

# Reactive Compatibilization of Polyamide-6 (PA 6)/Polybutylene Terephthalate (PBT) Blends by a Multifunctional Epoxy Resin

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**ABSTRACT:** A multifunctional epoxy resin has been demonstrated to be an efficient reactive compatibilizer for the incompatible and immiscible blends of polyamide-6 (PA 6) and polybutylene terephthalate (PBT). The torque measurements give indirect evidence that the reaction between PA and PBT with epoxy has an opportunity to produce an *in situ* formed copolymer, which can be as an effective compatibilizer to reduce and suppress the size of the disperse phase, and to greatly enhance mechanical properties of PA/PBT blends. The mechanical property improvement is more pronounced in the PA-rich blends than that in the PBT-rich blends. The fracture behavior of the blend with less than 0.3 phr compatibilizer is governed by a particle pullout mechanism, whereas shear yielding is dominant in the fracture behavior of the blend with more than 0.3 phr compatibilizer. As the melt and crystallization temperatures of the base polymers are so close, either PA or PBT can be regarded as a mutual nucleating agent to enhance the crystallization on the other component. The presence of compatibilizer and *in situ* formed copolymer in the compatibilized blends tends to interfere with the crystallization of the base polymers in various blends. © 2000 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 38: 23–33, 2000

**Keywords:** PA; PBT; compatibilizer; morphology; mechanical properties; crystallization

## INTRODUCTION

From the practical and economical points of view, polymer blending from existing polymers is the most effective and convenient route to create new and useful materials with greater versatility and flexibility than the development of new polymers. However, most randomly selected polymer pairs usually are immiscible and incompatible, resulting in products with more inferior properties than the average of the base polymers. In these incompatible polymer blends, the control of interfacial

tension plays an important role to govern the blend morphology and associated mechanical properties. The dispersed phase size reduction with decreasing interfacial tension is important for obtaining uniform blend properties, while retaining the physical properties of both of the homopolymers. During the last two decades, research activities on polymer compatibilization have grown at an exponential rate and have been the subject of some recent reviews.<sup>1–7</sup>

The block and graft polymers are well known as efficient compatibilizers to reduce the interfacial tension of polymer blends. In addition, the compatibilizer plays an important role in suppressing coalescence of the dispersed domains.<sup>8–11</sup> However, the microphase separation inherent to most block copolymers has high vis-

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cosities, making it difficult to disperse them into binary homopolymer blends. And, block copolymers with high molecular weights may prefer to micellize within one of the homopolymers phases rather than reside at the interface. In order to overcome many of the shortcomings of block copolymers, research activities in the area of the reactive type compatibilization have been stimulated and clearly become the main stream in compatibilizing incompatible polymer blends during the past few years.<sup>7</sup> The main advantage of using compatibilizers in polymer blends is the suppression of coalescence achieved through stabilizing the interface.

Polyamide (PA 6 or PA 6,6) and polyester (PBT or PET) are both high volume commercial products. Blends from them should be an ideal choice to create new and useful polymeric products possessing certain specific properties from base polymers. Utracki et al.<sup>12–14</sup> have studied the melt rheologies of PA/PET blends and their results showed the presence of a degree of association and/or crystallization among these two polymers. Kamal et al.<sup>15</sup> reported that both neat PA 6,6 and PET exhibit ductile failure under both tensile and impact tests, but the blends show brittle behavior. The brittleness originates in the poor interphase adhesion of the incompatible PA 6,6/PET system. It has been reported that polyester–polyamide copolymers are formed through ester–amide interchange reaction in melt blending of PET and PA.<sup>16–18</sup> Pillon et al.<sup>19,20</sup> characterized the ester–amide interchange reaction of PET and PA catalyzed by *p*-toluenesulfonic acid by DSC, <sup>1</sup>H and <sup>13</sup>C NMR. Watanabe et al.<sup>21</sup> reported that PBT and PA 6 were an incompatible polymer pair. Wakita<sup>22</sup> studied the melt elasticity of incompatible blends of PBT/PA 6 and reported that the extrudate swells vary with the viscosity ratios and compositions. Fakirov et al.<sup>23, 24</sup> studied the relation between crystallinity and compatibility of the blends of polyamide-6 (PA 6)/polyesters (including PBT and PET). Huang et al.<sup>25</sup> reported that a solid epoxy resin with intermediate molecular weight is a good reactive compatibilizer for PBT/PA 6,6 blends. Component phase separation due to crystallization leads to reduced mechanical properties of the blends. Some indirect evidence showed that the copolymer layers formed between the base polymers in the blends improve the compatibility and change the resultant morphology of the system.

We had previously reported that a multifunctional epoxy resin is able to act as a coupler to

function as an excellent reactive compatibilizer for the blends of PPE/PA 6<sup>26</sup> and LCP/PET.<sup>27</sup> An et al.<sup>28</sup> also reported that the ultimate mechanical properties of the PA 6/PBT blends showed significant improvement on addition of an epoxy resin E-44. In this study, we utilize the same multifunctional epoxy resin by functioning as a coupling agent to compatibilize the PA 6/PBT blends.

## EXPERIMENTAL

### Materials

Polyamide-6 (PA) is a general-purpose grade, 1013NW8, purchased from UBE Industries Ltd. of Japan. The number-average molecular weight is 13,000. Polybutylene terephthalate (PBT), D-201, is a natural grade product from Shin-Kong Synthetic Fibers Corp. of Taiwan. The number-average molecular weight is 25,000. The reactive compatibilizer, a tetrafunctional epoxy resin, *N,N,N',N'*-tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM), was obtained from Ciba-Geigy of Switzerland. The epoxy equivalent weight of the epoxy is 110–130 g/eq. The corresponding data were given from the suppliers.

