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The phase transformation toughening and synergism in poly(butylene terephthalate)/poly(tetramethyleneglycol) copolymer-modified epoxies

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The toughening of epoxy modified with poly(butylene terephthalate)/poly(tetramethylene glycol) (PBT–PTMG) copolymers of various chemical composition was investigated. The fracture toughness of the brittle epoxy was highly enhanced by the inclusion of PBT–PTMG copolymer without loss of other intrinsic mechanical properties, such as modulus and yield stress. These modified epoxies also exhibited synergism in toughening. The remarkable enhancement and the synergism in fracture toughness of PBT/PTMG-modified epoxies is possibly due to the enhancement of the degree of phase transformation toughening, which is a result of the enhancement of the degree of perfectness of PBT spherulites in the presence of PTMG segments. The changes in micro-morphology of PBT/PTMG phases induced by the different chemical composition of copolymer is the most important cause of the dependency of the fracture energy on the processing variables, such as the relative PBT/PTMG composition and total amount of modifiers. Other toughening mechanisms, such as crack bifurcation, ductile fracture of PBT/PTMG phases, main crack-path alteration, and crack bridging, also contributed to toughness enhancement of the modified epoxies. © *1998 Chapman & Hall*

1. Introduction

Epoxies are often used as the matrix in structural composites because of their high stiffness, high strength, chemical resistance, and excellent dimensional stability [1, 2]. However, their low toughness, especially in the presence of sharp cracks, detracts from this usage. Hence, an improvement in toughness of brittle epoxies is greatly desired. Toughness of epoxies has often been remarkably enhanced by the incorporation of rubber phase, but not all epoxies are successfully toughened by rubber [3–8]. Because the improved toughness has been reported to be mainly due to an enhanced shear deformation of the matrix material followed by rubber cavitation, epoxies with low cross-linking density can have their toughness greatly increased by the inclusion of rubber, but highly cross-linked epoxies usually cannot. Thus, recently, rigid polymers have been used as the second phase for better process and morphology control [9–16]. Among the polymers used, it has been reported that poly(butylene terephthalate) (PBT) is one of the most effective, especially in the particulate form [16]. The enhanced toughness is possibly due to the phase transformation toughening, which is known in zirconia-containing ceramics [17–24]. In view of the considerable increase in toughness of the poly(butylene terephthalate) (PBT)–epoxy system over that of the epoxy alone, it is of interest to understand the toughening mechanism to optimize the process and to apply it to other brittle polymer systems. However, owing to a reverse phase transformation on release of the applied stress, a direct confirmation of phase transformation of the PBT in the epoxy has been difficult to obtain, even though, several phenomena strongly support the possibility of the phase transformation toughening mechanism.

In the present study, epoxy blends with PBT copolymer having a soft poly(tetramethyleneglycol) (PTMG) segment were investigated to discuss the effect of PTMG segment on the morphology of the PBT phase and its effects on the fracture behaviour of modified epoxies. In addition, the possibility of

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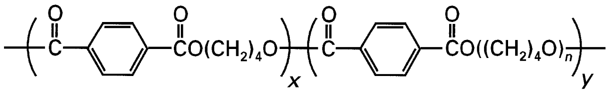

Figure 1 Chemical structure of PBT–PTMG copolymer.

TABLE I The chemical composition of PBT–PTMG copolymer

	Hard segment (PBT) content (wt %)[a]	Soft segment (PTMG) content (wt %)[a]
H87	87.5	12.5
H66	66.0	34.0
H46	46.5	53.5
H15	15.7	84.3

[a] Measured by ^{1}H-NMR.

phase transformation toughening mechanisms was investigated.

2. Experimental procedure

2.1. Materials

The epoxy and curing agent used in this study was diglycidyl ether of bisphenol A (DGEBA) epoxy (Epon 828) and piperidine, respectively. The optimum concentration of curing agent, 5 p.h.r., was used. The tougheners used in this study were thermoplastic polymers, such as poly(butylene terephthalate) (PBT) and poly(tetramethylene glycol) (PTMG) homopolymers and a copolymer with four different chemical compositions. The chemical structure and composition of the copolymers are shown in Fig. 1 and Table I.

