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The effect of crystalline morphology of poly (butylene terephthalate) phases on toughening of poly(butylene terephthalate)/epoxy blends

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In an effort to investigate the effect of the crystalline morphology of a poly(butylene terephthalate) (PBT) phase on the toughening of PBT/epoxy blends, the blends, having different degrees of perfectness of the PBT crystalline phase, were prepared by blending PBT and epoxy at various temperatures ranging from 200 to 240 °C. As the blending temperature decreases, the degree of perfectness of the PBT crystalline phase increases as a result of the increase of crystal growth rate. For PBT/epoxy blends, the change in crystalline morphology induced by processing may be the most important cause for the dependency of the fracture energy on blending temperatures. It has been found that PBT phases with a well-developed Maltese cross are most effective for epoxy toughening. This dependency reveals the occurrence of a phase transformation toughening mechanism. Also, the higher relative enhancement of fracture energy of a higher molecular weight epoxy system is further indirect evidence for a phase transformation toughening mechanism. Some other toughening mechanisms observed from the fracture surfaces, such as crack bifurcation, crack bridging, and ductile fracture of PBT phases, have been found to also be affected by the blending temperatures. © *1999 Kluwer Academic Publishers*

1. Introduction

Epoxies are often used as matrices in structural composites because of their high stiffness, high strength, good chemical resistance, and excellent dimensional stability. In spite of their outstanding properties, the use of epoxies is sometimes limited because of their low toughness, especially in the presence of sharp cracks. Hence, the improvement in toughness of brittle epoxies is strongly desired. In general, toughness of epoxies has been remarkably enhanced by the incorporation of rubber, but epoxies with high crosslink density cannot be successfully toughened [1]. Moreover, desirable intrinsic properties of the matrix, such as high strength and high stiffness, are inevitably lowered due to the low stiffness and strength of the added elastomeric materials. This limits the number of high performance applications such as aerospace, transportation, and building construction.

Recently, it has been reported that brittle epoxies can be successfully toughened by the inclusion of thermoplastic polymers without sacrificing the inherent properties of epoxies [2, 3]. Among them, PBT has been found to be the effective for toughening of high crosslinked epoxies [4]. It has been suggested that this exceptional increase of toughness might be due to the phase transformation toughening mechanism, which has been known in zirconia-containing ceramics [5–12]. Among crystalline polymers, only the PBT exhibits a stress-induced transformation with volume expansion like zirconia [4]. The normal α-structure of PBT can be transformed to a more extended β-crystal under applied stress that is thought to occur because of a change in butylene chain conformation from TGTG to TTTT.

Until now, direct experimental evidence for the occurrence of phase transformation toughening during the fracture of PBT/epoxy blends has not been obtained because of the immediate reverse phase transformation of PBT on release of the applied stress. Some results, such as morphology sensitivity and synergism on fracture toughness of PBT/epoxy blends, however, support the phase transformation toughening hypothesis indirectly [4, 13–15]. The synergism is believed to be due to the enhancement of degree of perfectness of PBT crystalline phases, which possibly affects phase transformation toughening. The high effectivness of premade powders in fracture toughness also supports the hypothesis [4, 15].

In the present study, PBT/epoxy blends having controlled crystalline morphology were investigated

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to discover the effect of degree of perfectness of the PBT crystalline phase on the fracture toughness of the blends. Also, the possibility of the phase transformation toughening mechanism was investigated.

2. Experimental

2.1. Materials

Two epoxy systems with different molecular weight and crosslinking density have been investigated: (1) diglycidyl ether of bisphenol A (DGEBA)/4,4′-diaminodiphenylmethane (DDM) and (2) tetraglycidyl-4,4′-diaminodiphenylmethane (TGDDM)/4,4′-diaminodiphenylsulfone (DDS). The optimum concentrations of DDM and DDS were 20 and 35 phr, respectively. PBT was used as a modifier, the molecular weight of which was 36,000.

For blending of PBT and epoxies, the mixture of PBT pellets and epoxies were heated, with stirring, to specific temperatures ranging from 200 to 240 °C, referred to here as the blending temperature (T_b). After complete dissolution of the PBT in the epoxies, the mixtures were cooled to room temperature at 10 °C/min. Before curing, the mixtures were degassed under vacuum at 80 °C and poured into preheated molds. The DGEBA/DDM system was cured at 80 °C for 2 h and postcured at 150 °C for another 2 h; the TGDDM/DDS system was cured at 180 °C for 2 h without postcuring. All blends studied contained 5% of PBT by weight.

2.2. Property measurements

The fracture toughness was measured by applying linear elastic fracture mechanics (LEFM). The critical strain energy release rate, G_{Ic}, was determined using a single-edge notched (SEN)–type specimen (4 mm × 11 mm × 100 mm) in a three-point bending geometry. The precrack of the specimen was generated by tapping into the specimen a razor blade chilled in liquid nitrogen. The specimens were tested on a universal testing machine at the crosshead speed of 0.5 mm/min. The following relationship was used to calculate G_{Ic} from sample and crack dimensions:

$$W = G_{Ic} \times B \times D \times \Phi,$$

$$\Phi = 0.5 \times (a/D) + (1/18\pi) \times (2L/D) \times (a/D)^{-1},$$

where W is the fracture energy, B is the sample thickness, D is the sample width, a is the initial crack length, and L is the span length (66 mm) [16].

