched impact strength. The key to preparation of commercially useful blends based on immiscible polymer pairs is compatibilization. To improve the compatibility between PBT and PA, the ester-amide interchange reaction was carried out in the melt so that good interphase adhesion between PBT and PA was achieved.¹⁻³ But the complexity of the process and the exact reacting conditions devalue its application. The objective of this study was to investigate the effect on enhancing mechanical properties and the compatibility of PBT/PA-6 blends by adding low molecular weight epoxy resin E-44.

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EXPERIMENTAL

Materials and Preparation of Blends

Materials used in this study included PBT, PA-6, and epoxy resin E-44. All were commercial grades. PBT ($[\eta] = 0.90$ dL/g, measured in a 1/1 w/w phenol : tetrachloroethane solvent, 25°C) was supplied by the Ba-Lin Petroleum Chemical Co. (China), epoxy resin E-44 (low molecular weight) was supplied by the Shanghai Chemical Reagent Plant (China), and PA-6 (1013B) was supplied by Ube Industries Ltd.

Prior to compounding, PBT and PA-6 were dried at 120°C for 6 h in a vacuum oven; epoxy resin E-44 was dried in a hot air drier at 120°C for 4.5 h. All the blends were prepared by melt mixing in an SHJ-30 twin-screw extruder (Nanjing Rubber and Plastic Machinery Co., China) in a temperature range of 230–250°C with a screw speed at 150 rpm, $L/D = 28$.

Preparation of Test Specimens

The test specimens for the measurement of mechanical properties were prepared by injection molding on a Windsor SP-1 screw-type machine using the screw speed of 30 rpm and injection pressure of 200 kg/cm² with a barrel temperature of 230 ± 5°C. The mold was kept at ambient temperature (25 ± 2°C).

Measurement of Mechanical Properties

The notched Izod impact strength was measured on an FIE impact tester Model IT according to the ASTM D256 test procedure. Flexural strength was measured on an Instron universal tester Model 1211 using a three-point bending method with center loading on a simply supported beam. The support span length was 7 cm. Five samples were tested in each case, and the average value was reported. All the tests were performed at ambient temperature, i.e., 25 ± 2°C.

Scanning electron micrographs of impact fracture surfaces were recorded on a Hitachi S-570 scanning electron microscope compared with notched impact fracture surfaces etched out by formic acid. Prior to microtoming, all the fracture surfaces were made conductive by the deposition of a layer of gold in a vacuum chamber.

Thermal analysis were made with a DSC instrument (Perkin-Elmer, DSC-7C). All samples were quenched in liquid nitrogen and dried previously.

The samples were heated at a rate of 15°C/min in a nitrogen atmosphere up to 250°C to obtain the heating curve and were held at this temperature for 3 min, then subsequently cooled at 15°C/min down to 100°C to obtain the cooling curve.

Dynamic mechanical thermal analysis was carried out using the Rheovibron-DDV-II-EA-type viscoelasticimeter with a temperature ranging from –150 to 250°C at a frequency of 110 Hz and heating rate of 2°C/min.

Wide-angle X-ray diffraction plots were taken 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 150°C for 5 min.

RESULTS AND DISCUSSION

Mechanical Properties

The mechanical properties of polymer blends are greatly influenced by their miscibility. In developing commercially useful polymer blends based on immiscible components, the objective is to compatibilize immiscible polymer blends. Values of the various notched Izod impact strengths and flexural strengths at varying epoxy resin E-44 content for PBT and PBT/PA-6 (100/20)–E-44 blends are given in Table I. Because of poor compatibility of PBT/PA-6 blends, the mechanical properties of PBT/PA-6 blends are less desirable. The notched impact strength of PBT/PA-6 (sample 1) is 3.0 kg m/m, lower than that of PBT (4.2 kg m/m). On adding a small amount of epoxy resin E-44, the mechanical properties of PBT/PA-6 blends increased dramatically. The maximum increase of notched impact strength ($\approx 600\%$) is obtained at 3% (weight) epoxy resin E-44 (Fig. 1), but the mechanical properties of PBT increased slightly on adding a small amount of epoxy resin E-44 (Fig. 2). The compatibilizing of PBT/PA-6 blends was attributed to the improved mechanical properties. Moreover, it was found that the addition of epoxy resin E-44 not only enhances the impact toughness but also the mechanical strength, which is different from rubber-toughened plastics. We will discuss this further.