2.2. Specimen preparation

Two processes have been used for preparing the specimens: (1) the dissolution/precipitation process, and (2) the powder process. For the dissolution/precipitation process, all the specimens were made by the following schedule: (1) the mixture of epoxy and thermoplastic modifiers, such as PBT/PTMG homo- and copolymers, was heated to approximately 220 °C to dissolve them completely; (2) the homogeneous mixture was cooled down to room temperature (during this stage, mainly, phase separation/recrystallization occurs); (3) the curing agent was added at room temperature; (4) the mixture was degased and poured into a preheated mould at 80 °C; (5) the epoxy was cured at 120 °C for 16 h. Most of the specimens were prepared by the dissolution/precipitation process. For the powder process, the epoxy, curing agent, and pre-made PBT–PTMG copolymer powder were mixed at room temperature and cured following the same schedule as the dissolution/precipitation process.

2.3. Powder-making process

Figure 2 Scanning electron micrograph of pre-made PBT–PTMG copolymer powder.

The powder of crystalline PBT homopolymer and PBT–PTMG copolymer was made by the following schedule: (1) the polymers with various chemical composition were completely dissolved in DGEBA epoxy at high temperature; (2) the solution was cooled down to room temperature (during this stage, thermoplastics are crystallized as isolated spherulites); (3) after complete crystallization and phase separation, the solution was washed by acetone more than three times with high mechanical agitation for complete dissolving out of the solvent; (4) the washed powders were filtered and dried at room temperature.

For the powders made by above process, each powder was a single spherulite. The size of the powders can be easily controlled by changing the solution concentration and cooling rate. A scanning electron micrograph of PBT–PTMG powder is shown in Fig. 2. After the powder making process, the thermal properties, such as melting temperature, glass transition temperature, and crystallinity, essentially remained unchanged.

2.4. Mechanical test

In this study, 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. These specimens were precracked by tapping with a fresh razor blade chilled in liquid nitrogen. The specimens were tested on a screw-driven Instron machine at $0.01\,\mathrm{mm\,s^{-1}}$ crosshead speed. The following relationships were used to calculate G_{IC} from each sample and crack dimension [25]

$$U = G_{IC} B D \phi \tag{1}$$

$$\phi = 0.5(a/D) + (1/18\pi)(2L/D)(a/D)^{-1} \tag{2}$$

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

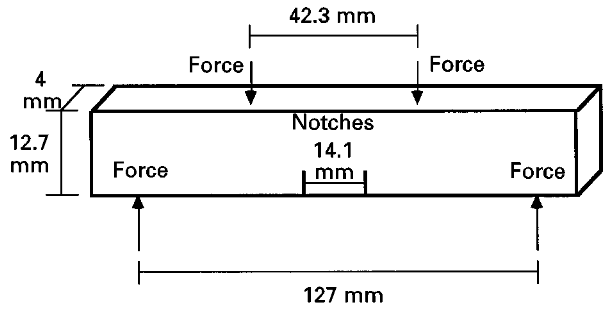

Figure 3 Double notch four-point bending (DN-4PB) specimen geometry.

To examine the yielding behaviour of the materials, specimens were deformed in uniaxial compression. Rectangular rod-shaped specimens were used with a height-to-width ratio of 2 : 1. The uniaxial compression tests were performed at a constant crosshead speed of $0.01\,\mathrm{mm\,s^{-1}}$. The load from the measured load–displacement curve was converted to stress using the initial specimen's cross-sectional area. Then the compressive modulus, E, and the compressive yield stress, σ_y were also determined.