The specimens were deformed under uniaxial compression to examine their yielding behavior. A constant displacement rate of 0.5 mm/min was used. The load measured from the load-displacement curve was converted to stress using the initial cross-sectional area of the specimen. Then the compressive modulus, E, and the compressive yield stress, σ_y, were determined.

Thermal properties were measured by using a differential scanning calorimetry (DSC) with a 10 °C/min scanning rate. The glass transition temperature (T_g) was determined with a dynamic mechanical thermal analyzer (DMTA). The viscosity of the blends was monitored with a rheometric mechanical spectrometer (RMS) equipped with a coni-cylinder. Dynamic experiments were performed under oscillatory stress at 10% strain and 1 rad/s frequency.

2.3. Fractographic study

Scanning electron microscopy (SEM) was used to study and record the fractured surfaces of the pure and modified epoxies. The fractured surfaces were coated with a thin layer of gold-palladium.

In order to examine a process zone at a crack tip, polarized transmission optical microscopy was used to investigate plastic deformation of the matrix near the crack tip. The specimens used for optical microscopy study were broken by a double-notched four-point bending (DN-4PB) method. The thin section including this stationary crack was made by using the petrographic polishing technique [16]. The section plane was parallel to the crack propagation direction and normal to the fracture surface.

3. Results

Near and above its melting point, PBT is soluble in uncured epoxy resins. The temperatures at which the dissolution process begins and reaches completion are of interest, because the crystallization behavior depends on these. In Fig. 1, DSC thermograms of epoxy blends containing 5 wt % of PBT are compared with the thermogram of pure PBT. On blending with epoxies, there occurs a lowering of the endothermic dissolution peak of PBT, the amount of which depends on the molecular weight of the epoxy. The onset of the dissolution peak in the TGDDM system is about 15 °C higher than that in the DGEBA system. Also, the peak in the TGDDM system is sharper and narrower.

On blending PBT and epoxy, under high agitation transparent mixtures can be obtained when the T_b for the DGEBA and TGDDM systems are above 200 °C and 210 °C, respectively. Cooling causes the PBT to crystallize from these mixtures. The crystallization temperature of PBT in epoxies on cooling depends on T_b, as

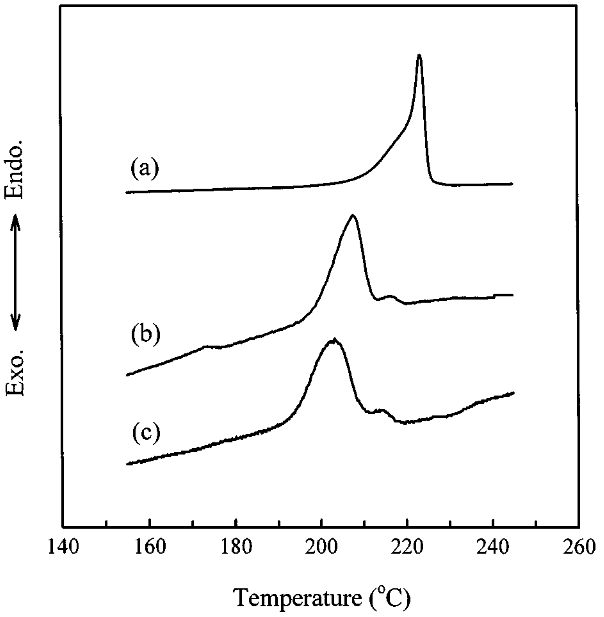


Figure 1 DSC thermograms of PBT (5 wt %) and epoxy blends without curing agents: (a) pure PBT, (b) PBT/TGDDM, (c) PBT/DGEBA.

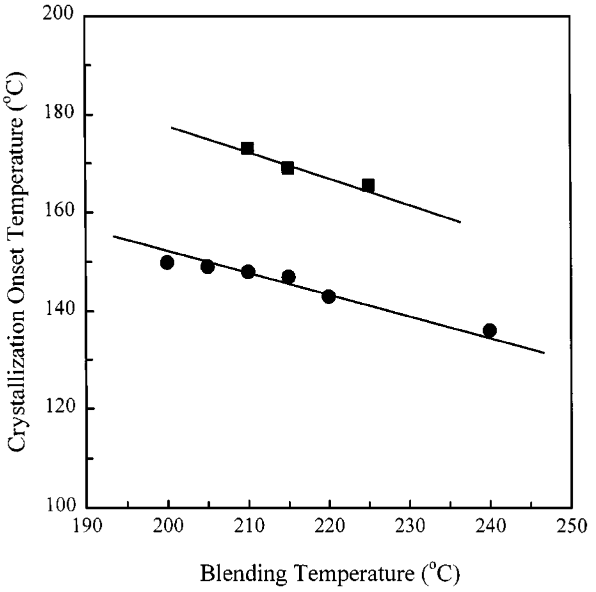


Figure 2 The effects of the T_b on the crystallization onset temperature of PBT in epoxy: (●) DGEBA/DDM system, (■) TGDDM/DDS system.

shown in Fig. 2. As T_b increases from 200 to 240 °C, the crystallization onset temperature decreases from 150 to 135 °C.