SEM

A scanning electron microscope was used to investigate the morphology of PBT/PA-6 blends and PBT/PA-6 blends containing epoxy resin E-44.

Table I The Mechanical Properties of PBT and PBT/PA-6 100/20 Blends at Varing Epoxy Resin E-44 Content

	Sample No.							
	1	2	3	4	5	6	7	8
E-44 content (%)	0	0.5	1.0	1.5	3.0	6.0	9.0	12.0
Flexural strength (MPa)								
PBT/PA-6	79	92	98	104	118	112	103	93
PBT	73		89	102	104	95	87	77
Notched impact Izod strength (kg m/m)								
PBT/PA-6	3.0	8.3	12.6	15.1	19.3	15.9	13.2	9.8
PBT	4.2		4.4	4.7	4.5	3.9	3.3	3.1

Figure 3(a) shows the SEM micrograph of a fracture surface of the PBT/PA-6 blend (sample 1). Two-phase morphology is observed on the fracture surface of the blend. PA-6 was dispersed in a spherical shape in the continuous phase of PBT. Cavities can be seen clearly wherein the slippage of PA-6 particles occurred during the fracturing process. It is smooth around these cavities, and there is no evidence of the presence of adhesion between the minor phase and the matrix, so the mechanical properties of the PBT/PA-6 blend were relatively poor (Table I). Figure 3(b) shows the SEM micrograph of the fracture surface of the PBT/PA-6 blend containing 3.0%

(weight) epoxy resin E-44 (sample 5). By comparing the morphology of the uncompatibilized PBT/PA-6 blend with the morphology of the PBT/PA-6 blend containing 3.0% epoxy resin E-44, it can be seen immediately that important morphological changes occurred on addition of epoxy resin E-44 [Fig. 3(b)]. The two-phase morphology is less distinct. No dispersed PA-6 particles were found and no cavities are shown in Figure 3(b). A ductile type of fracture is observed on the fracture surface of the PBT/PA-6 blend containing epoxy resin E-44, indicating an excellent interfacial adhesion. Figure 3(c) is the SEM micrograph of the etched fracture surface of

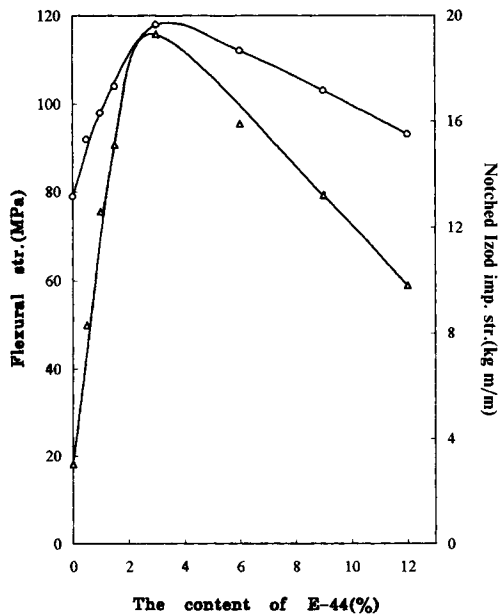


Figure 1 Mechanical properties (PBT/PA-6/E-44) vs. % epoxy resin E-44 content: (○) flexural strength; (△) notched Izod impact strength.

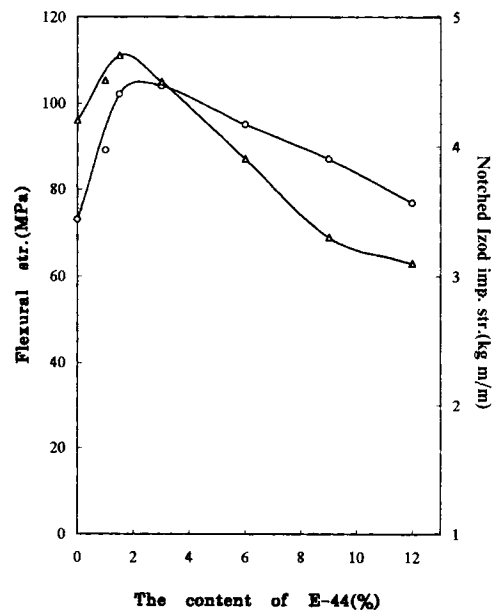


Figure 2 Mechanical properties (PBT/E-44) vs. % epoxy resin E-44 content: (○) flexural strength; (△) notched Izod impact strength.