### Preparation of Test Specimens

Melt blending was carried out on a corotating 30 mm twin-screw extruder with a decompression zone. The extruded pellets were dried at 100 °C for over 24 h and molded into standard 1/8 inch thickness ASTM specimens using an Arburg 3 oz injection molding machine. The detailed processing conditions for extrusion and injection molding are listed in Table I.

### Characterization

To verify the reactions of PA and PBT with epoxy based on viscosity increase, torque versus time measurements were carried out under a loading of 5 Kg in a Brabender Plastic-Corder mixer from Germany with a capacity 30 mL. The rotational speed was 30 rpm and the temperature was controlled at 260 °C.

Thermal properties were investigated by the differential scanning calorimetry (DSC) from 25 to 280 °C at a heating rate of 10 °C/min on a DSC instrument model SSC-5200 from Seiko Co. of Japan. Capillary rheological measurements of

**Table I.** Processing Conditions

Extrusion Blending:										
Stage	1	2	3	4	5	6	7	8	9	Die
Temp. (°C)	210	240	245	250	255	255	255	240	240	240
Injection Molding:										
Stage	1			2			3			4
Temp. (°C)	250			260			260			250

matrices and the blends were carried out at 260 °C using a Kayeness Galaxy Calillart Rheometer (L/D = 40, orifice radius = 0.02 inch, and orifice length = 0.8 inch).

Morphologies of the cryogenically fractured surfaces were examined by a Hitachi S-570 scanning electrons microscopy (SEM) on the plane perpendicular to the injection flow direction at the central region of the specimen near the notch tip front.

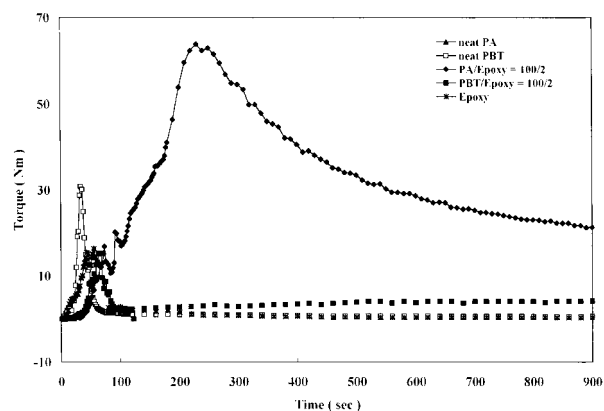
Standard tensile tests (ASTM-D638) were carried out at a crosshead speed of 50 mm/min. Standard flexural tests (ASTM-D790) were carried out at a crosshead speed of 1.2 mm/min and a span length of 50 mm. Notched Izod impact tests were carried out at ambient conditions according to the ASTM-D256 standard method. The procedures of the previously developed method to determine impact critical strain energy release rate (Gc) were carried out at ambient conditions by varying depth of a notch.<sup>29</sup>

## RESULTS AND DISCUSSION

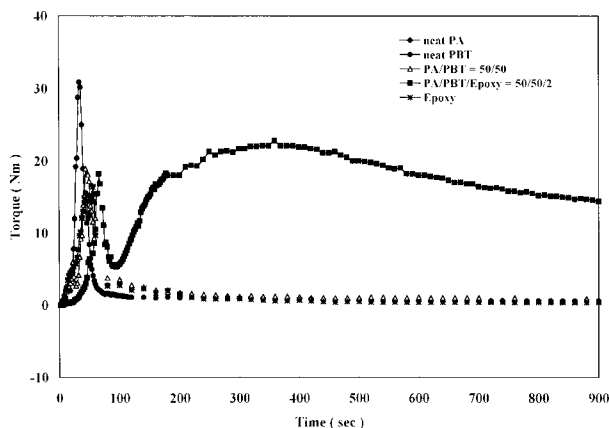
### Torque Versus Time

Torque measurements have been successfully used to obtain qualitative information concerning the chemical reactivity and the extent of reaction in reactively compatibilized blends. Figure 1 gives the relationship between torque with time for PA, PBT, epoxy, PA/epoxy = 100/2 and PBT/epoxy = 100/2 mixtures tested at 260 °C. The torques of the neat PA, PBT, and epoxy are all very low and remain almost constant after 200 s at this temperature. It means that ring opening or crosslinking reaction by this epoxy monomer does not occur at this temperature. The torque of the PA/epoxy = 100/2 mixture is drastically higher than that of neat PA but gradually decreases after about 250 s probably because of thermal degrada-

tion. On the other hand, the torque of the PBT/epoxy = 100/2 mixture is only slightly higher than that of the neat PBT. Therefore, we can conclude that both PA and PBT can react with epoxy and the reaction between PA and epoxy is significantly faster than that between PBT and epoxy. These results provide indirect evidence of molecular weight increase due to the anticipated reactions between end groups of PA and PBT with epoxy. Plots of torque versus time for PA, PBT, epoxy, PA/PBT = 50/50 and PA/PBT/epoxy = 50/50/2 mixtures are shown in Figure 2. The torques of PA, PBT, epoxy and PA/PBT = 50/50 are very low and remain almost constant after 200 s at 260 °C. The occurrence of the potential complexation between amine and carboxyl end groups is insignificant based upon the observed viscosity results. The compatibilized blend, PA/PBT/epoxy = 50/50/2, possesses a significantly higher torque than the corresponding uncompatibilized blend, PA/PBT = 50/50. These results give indirect evidence that the reaction between PA and PBT with epoxy may have an opportunity to produce the *in*