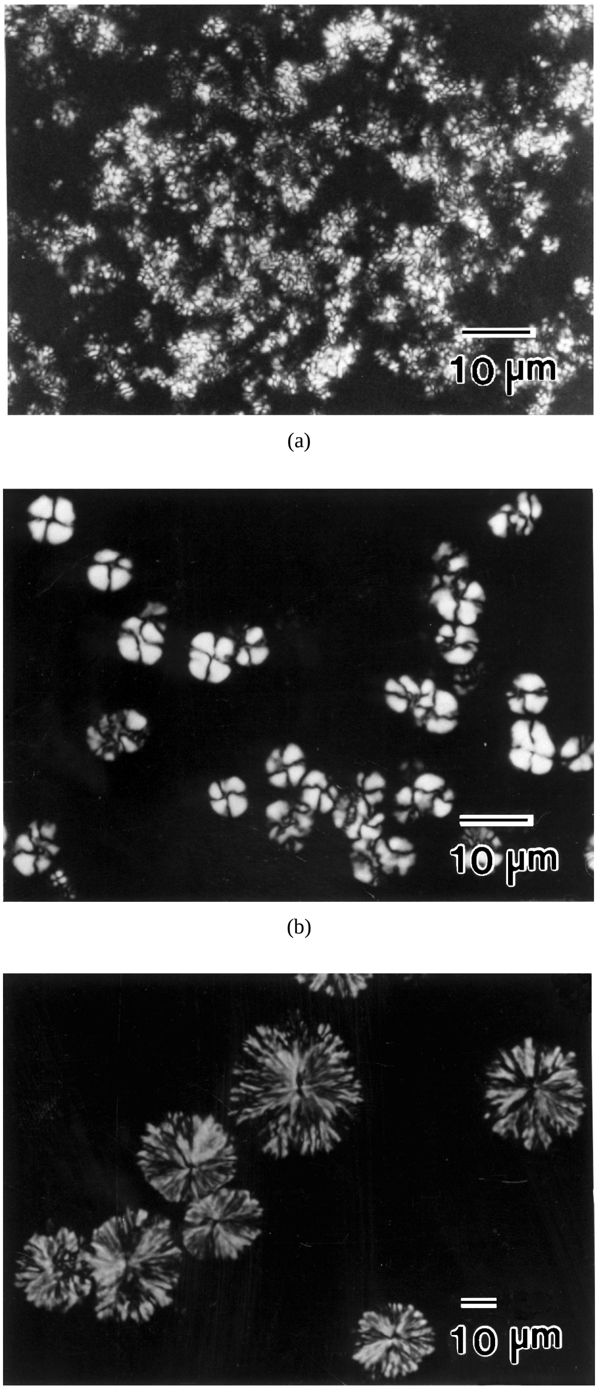
On cooling, the PBT forms isolated spherulites as seen in transmitted optical micrographs. The crystalline morphology of the PBT spherulites that develops also depends on T_b. As shown in Fig. 3 for the DGEBA and TGDDM systems, the most well-developed Maltese crosses, indicating the highest degree of perfectness, can be seen when T_b is 210 and 215 °C, respectively. Above those temperatures, the developed spherulites do not exhibit well-developed Maltese crosses, although they do have the circular and fibrous characteristics of spherulites. On the other hand, below those temperatures, no crystalline phase separation is apparent. The agglomerations of tiny crystals dominate the fields of view in optical micrographs of thin section as seen in Fig. 3a and d.

The effect of T_b on the thermal properties of blends after curing is shown in Table I. The melting temperature (T_m) and heat of fusion (ΔH) of PBT have remained unaffected by changing T_b, irrespective of which epoxy is used. The single melting of PBT indicates no occurrence of partial melting/dissolution of PBT in epoxy during blending process. Fig. 4 shows that the T_g of the epoxy decreases almost linearly with an increase of T_b. The viscosity change of PBT/epoxy blends on cooling is shown in Fig. 5. As seen in the figure, there occurs a sudden increase of viscosity of PBT/epoxy blends at temperatures lower than 90 °C, which is far below the crystallization temperatures of PBT in the blends.

The effect of T_b on the mechanical properties of PBT/epoxy blends, such as modulus and yield stress, is shown also in Table I. Both modulus and yield stress

TABLE I Effects of blending temperature on thermal and mechanical properties of PBT-modified epoxies

T_b (°C)	T_m (°C)	ΔH (J/g)	E (GPa)	σ_y (MPa)
DGEBA/DDM				
neat	—	—	2.80	118
200	218	67.8	2.79	118
205	218	67.9	2.86	121
210	219	67.9	2.74	117
215	219	67.8	2.80	120
220	217	67.8	2.79	119
240	217	67.8	2.83	118
TGDDM/DDS				
neat	—	—	2.94	148
210	211	65.4	2.90	144
215	212	64.3	2.93	147
225	209	66.6	2.90	147