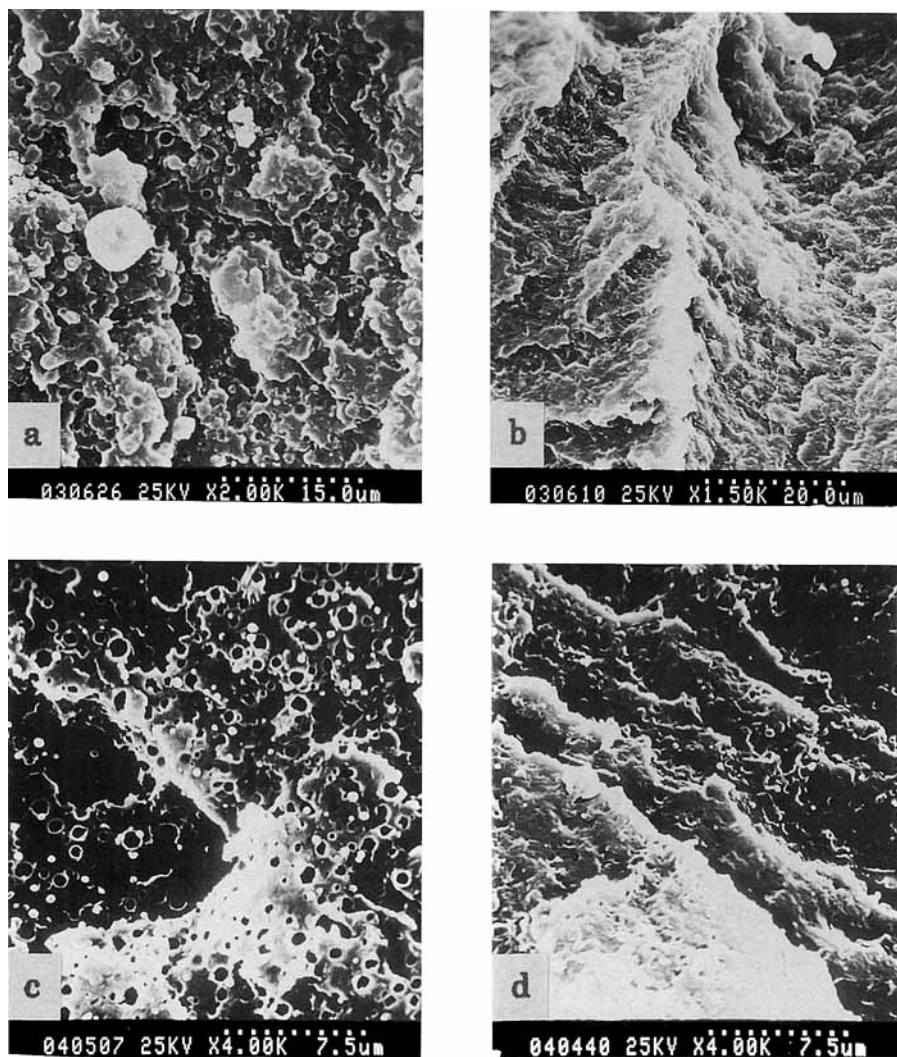


Figure 3 SEM micrographs of impact fracture surfaces: (a) PBT/PA-6; (b) PBT/PA-6/E-44 (3.0%); (c) etched surface of PBT/PA-6 system; (d) etched surface of PBT/PA-6/E-44 (3.0%) system.

the PBT/PA blend (sample 1). It exhibited vigorous cavities which formed by dissolving PA-6 with formic acid. This reveals that the adhesion between PA-6 and PBT was very poor. Figure 3(d) is the SEM micrograph of the etched fracture surface of PBT/PA-6 blends containing 3.0% (weight) epoxy resin E-44 (sample 5). The shape, size, and distribution of the cavities varied tremendously [compared with Fig. 3(c)]. The morphology suggests that epoxy resin E-44 appears to span the interfaces between regions of PBT and PA-6, thus enhancing the adhesion and compatibility of the blend, indicating that E-44 acted as a kind of interfacial agent.