**Figure 1.** Plots of torque versus time for PA, PBT, epoxy, PA/epoxy = 100/2 and PBT/epoxy = 100/2 mixtures.

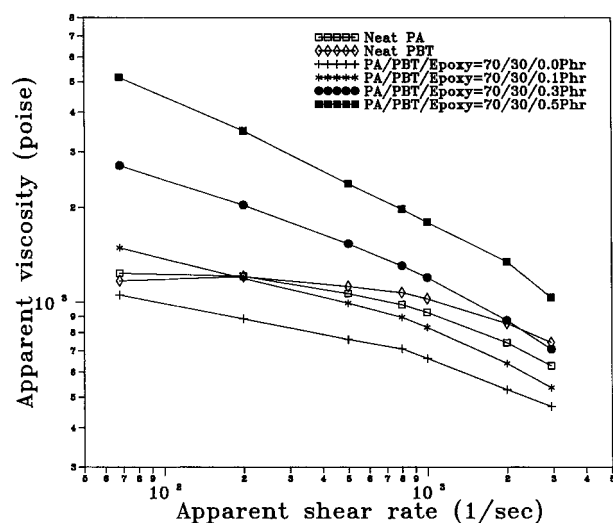


**Figure 2.** Plots of torque versus time for PA, PBT, epoxy, PA/PBT = 50/50 and PA/PBT/epoxy = 50/50/2 mixtures.

*in situ* formed copolymer to act as the effective compatibilizer for PA/PBT blends.

### Capillary Rheometry

Figure 3 illustrates the apparent viscosity versus shear rate plots for the PA, PBT, uncompatibilized and compatibilized PA/PBT = 70/30 blends at 260 °C. All molten polymers present non-Newtonian fluid behavior. The uncompatibilized blends and the blend containing 0.1 phr compatibilizer have lower viscosities than the pure components. The apparent viscosity of the blend increases with the increase of the compatibilizer



**Figure 3.** Plots of apparent viscosity versus shear rate for the uncompatibilized and compatibilized PA/PBT = 70/30 blends at 260 °C.

**Table II.** Summary of the Power Law Index of the PA6/PBT Blends at 260°C

Composition	Power Law Index (n)
PA6	0.87
PBT	0.94
PA6/PBT = 70/30	0.82
PA6/PBT/epoxy = 70/30/0.1 phr	0.77
PA6/PBT/epoxy = 70/30/0.3 phr	0.68
PA6/PBT/epoxy = 70/30/0.5 phr	0.61
PA6/PBT = 50/50	0.87
PA6/PBT/epoxy = 50/50/0.1 phr	0.82
PA6/PBT/epoxy = 50/50/0.3 phr	0.70
PA6/PBT/epoxy = 50/50/0.5 phr	0.51
PA6/PBT = 30/70	0.87
PA6/PBT/epoxy = 30/70/0.1 phr	0.80
PA6/PBT/epoxy = 30/70/0.3 phr	0.67
PA6/PBT/epoxy = 30/70/0.5 phr	0.57

content. In the reactive compatibilized blending systems, the effect of the compatibilizer on the apparent viscosity of the blend is very complicated. There are several variables such as composition, viscosity ratio, functionality, compatibilizer quantity, and plasticization. Molecular weight increases through *in situ* reactions are mainly responsible for such viscosity increase after compatibilization.

The viscosity of PA is so close to that of PBT and the apparent viscosity versus shear rate of the rest compositions has a similar trend as that of the PA/PBT = 70/30 series. The plasticization is not an important effect to the viscosity change because the added amount of epoxy is very small. So, functional end groups and quantity of the resins play determinant roles. The constant parameters (n) of the blends according to the power law model are summarized in Table II. Shear thinning of a molten blend is well demonstrated by the deduced power law index ( $n < 1$ ). From these power law indices, it shows that the apparent viscosity of the blend increases with increasing epoxy content at the processing conditions. In other words, the epoxy is really effective as a compatibilizer to result in reducing the domain size of the dispersed phase and molecular weight increase.

The uncompatibilized blend has the expected lowest viscosity in the incompatible blend. From

**Table III.** Summary of Functional End Groups of All Blends<sup>a</sup>

	PA6 ( $f = 3$ ) PA6-NH <sub>2</sub>	(mole*10 <sup>-4</sup> ) PA6-COOH	PBT ( $f = 2$ ) PBT-COOH	(mole*10 <sup>-4</sup> ) PBT-OH	Epoxy ( $f = 4$ ) (mole*10 <sup>-4</sup> )
PA6/PBT = 70/30	42	21	6	18	—
PA6/PBT/epoxy = 70/30/0.1 phr	42	21	6	18	33
PA6/PBT/epoxy = 70/30/0.3 phr	42	21	6	18	100
PA6/PBT/epoxy = 70/30/0.5 phr	42	21	6	18	167
PA6/PBT = 50/50	30	15	10	30	—
PA6/PBT/epoxy = 50/50/0.1 phr	30	15	10	30	33
PA6/PBT/epoxy = 50/50/0.3 phr	30	15	10	30	100
PA6/PBT/epoxy = 50/50/0.5 phr	30	15	10	30	167
PA6/PBT = 30/70	18	9	14	42	—
PA6/PBT/epoxy = 30/70/0.1 phr	18	9	14	42	33
PA6/PBT/epoxy = 30/70/0.3 phr	18	9	14	42	100
PA6/PBT/epoxy = 30/70/0.5 phr	18	9	14	42	167