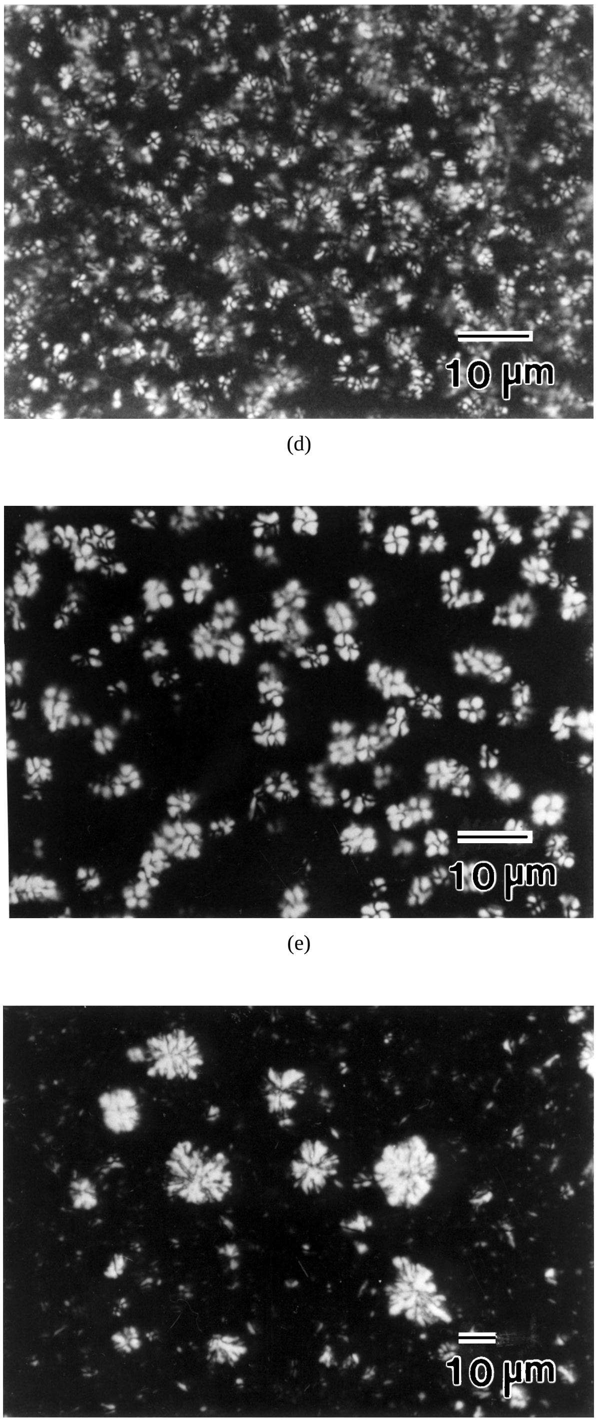


(a)

(b)

(c)

Figure 3 Polarized transmission optical micrographs of thin section of PBT/epoxy blends for the DGEBA/DDM system (a) T_b: 200 °C, (b) T_b: 210 °C, (c) T_b: 240 °C and for TGDDM/DDS system: (d) T_b: 210 °C, (e) T_b: 215 °C, (f) T_b: 225 °C.



(d)

(e)

(f)

Figure 3 (*Continued*).

of the modified epoxies have remained at essentially the same values the epoxies show without PBT. The fracture toughness exhibits strong dependency on T_b and epoxy molecular weight, as seen in Fig. 6, however. For the DGEBA system, the toughness increases rapidly when T_b increases up to 210 °C. For higher T_b, the toughness slowly decreases. For the TGDDM system, however, the maximum fracture toughness was obtained when T_b was 215 °C. The temperature range affecting the toughness for the TGDDM system is much narrower than that for the DGEBA system. Fig. 7 shows the relative fracture toughness enhancement of PBT/epoxy blends over neat epoxies. From this figure, it should be noticed that the relative enhancement of toughness of the TGDDM system is much higher than that of the DGEBA system.

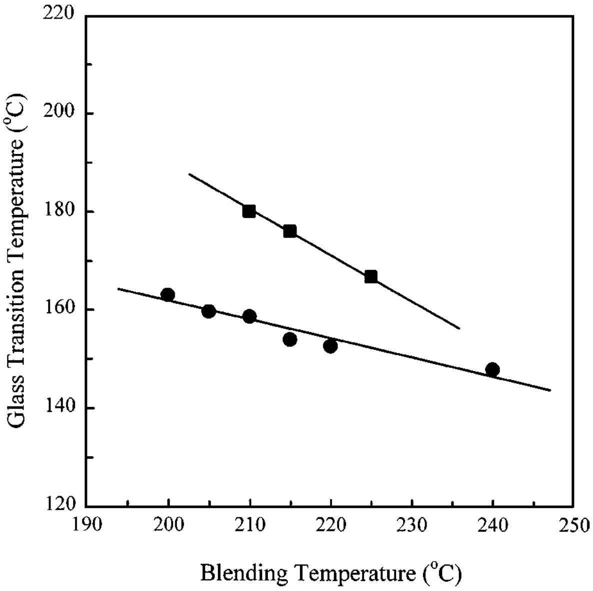


Figure 4 The effects of the T_b on the T_g modified epoxies after curing: (●) DGEBA/DDM system, (■) TGDDM/DDS system.