DSC

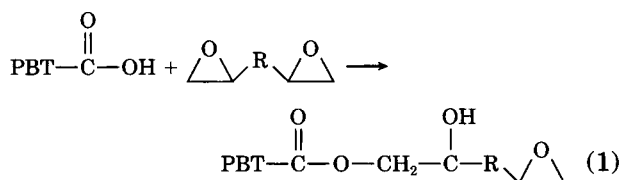
DSC dynamic crystalline data of the PBT-E-44 system and the PBT/PA-6-E-44 system are illustrated in Table II. For the PBT-E-44 system, because of the "dilution" effect of small moleculars, the melting temperature of PBT decreases with increasing content of epoxy resin E-44. Moffett and Dekkers⁴ studied dynamically vulcanized thermoplastic elastomer blends of PBT and EPDM upon melt mixing. The epoxy groups of the EPDM-*g*-GMA react predominantly with the carboxylic acid end groups of PBT, which results in the *in situ* formation of the PBT-EPDM graft copolymer. In the present system,

Table II Crystalline Data of DSC

	Sample No.							
	1	2	3	4	5	6	8	
E-44 content (%)	0	0.5	1.0	1.5	3.0	6.0	12.0	
PBT								
T_m (°C)	228.7		227.6	226.5		223.7		
T_c (°C)	196.8		195.2	191.4		181.7		
ΔH_c (J/g)	-44.6		-42.3	-41.5		-41.9		
PA-6 in PBT/PA-6 ^a								
T_m (°C)	228.3	228.6	227.5	227.2	226.5	226.6	224.0	
T_c (°C)	176.7	172.7	172.5	172.1	160.3	154.7	145.6	
ΔH_c (J/g)	-8.7	-8.3	-7.9	-6.8	-6.4	-5.9	-3.6	
PBT in PBT/PA-6								
T_m (°C)	228.3	228.6	227.5	227.2	226.5	226.6	224.0	
T_c (°C)	188.9	189.4	189.3	188.2	187.4	184.8	184.0	
ΔH_c (J/g)	-34.4	-35.1	-34.6	-33.8	-32.8	-31.9	-29.4	

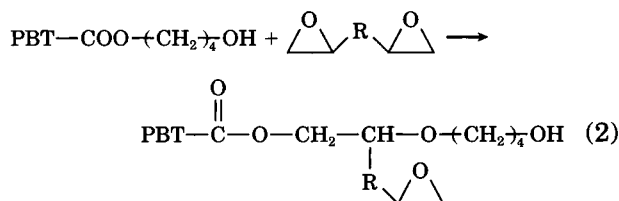
^a 100/20 PBT/PA-6 blends.

epoxy resin E-44 reacts with the carboxylic acid end groups of PBT at a low content of epoxy resin E-44 as follows:



Thus, the PBT molecular chains were longer, resulting in an enhanced cohesive energy so that the notched impact strength and flexural strength of PBT show an increasing trend (Table I). Over a small content of epoxy resin E-44, there were few carboxylic acid end groups of PBT left; the PBT molecular chains cannot be prolonged by the reaction of carboxylic acid end groups with epoxy groups. Zaitseva et al.⁵ studied the reactivity of different groups on crosslinking with epoxy resins. It was found that the reactivity of the dicarboxylic esters was active. Concerning that, it is suggested that

there is another reaction between epoxy groups and the PBT molecular chains as follows:



The side-chain groups of epoxy resin E-44 in PBT chains destroyed the regularity of PBT molecular chains, so the crystallizing of PBT was difficult relatively. On the other hand, the chain segments around side-chain groups can be the sites of stress concentration. Under stresses, initiation of the fracture occurred on these sites. As a result, at above an $\sim 2.0\%$ content of epoxy resin E-44, the notched impact strengths and flexural strengths of PBT showed a decreasing trend (Fig. 2).