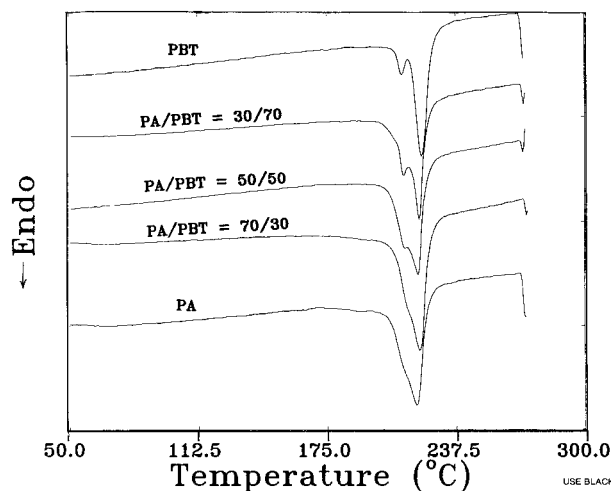
<sup>a</sup> The base of the calculation is 100 ( $f$ : the functionality of a resin):  $M_n$  of PA6 = 33,000 ( $-\text{NH}_2/-\text{COOH} \approx \frac{1}{1}$ );  $M_n$  of PBT = 25,000 ( $-\text{OH}/-\text{COOH} \approx \frac{3}{1}$ ); EEW of epoxy = 110–130 g/eq.

Table III, the amount of functional end groups of epoxy is less than the sum of PA and PBT when the epoxy content is just added 0.1 phr. The compatibilizer is probably consumed by the PA to increase its molecular weight and does not contribute to lower interfacial tension. At 0.3 phr compatibilizer, the amount of functional end groups of epoxy is very close to the sum of the neat resins. All of the functional end groups of the neat resins are not completely consumed. Certain PA-co-epoxy-co-PBT copolymers are expected to be formed at the interface. Higher viscosity from a better compatibilized blend can be related to the expected higher molecular weight from coupling reactions and the increased interfacial friction of the *in situ* formed copolymers anchoring along the interface.

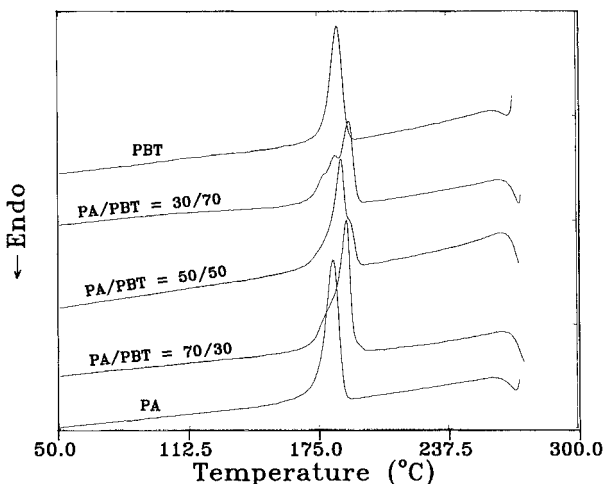
#### Differential Scanning Calorimetry (DSC)

Figures 4 and 5 show the second heating and the first cooling DSC scans of PA, PBT, and various uncompatibilized PA/PBT blends. The glass-transition temperatures of pure PA and PBT cannot be detected by these thermograms. Two endo-

therms can be seen in the pure PBT as shown in the heating thermograms (Fig. 4). Similar results were also observed previously by Huang<sup>25</sup> and Nadkarni et al.<sup>30</sup> PBT is one of the fastest crystallizing polymers and the crystallization kinetics



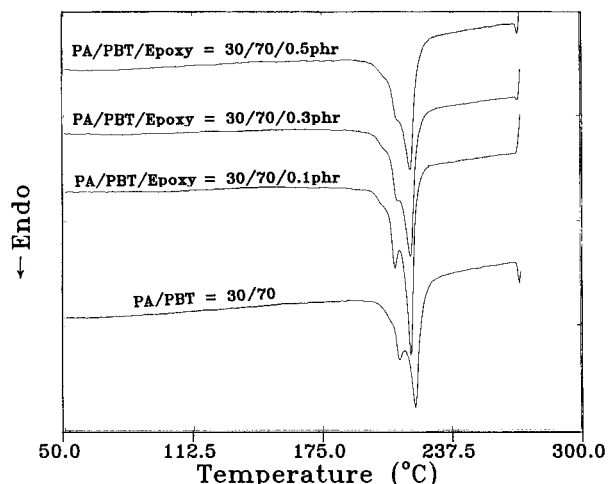
**Figure 4.** DSC thermograms at second heating of the base polymers and the uncompatibilized blends.



**Figure 5.** DSC thermograms at first cooling of the base polymers and the uncompatibilized blends.

have only been partially investigated.<sup>31</sup> PBT is known to possess two crystalline structures,  $\alpha$  and  $\beta$  forms, which can undergo a reversible transformation at a low level of applied stress.<sup>32</sup> The appearance of two endotherms can be interpreted reasonably as the result of sequential melting of the two different crystalline structures. PA and PBT are both highly crystalline polymers that can crystallize rapidly even under a quenched condition. Since the melt temperature of pure PA is so close to the major melt temperature of pure PBT (218.4 vs. 221.2 °C), the melt temperature of blends tend to fuse together. Crystallization temperatures (cooling scans) of pure PA and PBT are very close and the crystallization temperatures of all uncompatibilized blends are higher than those of the base polymers as shown in Figure 5. Therefore, either PA or PBT can be considered a mutual nucleating agent to enhance the crystallization on the other component.