Fig. 8 shows the SEM micrographs of fracture surfaces of PBT/epoxy blends. The toughening mechanisms observed from the fracture surfaces of modified epoxies are crack bifurcation, crack bridging, and ductile fracture of PBT phases. As seen on fracture surfaces, several tails or crack bifurcation lines behind every PBT phase are observed that indicate the crack bifurcation and crack bridging mechanisms. With an increase of degree of perfectness of the PBT crystalline phase, the size of the tails increases and the number of tails decreases, which reveals the strengthening of crack bifurcation and primary crack bridging mechanisms.

4. Discussion

The fracture toughness of PBT/epoxy blends has been found to be highly affected by the crystalline morphology of PBT phases [4, 13–15]. Thus, it is

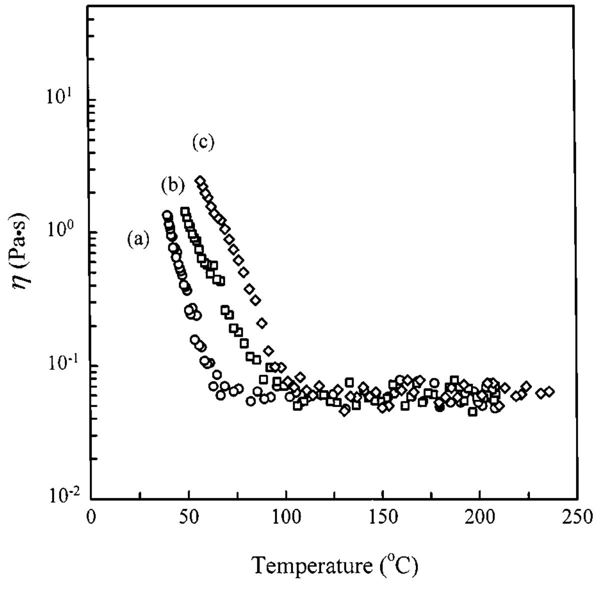


Figure 5 The viscosity change of PBT/DGEBA epoxy blends on cooling: (a) pure epoxy, (b) T_b: 210 °C, (c) T_b: 240 °C.

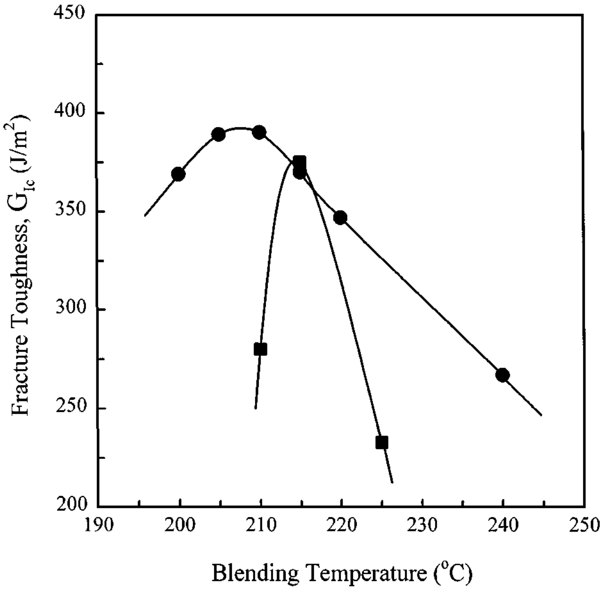


Figure 6 The effects of T_b on the fracture toughness of PBT-modified epoxies: (●) DGEBA/DDM system, (■) TGDDM/DDS system.

necessary to understand the crystallization and phase separation behavior of PBT in blends with epoxies. The blends of PBT and epoxies are expected to exhibit the upper critical solution temperature (UCST) behavior like many other polymer solutions. In the phase diagram for PBT/epoxy blends, the melting or crystallization line is thought to be higher than the binodal decomposition line is because it is observed that the PBT is crystallized first on cooling. Fig. 9 shows the schematic phase diagram for PBT/epoxy blends. For binary blends, the critical volume fraction, Φ_C, can be calculated from $\Phi_C = N_B^{1/2}/(N_A^{1/2} + N_B^{1/2})$, where N_A and N_B are the degrees of polymerization of the two components [17]. For the PBT/epoxy blends investigated, the calculated Φ_C is 0.078, which is too low a value to expect liquid–liquid phase separation before crystallization. For example, on cooling from point A, the crystallization of PBT mostly takes place well below the melting curve because of supercooling. As the crystallization proceeds, PBT molecules in homogeneous mixture move to the nuclei of PBT nearby and continuously grow to form spherulites. As a result, the composition of PBT in the homogeneous region is decreased along the dashed line, instead of