2.5. Fractography

Scanning electron microscopy (SEM), Hitachi S-2500C, 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 the double-notched four-point bending method (DN-4PB) [26, 27]. Fig. 3 is a schematic drawing showing details of the test. Owing to stress intensification at the crack tips, processing zones are formed at each crack tip upon loading. Because both cracks can never be identical, one of the cracks propagates in an unstable manner and then the other crack immediately becomes unloading and stationary. The thin section including this stationary crack was made by using the petrographic polishing technique [25]. The section plane was parallel to the crack propagation direction and normal to the fracture surface.

3. Results

3.1. Phase separation behaviour of epoxy/PBT/PTMG blends

For the blends of epoxy and thermoplastic modifiers, such as poly(butylene terephthalate)(PBT)/poly(tetramethyleneglycol) (PTMG) homo- and copolymers with various chemical compositions, homogeneous mixtures can be obtained at temperatures above 200 °C. The phase separation of modifiers in epoxy occurs during cooling of the homogeneous mixture of the blends. After phase separation, within the composition of this study, the epoxy is continuous phase and the thermoplastic modifiers are dispersed phases, as seen in Fig. 4. The dispersed phases are spherical in shape. The Maltese cross under crossed polars reveals that the dispersed phases are isolated spherulites. For the blend of epoxy and PTMG oligomer, the molecular weight of which is $1000\,\mathrm{g\,mol^{-1}}$, however, the phase separation cannot be observed even after curing.

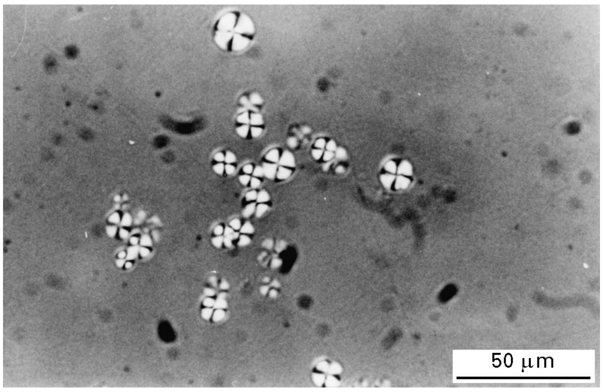

Figure 4 Polarized transmission optical micrograph of thin section of 10 wt % PBT–PTMG-modified epoxy (H46).

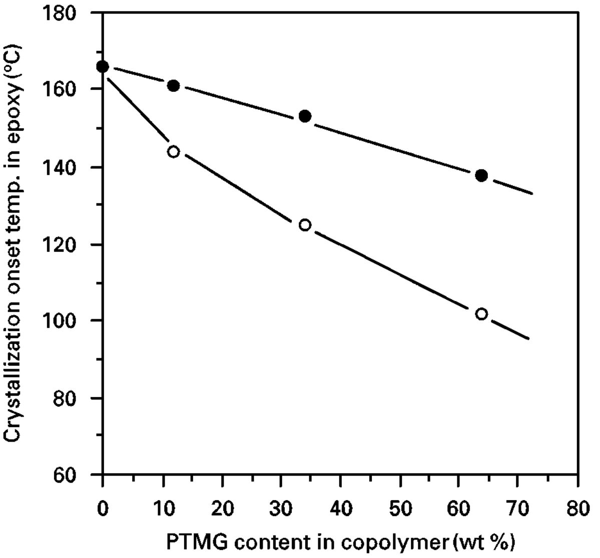

Figure 5 The effects of relative chemical composition of PBT/PTMG on the crystallization onset temperature of PBT in PBT/PTMG/epoxy blends before cure. (○) PBT-PTMG copolymer, (●) PBT and PTMG homopolymer.

For PBT–PTMG copolymer/epoxy blends, it has been found that the phase separation behaviour and the morphology of dispersed phase are sensitive to the relative composition of PBT/PTMG and the total amount of copolymer. For epoxy blends with a copolymer of high PTMG composition, the phase separation/crystallization occurs only when using a high amount of copolymer. Thus, for modified epoxy with copolymer with 84.3 wt % PTMG(H15), the phase separation/crystallization has been observed only when the composition of copolymer is above 20 wt %.