The DSC scans of second heating of the uncompatibilized and compatibilized PA/PBT = 30/70 blends are given in Figure 6. The lower-temperature endotherm gradually decreases with the increase of the compatibilizer quantity. Figure 7 represents the first cooling DSC scans of the uncompatibilized and compatibilized PA/PBT = 30/70 blends. These two exotherms of all blends shift to lower temperatures with the increase of the compatibilizer quantity. From Table IV, we can deduce that PBT mainly contributes to the lower-temperature crystalline structure formation and the higher-temperature crystalline formation comes from the overlap between PA and PBT crystallization. Because the compatibilizer is

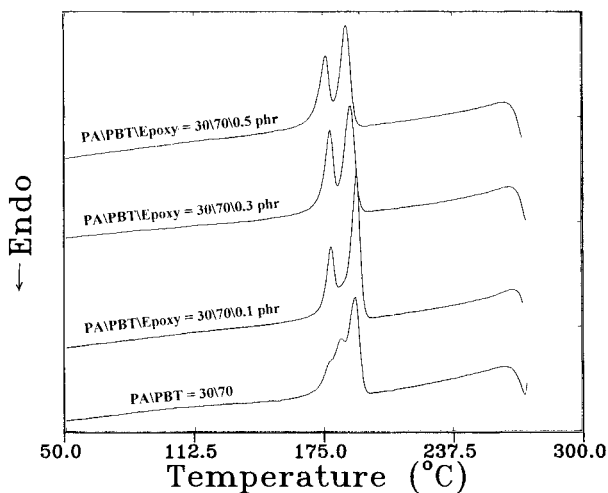


**Figure 6.** DSC thermograms at second heating of the uncompatibilized and compatibilized PA/PBT = 30/70 blends.

more compatible with PBT than with PA, it can be regarded as a heterogeneous nucleating agent in the PA phase and a crystallization retarder in the PBT phase. Therefore, the melt temperature range gradually becomes broader and the crystallization degree decreases with the increase of the compatibilizer quantity. In other words, the compatibilizer or the *in situ* formed copolymer tends to interfere with the crystallization of the base polymers in various blends.

### Morphologies

Figures 8–10 give some selected SEM micrographs of the uncompatibilized and compatibi-



**Figure 7.** DSC thermograms at first cooling of the uncompatibilized and compatibilized PA/PBT = 30/70 blends.

**Table IV.** Summary of DSC Data

Composition	$\Delta H_c$ (J/g)	$T_c$ (°C)		$\Delta H_m$ (J/g)	$T_m$ (°C)		Lower Temperature	Higher Temperature
							Crystalline Structure	Crystalline Structure
							Form (%)	Form (%)
PA6	-50.3	181.9		42.3	218.4		—	—
PBT	-36.5	184.7		32.5	211.6 221.2		—	—
PA6/PBT = 70/30	-51.7	188.6		46.8	220.0		—	—
PA6/PBT/epoxy = 70/30/0.1 phr	-49.6	173.0 185.9		49.2	218.4		28.57	71.43
PA6/PBT/epoxy = 70/30/0.3 phr	-48.7	170.2 184.7		34.5	217.3		30.08	69.92
PA6/PBT/epoxy = 70/30/0.5 phr	-46.8	168.5 184.2		30.6	217.8		31.67	68.33
PA6/PBT = 50/50	-49.2	186.4		47.6	212.8 219.5		—	—
PA6/PBT/epoxy = 50/50/0.1 phr	-45.9	173.5 185.3		32.2	212.2 219.6		24.78	75.22
PA6/PBT/epoxy = 50/50/0.3 phr	-45.3	170.2 183.1		30.6	210.5 217.8		28.77	71.23
PA6/PBT/epoxy = 50/50/0.5 phr	-38.6	173.6 183.0		30.3	210.5 217.3		47.98	52.02
PA6/PBT = 30/70	-41.5	183.1 189.8		33.1	212.2 220.1		45.98	54.02
PA6/PBT/epoxy = 30/70/0.1 phr	-47.2	178.6 190.9		39.8	210.5 217.9		32.63	67.37
PA6/PBT/epoxy = 30/70/0.3 phr	-43.6	177.5 188.1		35.0	211.7 217.8		45.54	54.46
PA6/PBT/epoxy = 30/70/0.5 phr	-41.9	175.8 185.9		34.1	211.7 217.8		45.91	54.09

$T_c$ : crystallizing point.

$T_m$ : melting point.

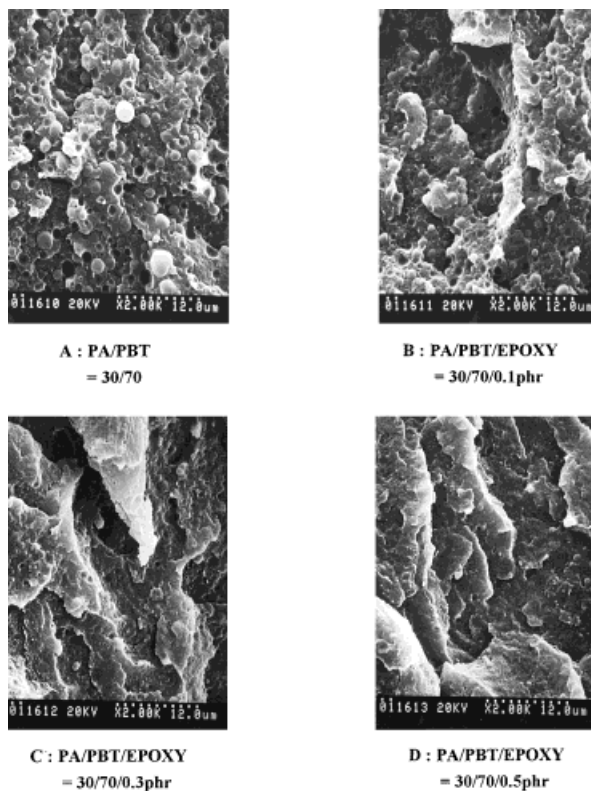
$\Delta H_c$ : enthalpy of crystallization.