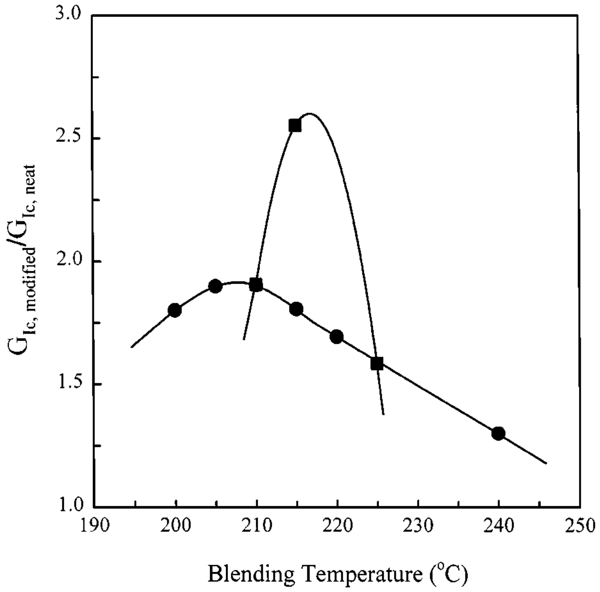
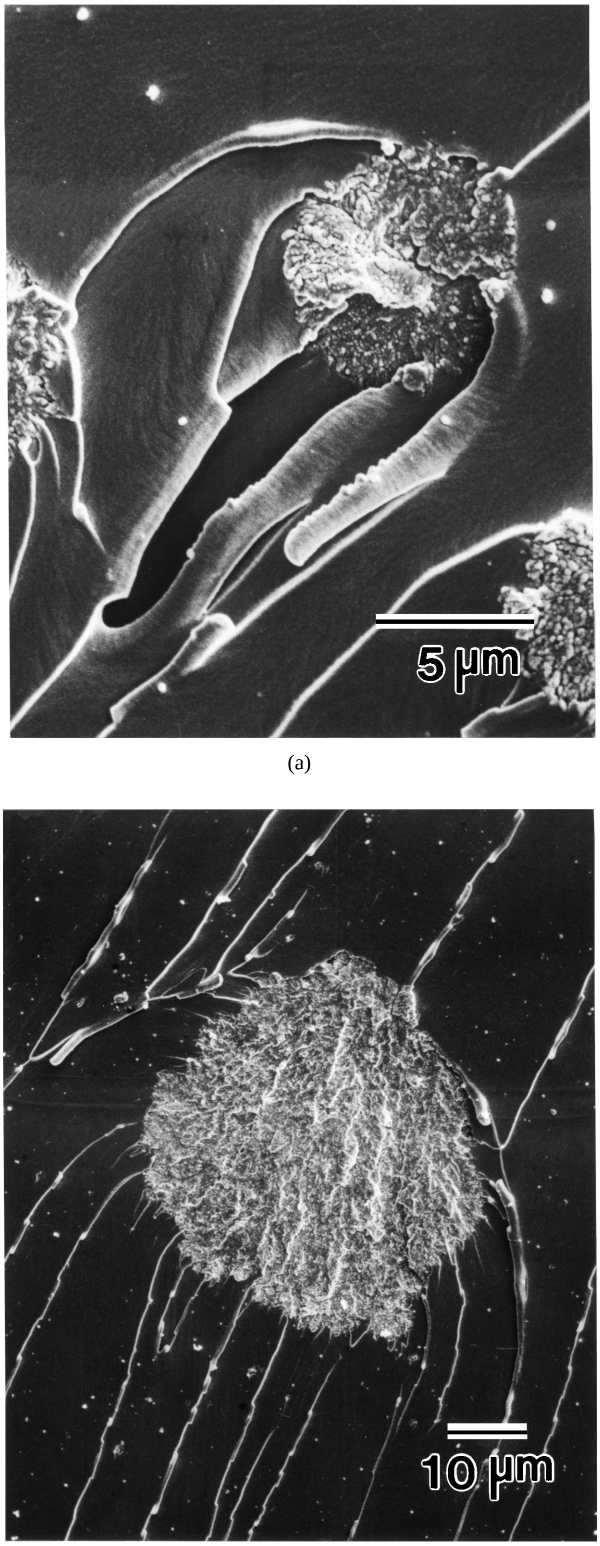


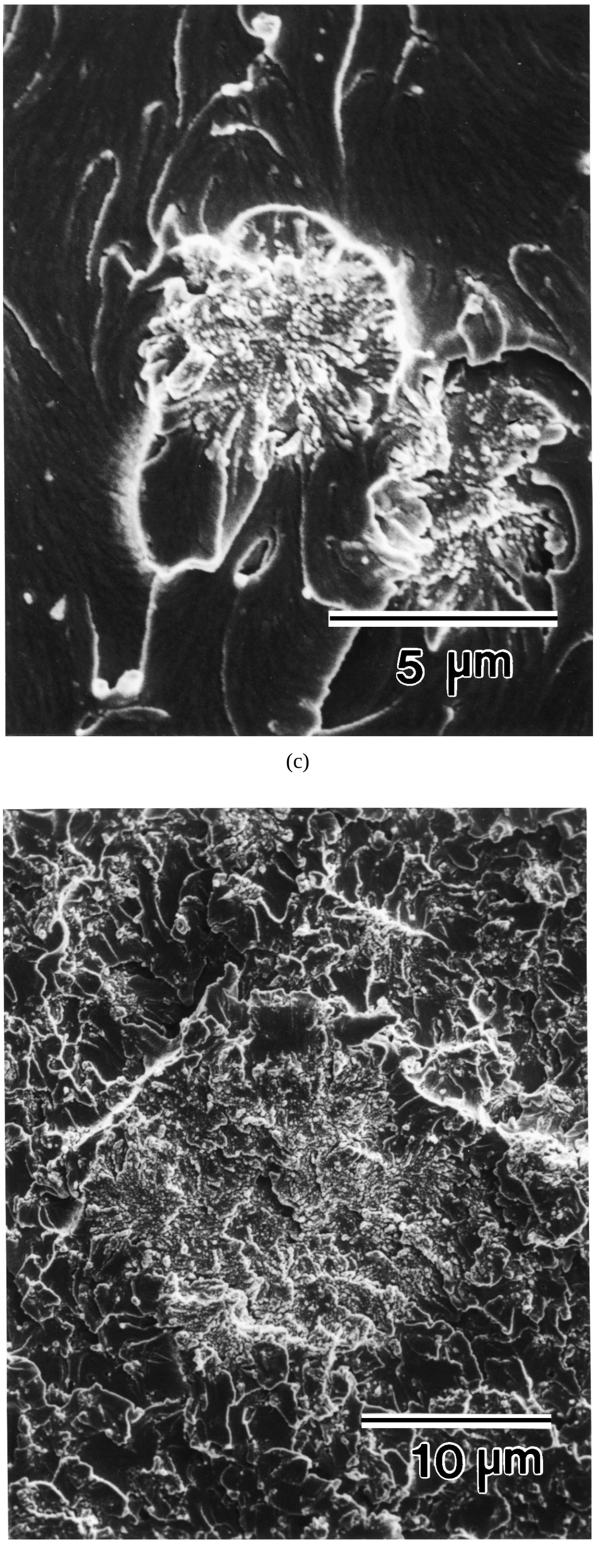
Figure 7 The effects of T_b on the relative fracture toughness enhancement of modified epoxies over neat epoxies: (●) DGEBA/DDM system, (■) TGDDM/DDS system.