The phase separation in the epoxy blend with PBT–PTMG copolymer seems to be initiated by the crystallization of the PBT segment. The crystallization onset temperature, T_{COT}, of PBT in epoxy is affected by the relative composition of PBT/PTMG and the total amount of copolymer. Fig. 5 shows the effects of relative composition of PBT/PTMG on T_{COT} when the total amount of copolymer is 10 wt %. As seen in figure, T_{COT} almost linearly decreases with increasing PTMG composition in the copolymer. When using a copolymer with 53.5 wt % PTMG(H46), T_{COT} is more than 60 degrees lower than PBT homopolymer. As mentioned, for the modified epoxy with copolymer, with 84.3 wt % PTMG(H15), however, the crystallization peak is not observed. The dependency of T_{COT} on relative composition of PBT/PTMG is also observed when homopolymers were added to the epoxy separately. But, in this system, as seen in Fig. 5, the amount by which T_{COT} is reduced with PTMG composition is much smaller than in the copolymer system.

The size and morphology of precipitated phases also have been found to be affected by the relative composition of PBT/PTMG. The size of spherulites increases with an increase of PBT composition in the copolymer. As seen in Fig. 6, for 10 wt % copolymer modified epoxies, the size of the precipitated phases is changed from 7 μm to 20 μm, when the PBT composition in the copolymer is changed from 46 wt % to 87 wt %. The morphology and the degree of perfection of precipitated spherulites are also affected by PBT/PTMG composition. With an increase of PTMG composition, the morphology of the spherulites becomes more perfect. The well-developed Maltese cross under crossed polars can be observed only when the PBT/PTMG composition is 46/54(H46). For epoxy blend with a higher composition of PTMG, the crystallization of PBT was not observed. However, for higher total modifier composition, such as 20 wt %, the crystallization can be observed in epoxy blends with higher composition of PTMG.

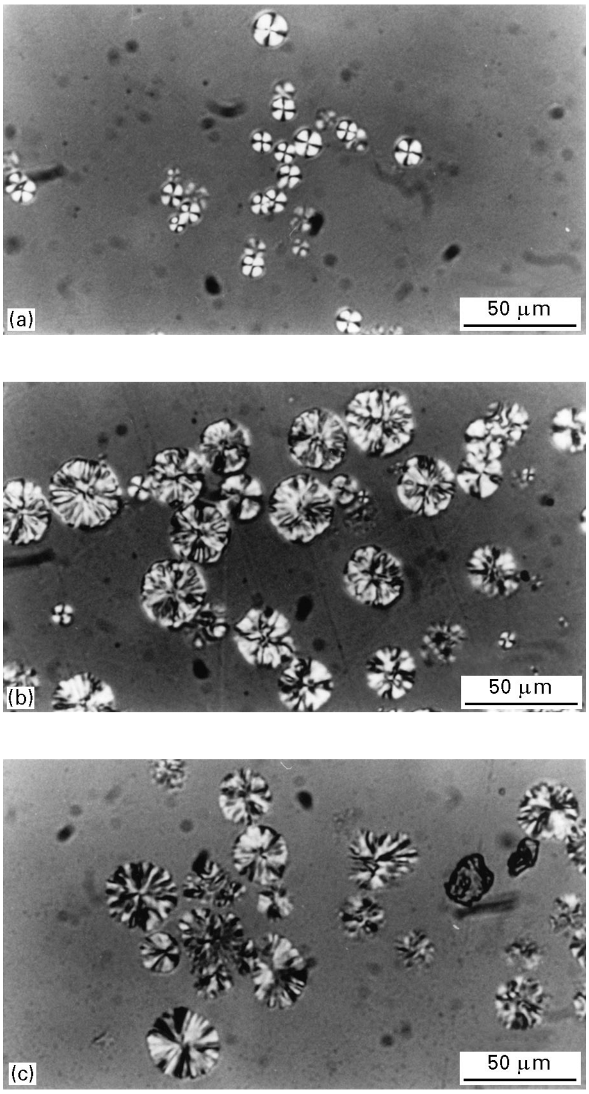

Figure 6 Polarized transmission optical micrographs of a thin section of modified epoxies with 10 wt % PBT–PTMG copolymer of various chemical compositions: (a) H46 (b) H66, (c) H87.