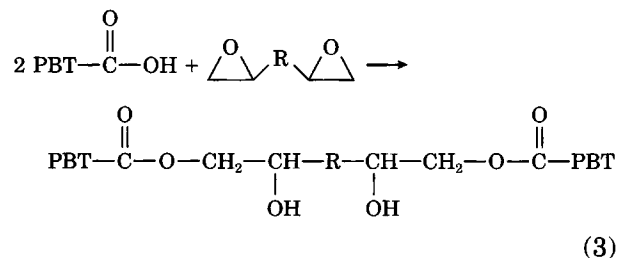
Table III shows the intrinsic viscosity of PBT containing different amounts of epoxy resin E-44. It was found that the intrinsic viscosity of PBT con-

Table III The Intrinsic Viscosity of PBT at Different Epoxy Resin E-44 Content

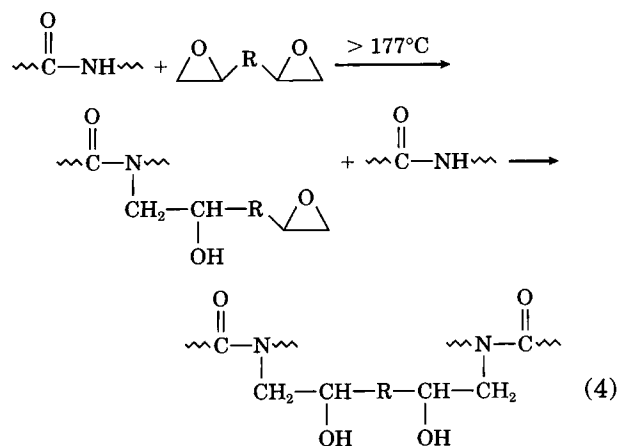
	Sample No.						
	1	2	3	4	5	6	7
E-44 content (%)	0	1	1.5	3.0	6.0	9.0	12.0
PBT $[\eta]$ (dL/g) ^a	0.766	0.911	0.954	0.921	0.794	0.772	0.751

^a Measured in 1/1 w/w phenol : tetrachloroethane solvent, 25°C.

taining only a 1% (weight) amount of epoxy resin E-44 was higher than that of the PBT material ($[\eta] = 0.90 \text{ dL/g}$). The presence of the following reaction is suggested:

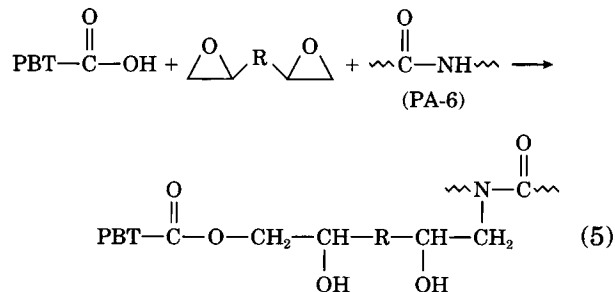


In consequence, the PBT molecular chains are prolonged. The intrinsic viscosity of PBT increased. Above a 1.5% (weight) content of epoxy resin E-44, the intrinsic viscosity of PBT decreased with increasing amount of epoxy resin E-44. The explanation given is that, owing to the introduction of side chains by chemical bonding, the solubility of PBT diminished in the solvent and the intrinsic viscosity of PBT decreased, as shown in Table II. With increasing E-44 content, the influence on melting temperature and enthalpy of PA-6 is greater than on that of PBT. At a temperature of 177°C , the epoxy groups react with polyamide without a catalyst,⁶ as follows:



The presence of the crosslinking reaction of epoxy resin E-44 with PA-6 was proved by the phenomenon that adding a small amount of epoxy resin E-44 in melted PA-6 resulted in the gelation of PA-6.