(a)

(b)

Figure 8 SEM of the fracture surfaces of PBT/epoxy blends for DGEBA/DDM system: (a) T_b: 210 °C, (b) T_b: 240 °C and for TGDDM/DDS system: (c) T_b: 215 °C, (d) T_b: 225 °C.



(c)

(d)

Figure 8 (*Continued*).

the straight line shown in Fig. 9. When the binodal line is far below the melting curve, it is difficult for phase separation to take place due to the low chain mobility. Consequently, for this system liquid–liquid phase separation after crystallization may not occur.

The PBT and epoxies form uniform mixtures due to their miscibility when mixed at temperatures above 210 °C with high agitation. On cooling the homogeneous mixtures, reprecipitation/crystallization of the PBT as isolated spherulites occurs. Uniformly space-filled spherulites must be made of a crystalline structure that radiates from a center, branching with a small angle, and space-filling amorphous phase. After the reprecipitation/crystallization stage, inside the spherulite, the PBT crystalline phase is surrounded by a mixture of epoxy and PBT molecules that cannot be crystallized. In general, the degree of perfectness of the spherulites is related with the concentration of impurities and is determined by D/G, where D is the average diffusion coefficient of the impurities and G is the radial growth rate of the spherulites. Higher D/G ratios correspond to lower degrees of perfectness [18, 19]. The radial growth rate may be described by the equation, $G = G_0 \exp(-\Delta E/RT) \exp(-\Delta F^*/RT)$, where ΔE is the free energy of activation for a chain crossing the barriers to the crystal, and ΔF^* is the free energy of formation of a surface nucleus of critical size [20]. The third factor expresses the temperature dependence of the nucleation rate. For PBT/epoxy blends, when the blending temperature is not sufficiently high enough, there possibly exists a large number of undissolved living nuclei of PBT that affect the crystal growth rate by lowering the ΔF^*. For PBT/epoxy blends studied, when the T_b is lowered, the crystal growth rate increases as the result of the increasing number of residual living nuclei. The results of the increase of the crystallization onset temperature with a decrease of T_b reveals the dependency of the growth rate on T_b (see Fig. 2). During crystallization, the diffusivity of epoxy may not be affected by T_b because an increase of viscosity of PBT/epoxy blends occurs at temperatures lower than 90 °C, which is far below the crystallization temperatures (see Fig. 5). Consequently, the parameter for the degree of perfectness of the PBT crystalline phase in epoxy, D/G, is mainly determined by the crystal growth rate, G. Therefore, for PBT/epoxy blends, as T_b decreases, the degree of perfectness of the PBT crystalline phase increases as a result of a lowering of the D/G value.

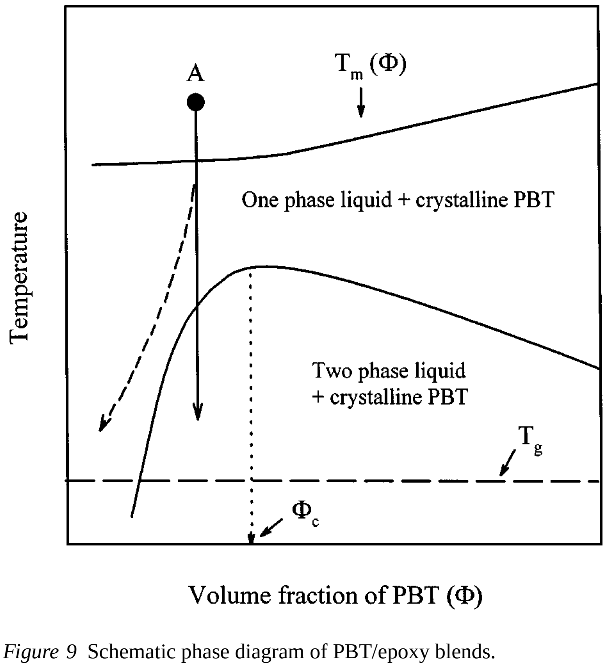


Figure 9 Schematic phase diagram of PBT/epoxy blends.