$\Delta H_m$ : heat of fusion.

lized PA/PBT = 30/70, 50/50, 70/30 blends, respectively. Phase contrast and the sizes of the dispersed spherical particles of all three blending series decrease with the increase of the compatibilizer quantity. At the same compatibilizer quantity, the size and the particle pullout of the dispersed phase are less in the PA-rich blends than in the PBT-rich blends. Particle pulling-out and phase contrast of the blends containing 0.3 and 0.5 phr compatibilizer disappear [Figs. 10(c) and 10(d)], similar to a single-phase morphology. The above morphological information clearly demonstrates that this epoxy resin is indeed an efficient emulsifying agent for the PA/PBT blends to suppress phase coalescence and result in smaller phase domain size. These SEM morphological results provide evidence to explain the observed trend of the mechanical properties.

An effective compatibilizer can improve the interfacial adhesion of a blend and consequently enhance its mechanical properties. However, ef-

fectiveness of a compatibilizer should consider both interfacial adhesion and matrix intrinsic property change of the base polymers. Most literature tends to emphasize only the interfacial properties but ignores the change of the matrix intrinsic properties induced by the compatibilizer. In a reactively compatibilized blending system, a fraction of the compatibilizer (unreacted, partially reacted, or fully reacted), more or less, is expected to be distributed and dissolved in both base matrices that certainly will affect the intrinsic properties of the base polymers. It may increase or decrease the matrix intrinsic properties depending on the systems and/or the reaction mechanism involved of the compatibilizer with matrices. An et al.<sup>28</sup> proposed a compatibilization mechanism of the PA 6/PBT blends to explain the improvement of the mechanical properties of their blends in terms of molecular weight increase of matrices, and the enhancement of the interfacial adhesion between the matrices by the *in situ*



**Figure 8.** SEM micrographs of the uncompatibilized and compatibilized PA/PBT = 30/70 blends.

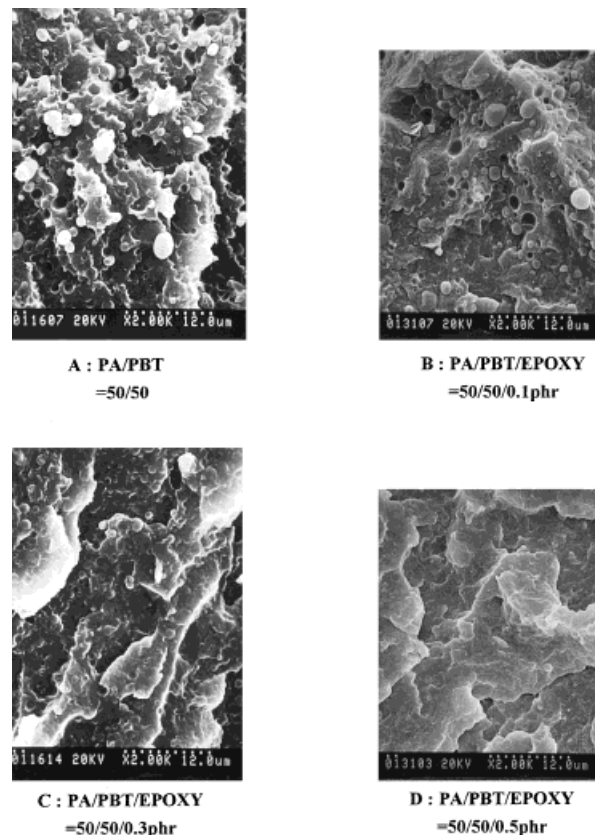
formed copolymer. In this reactively compatibilized PA/PBT system, a much greater fraction of the added epoxy is believed to be distributed in the PBT phase than that in the PA phase because the epoxy resin is more compatible with PBT than with PA. Not all of the epoxy initially dissolved in PBT has the chance to contact and reacts with PA at the interface. The presence of epoxy resin in the PBT phase, either in its original form or the *in situ* formed copolymer, tends to decrease the intrinsic properties of the PBT matrix. This is the reason why the observed mechanical property improvement of those PBT-rich blends is less substantial even with the expected improvement of the interfacial adhesion. In general, the matrix component of the blend has a determinant effect on the final properties of the blend, whereas the dispersed component plays a less important role. This is why the PA-rich blends show much better mechanical properties than the PBT-rich blends.

### Mechanical Properties

The material mechanical properties can roughly be classified into two categories: strength and

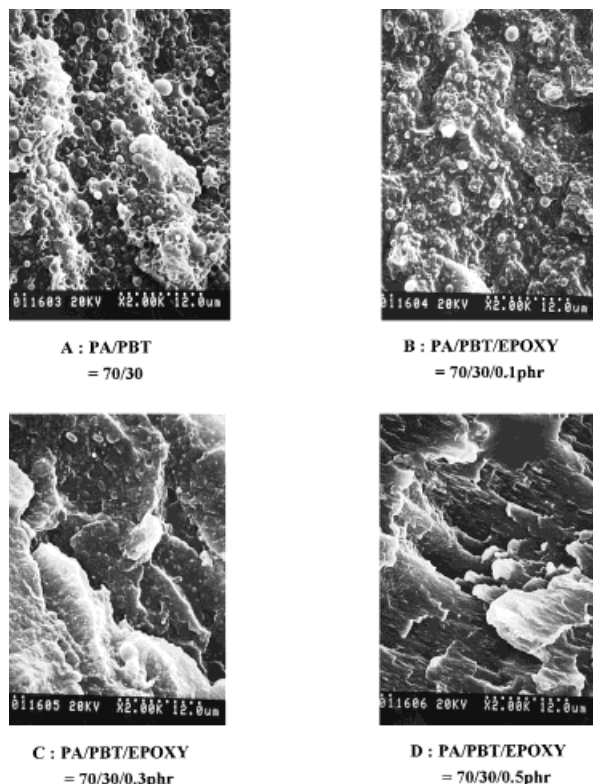
toughness. Tensile strength and flexural modulus can be considered the material strength, while tensile elongation and Izod impact energy are the material toughness. In general, modification of a polymeric material rarely results in improving both properties simultaneously. It usually results in one property being improved, while the other is not. This trend has also frequently existed in many compatibilized polymer blends relative to their uncompatibilized counterparts. Fortunately, improvement in both strength and toughness properties can be achieved in this compatibilized PA/PBT blend.