Epoxy resin E-44 was selective; it has greater reactivity but less compatibility with PA-6 than with PBT. There is an equilibrium between the reaction of epoxy groups with PA-6 and the reaction of epoxy groups with PBT. The most probable reaction on the interface between PBT and PA-6 during melt mixing is



From our viewpoint, E-44 acts actually as an interfacial agent. The SEM micrograph [Fig. 3(b)] shows a good compatibility between PBT and PA-6. Moreover, PA-6 dispersed uniformly in the PBT matrix, so that the probability of the crosslinking reaction of PA-6 with epoxy groups decreased greatly. When increasing the amount of E-44, a slight crosslink of PA-6 influences greatly the cooling crystalline velocity and crystalline enthalpy of PA-6 in the blends (Fig. 4). Nevertheless, a slight crosslink may be useful in improving mechanical properties. Kurauchi and Ohta⁷ first proposed that rigid SAN particles could toughen the ductile PC matrix. The large elongation of SAN in the blends is attributed to the cold drawing. Under the influence of the compressive stress on the dispersed SAN, rigid SAN deforms in a ductile manner. Therefore, the large absorbed energy of the blends is thought to result partly from the large elongation of SAN. It is different from the rubber-modifying plastics; rigid

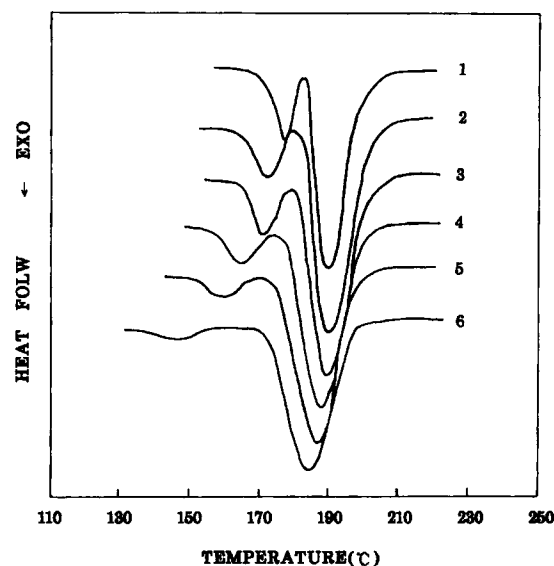


Figure 4 DSC plots for PBT/PA-6/E-44 system at varying content of epoxy resin E-44 (cooling cycle): (1) PBT/PA-6; (2) PBT/PA-6/E-44 (0.5%); (3) PBT/PA-6/E-44 (1.0%); (4) PBT/PA-6/E-44 (1.5%); (5) PBT/PA-6/E-44 (3.0%); (6) PBT/PA-6/E-44 (6%).

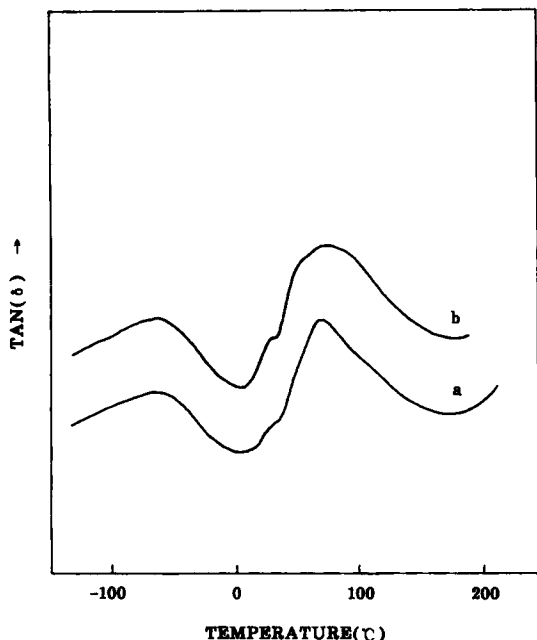


Figure 5 DMTA $\tan \delta$ -temperature plots: (a) PBT/PA-6; (b) PBT/PA-6/E-44 (3.0%).

organic fillers not only improve the toughness but also the rigidity and heat resistance of plastics. The compressive stress occurs only in a blend of having good interphase adhesion for stress transfer. The cold-drawing mechanism is available for explaining the PBT/PA-6 blends containing epoxy resin E-44.