For PBT/epoxy blends, the change in crystalline morphology induced by processing may be the most important cause for the dependency of the fracture energy on T_b. It has been found that PBT spherulites with a well-developed Maltese cross are effective for epoxy toughening. The dependency reveals the occurrence of a phase transformation toughening mechanism in PBT/epoxy blends. The PBT crystals have all orientations in a spherulite. For them to transform from a normal α-structure to a more extended β-structure, the crystals should be oriented with the axis of the applied load along the PBT chain axis. When PBT spherulites develop in an epoxy during cooling, some epoxies may be included inside the amorphous region of spherulite, and these cured epoxies tend to prevent the PBT crystals from rotating. In coarser PBT spherulites, the amount of epoxy inside the spherulite increases and the degree of isolation of the PBT crystal becomes greater. The rotation of the PBT crystal is more restricted by the three-dimensional crosslinked epoxy, and thus the phase transformation toughening mechanism is less operative.

When comparing the two epoxy systems studied, the temperature ranges affecting the fracture toughness are well-related to the dissolution ranges of PBT in each epoxy (see Figs 2 and 6). The results reveal the dependency of fracture toughness of PBT/epoxy blends on the crystallization behavior of PBT. Another result that should be noticed is the higher relative enhancement of the fracture energy of the TGDDM system than that of the DGEBA system (see Fig. 7). Compared with the DGEBA epoxy, the TGDDM epoxy is more viscous and less miscible with PBT due to its higher molecular weight and some branches. Thus, the PBT chains are more easily segregated when crystallized from the TGDDM epoxy solution during cooling, and the amount of epoxy inside the amorphous region of the PBT spherulites is less. The results of relative higher enhancement of fracture energy of high molecular weight epoxy system can be another indirect evidence for a phase transformation toughening mechanism in PBT/epoxy blends.

The morphology seen on the fracture surfaces reveals other causes for the dependency of the fracture energy on T_b. The toughening mechanisms observed from the fracture surfaces, such as crack bifurcation, crack bridging, and ductile fracture of PBT phases, are all affected by T_b. As seen on fracture surfaces, several tails or crack bifurcation lines behind every PBT phase are observed, which indicates a crack bifurcation and bridging mechanism. When the cracks pass around the two sides of PBT phases, the crack paths are locally and asymmetrically altered by PBT particles. Consequently, behind the particles they rejoin at the two different elevations, which results in a pair of steps on both sides of the fracture planes with a single welt between them. These steps and welts are also indications of the crack bifurcation and bridging. Crack bifurcation enhances the fracture energy partly by creating more crack area. The welt tends to hold both fracture surfaces together and is stretched until fractured as the two separate. Thus, as the size of the welt increases, the bridging effect becomes greater. The number of welts is another indication for toughening mechanisms. The increase of number of welts reveals the weakening of crack bifurcation and primary crack bridging by unfractured PBT phase. In PBT/epoxy blends, the size of the welts increases and the number of welts decreases with an increase of the degree of perfectness of PBT spherulites. The ductile fracture of the PBT phase, another indication of toughness enhancement, is also enhanced with T_b.

5. Conclusions

In an effort to investigate the effect of the crystalline morphology of the PBT phase on the toughening of PBT/epoxy blends, blends with different degrees of perfectness of the PBT phase can be prepared by blending PBT and epoxy at various temperatures. On cooling homogeneous PBT/epoxy blends formed at temperatures above 210 °C, crystallization of the PBT as isolated spherulites occurs. The degree of perfectness of the PBT crystalline phase in epoxy is mainly determined by the crystal growth rate, which is affected by the number of undissolved living nuclei. Thus, as the T_b decreases, the degree of perfectness of the PBT crystalline phase increases as a result of the increase of crystal growth rate.

For PBT/epoxy blends, the change in crystalline morphology induced by processing may be the most important cause for the dependency of the fracture energy on T_b. It has been found that PBT spherulites with a well-developed Maltese cross were most effective for epoxy toughening. This dependency reveals the occurrence of a phase transformation toughening mechanism that is affected by the degree of perfectness of PBT spherulites. As the degree of perfectness decreased, the amount of epoxy inside the amorphous region of the spherulite increased, the rotation of the PBT crystal was more restricted by the three-dimensional crosslinked epoxy, and thus the phase transformation toughening mechanism was less operative. The higher relative enhancement of fracture energy of the higher molecular weight epoxy system is further indirect evidence for a phase transformation toughening mechanism, because the PBT crystalline phase in the high molecular weight epoxy is more perfect due to the epoxy's higher viscosity and lower miscibility with PBT.

The toughening mechanisms observed from the fracture surfaces, such as crack bifurcation, crack bridging, and ductile fracture of PBT phases, are all affected by the T_b. The increase of size and the decrease of the number of welts with an increase of degree of perfectness of PBT spherulites indicate the strengthening of the crack bifurcation and bridging mechanisms.

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