Figure 11 shows the effect of the compatibilizer quantity on the tensile strength of the PA/PBT blends. Tensile strength in all different compositions increases with the increase of the compatibilizer quantity. Tensile strength improvement from these PA-rich blends is more effective than those PBT-rich blends after compatibilization. The effect of compatibilizer on the flexural modulus of the blends is less clear as shown in Figure 12. The trend in tensile elongation is similar but



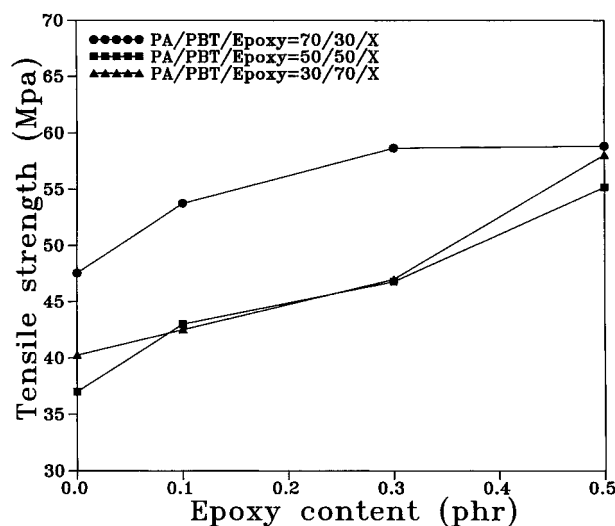
**Figure 9.** SEM micrographs of the uncompatibilized and compatibilized PA/PBT = 50/50 blends.



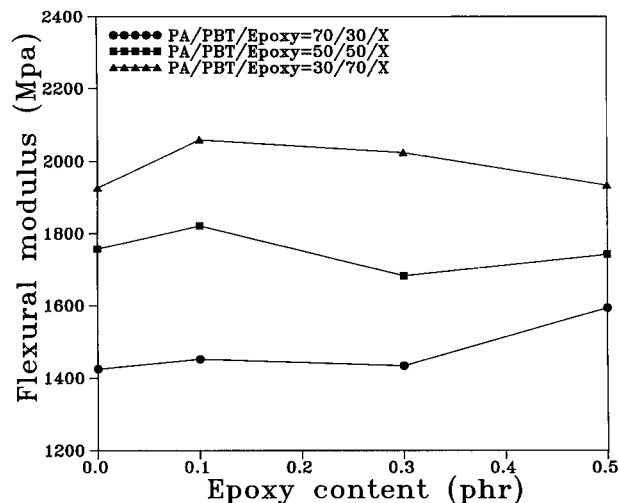


**Figure 10.** SEM micrographs of the uncompatibilized and compatibilized PA/PBT = 70/30 blends.

more drastic than that of the tensile strength as shown in Figure 13. Again, the PA-rich blends show better improvement than the PBT-rich blends when the same compatibilizer quantity is



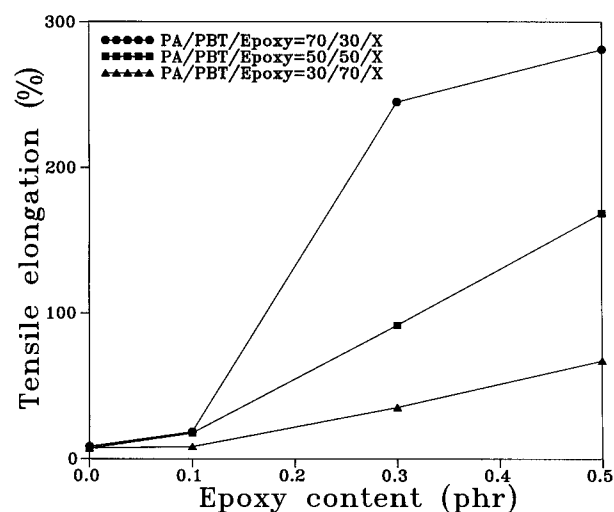
**Figure 11.** Effect of compatibilizer content on tensile strength.



**Figure 12.** Effect of compatibilizer content on flexural modulus.

employed. Figure 14 gives the effect of compatibilizer on the notched impact strength of the blends. The improvement of the impact strength is not substantial when the compatibilizer content is less than 0.3 phr. With addition of 0.5 phr compatibilizer, the impact strengths of all blends increase drastically.

Figure 15 shows the plot of  $BD\Phi$  versus impact energy of the uncompatibilized and compatibilized PA/PBT = 30/70 blends. The B is the uniform thickness of a specimen, D is the specimen length, and  $\Phi$  is the geometrical factor.<sup>29</sup> The slope of the regression line represents the critical