The brittle-to-ductile transition critical pressure⁸ of PA-6 rose due to enhanced rigidity of PA-6 by slight crosslinking. Thus, the notched impact strength and flexural strength of the blends were improved (Table I) with increasing the amount of epoxy resin E-44. The crosslink intensity of PA-6 increased on increase of the amount of epoxy resin E-44, so that the plastic deformation ability of PA-6 was weakened. Above 3.0% content, the notched impact strength and flexural strength diminished with increasing the amount of epoxy resin E-44. At the ratio 5 : 1 of PBT and PA-6, the optimum amount of epoxy resin E-44 is 3% (weight). On the other hand, above a 24% (weight) content of PA-6 in PBT/PA-6 blends, the addition of epoxy resin E-44 in the blends resulted in the gelation of PA-6. This supports the view of the presence of a slight crosslink of PA-6 in the blends on adding epoxy resin E-44.

DMA

Figure 5 shows the $\tan \delta$ - T curves of PBT/PA blends (sample 1) and PBT/PA blends containing epoxy resin E-44 (sample 5). Both curves show two glass transition temperatures, which confirms the pres-

ence of two phases. At a temperature of 65°C, a PBT α -relaxation peak appears. At a temperature of 43°C, a PA α -relaxation peak appears. Due to the presence of water, the glass transition temperature (T_g) of PA-6 shifted to a lower temperature for both blend systems. Compared with curve 1, the PBT α -relaxation peak of curve 2 became broader, indicating that the PBT amorphous region was affected by different crystalline regions, i.e., the PBT amorphous region was bound more, due to the presence of epoxy resin E-44. This result suggests that there is interfacial adhesion between PBT and PA-6.

Wide-angle X-ray Diffraction (WAXD)

Figure 6 gives WAXD plots for the PBT/PA-6 blend (sample 1) and the PBT/PA-6 blend containing 3.0% epoxy resin E-44 (sample 5). The characteristic peaks of PA-6 ($2\theta = 19.8, 23.5$) and of PBT ($2\theta = 16.0, 17.0, 20.8, 23.2, 25.2$) can be seen clearly in both WAXD plots (Fig. 5). Although the crystallization of PA-6 in the blends was hindered on adding epoxy resin E-44 (Fig. 3), at the condition of the samples' crystallizing isothermally at 150°C for 5 min, there is no obvious change shown in the WAXD plots (Fig. 5) on adding 3.0% epoxy resin E-44. Neither the PBT nor the PA-6 crystallization pattern was affected in the blends on adding epoxy resin E-44.

CONCLUSION

1. The mechanical properties of PBT/PA-6 blends can be improved greatly on adding a small amount of epoxy resin E-44.

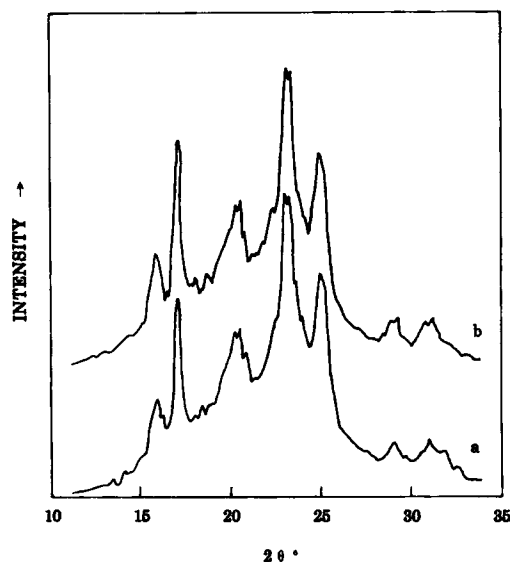


Figure 6 WAXD intensity vs. 2θ plots: (a) PBT/PA-6; (b) PBT/PA-6/E-44 (3.0%).

2. Through a reaction of epoxy groups with PBT and PA-6, the compatibility of the PBT/PA-6 blend was achieved.
3. Because of the special reactivity of epoxy resin E-44 with PBT and PA-6, not only was the notched impact strength improved significantly (the maximum value improved ~ 600%, but also the flexural strength, indicating a peculiar toughening mechanism.
4. The mechanical properties of PBT/PA (100/20) blends are optimum at the 3% weight content of epoxy resin E-44.

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