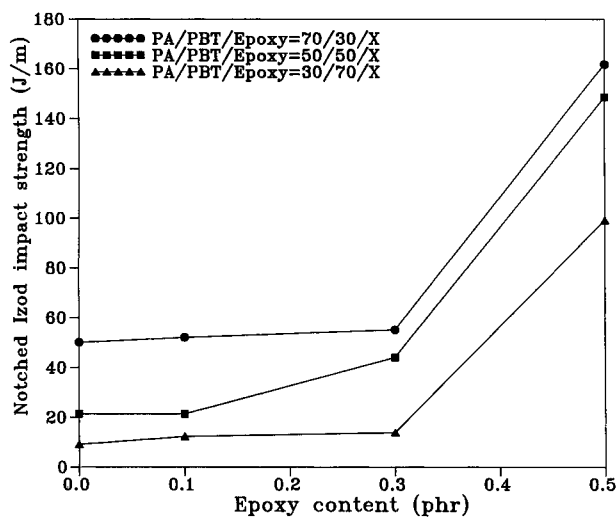


**Figure 13.** Effect of compatibilizer content on tensile elongation.

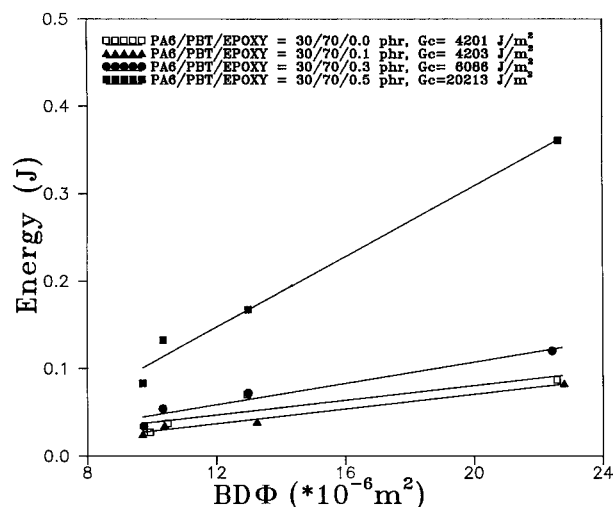
strain energy release rate ( $G_c$ ). The progressive improvement on  $G_c$  is achieved by increasing the amount of the compatibilizer. The presence of 0.5 phr compatibilizer results in about a five-fold increase on  $G_c$  as shown in Figure 15. Consequently, these mechanical properties can be related to the observed morphological results, shown in Figures 8–10. The fracture behavior of the blend with less than 0.3 phr compatibilizer is governed by a particle pullout mechanism, while shear yielding is dominant in the fracture behavior of the blend with more than 0.3 phr compatibilizer.

### *In Situ* Reactive Compatibilization Mechanism

In general, the reactive compatibilization system is more complicated than the traditional nonreactive system. The chemical structure of the nonreactive copolymer will not be altered during melt mixing and the copolymer prefers to reside thermodynamically at the interface with segments extending into both base polymer phases. A reactive copolymer is a precursor for the reactive compatibilizer and the final properties for the reactive compatibilized blend depend upon the structure and distribution of the *in situ* formed reactive compatibilizer.<sup>7</sup> To obtain an efficient *in situ* formed copolymer as a compatibilizer, several variables need to be considered such as composition, reactivity, blending sequence, processing condition, component mutual compatibility, and melting temperature.



**Figure 14.** Effect of compatibilizer content on notched impact strength.



**Figure 15.** Plots of impact energy versus  $BD\Phi$  to determine  $G_c$  for the uncompatibilized and compatibilized PA/PBT = 30/70 blends.

This multifunctional epoxy resin has low molecular weight with  $T_g$  significantly lower than the  $T_m$ s of PA and PBT. Epoxy resin is more compatible with PBT than with PA because it is miscible or nearly miscible with PBT.<sup>25</sup> Therefore, the epoxy resin is more likely to be dissolved or distributed in the PBT phase than in the PA phase during earlier stages of melt blending. Consequently, most of the epoxy has the first chance to make contact and react with the PBT end groups. Because the more reactive carboxyl end groups are made up of about 25% of the total PBT end groups, most epoxy groups remain free to react with amine and carboxyl end groups of the PA. Reactivity between epoxide with amine is pronouncedly greater than that with carboxyl. When 0.3 phr epoxy is added, the amount of the functional end groups of epoxy is very close to the sum of the neat resins and the formation of the copolymer is likely. At a small amount of epoxy, 0.1 phr, the improvement of mechanical properties of the compatibilized blends is not very substantial because the epoxy is almost consumed by reacting with amine groups. At 0.5 phr epoxy, the functional end groups of epoxy are greater than the sum of the neat resins and the formation of PA-co-epoxy-co-PBT copolymer is certain and results in drastic improvement in mechanical properties.

### CONCLUSION

This multifunctional epoxy resin has been demonstrated to be an efficient reactive compati-

lizer for the incompatible blends of PA and PBT. The torque measurements give indirect evidence that the reactions between PA and PBT with epoxy has an opportunity to produce the *in situ* formed mixed copolymer, which can be an effective compatibilizer to reduce and stabilize the size of the disperse phase, and to greatly enhance mechanical properties of PA/PBT blends.

The mechanical properties of PA/PBT blends have been substantially improved by adding a small quantity of the epoxy compatibilizer. The effect of the compatibilizer is more obvious on the PA-rich blends than on the PBT-rich blends. The nature of this epoxy compatibilizer is more compatible with the PBT phase than with the PA phase. A substantial fraction of the compatibilizer, reacted or unreacted, will reside in the PBT phase and thus decrease the intrinsic properties of the PBT matrix. On the other hand, the intrinsic properties of the PA phase may even be improved by molecular weight increase after compatibilization. Particle pullout is dominant in the fracture behavior of the blend containing less than 0.3 phr compatibilizer, whereas the fracture behavior of the blend with more than 0.3 phr is dominated by shear yielding.

Because the melt and crystallization temperatures of the base polymers are so close, either PA or PBT can be considered a mutual nucleating agent to enhance the crystallization on the other component. PBT mainly contributes to the lower-temperature crystalline structure formation and the higher-temperature crystalline structure formation comes from the overlap between PA and PBT crystallization in cooling DSC scans of various blends. Again, the compatibilizer and the *in situ* formed copolymer, along the interface and in the base polymers, will interfere with the crystallization of the base polymers in these compatibilized blends.

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