3.2. Properties of modified epoxies

The thermal properties of modified epoxy after curing, such as the T_g of the epoxy matrix and the T_m of the PBT, are shown in Table II. The T_m remained unaffected by the blending, while T_g was lowered. As is seen in Table II, the T_g of modified epoxies decreases almost linearly with an increase of PTMG composition in the copolymer.

The mechanical properties, such as modulus and yield stress of the modified epoxies, have remained unaffected by being blended with PBT–PTMG copolymers, regardless of the chemical composition of the copolymer, as illustrated in Fig. 7. However, the

TABLE II Thermal properties of modified epoxies with PBT/PTMG copolymers

Specimen[a]	T_g of epoxy matrix (°C)[b]	T_m of PBT (°C)[c]
Neat epoxy	95.8	–
PBT	95.2	223.3
H87	93.8	223.7
H66	87.8	223.4
H46	82.3	223.4
H15	75.5	–
PTMG	69.3	–

[a] Modifier content: 10 wt %.
[b] Measured by DMTA.
[c] Measured by DSC.

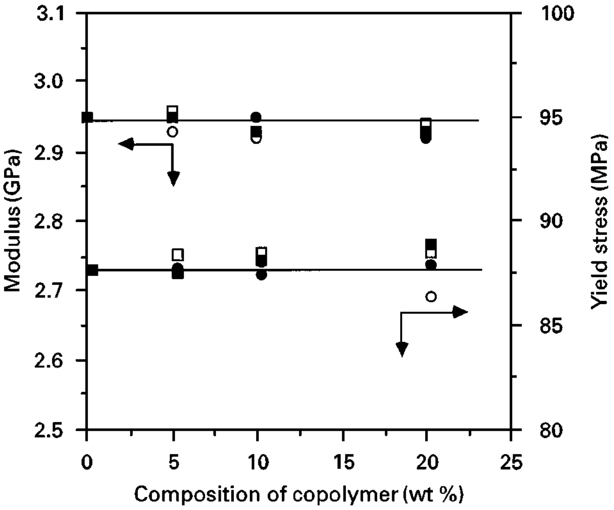

Figure 7 The effects of modifier composition on the modulus and yield stress of modified epoxies with PBT-PTMG copolymer of various chemical compositions: (○) H15, (●) H46, (□) H66, (■) H87.

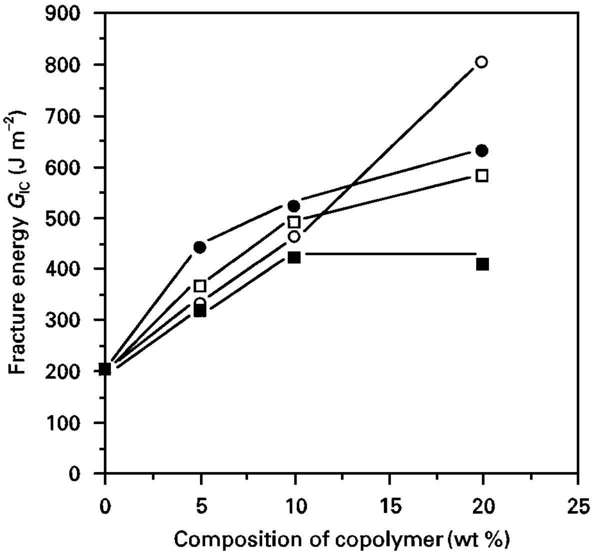

Figure 8 The effects of modifier composition on the fracture energy of modified epoxies with PBT-PTMG copolymer of various chemical compositions: (○) H15, (●) H46, (□) H66, (■) H87.

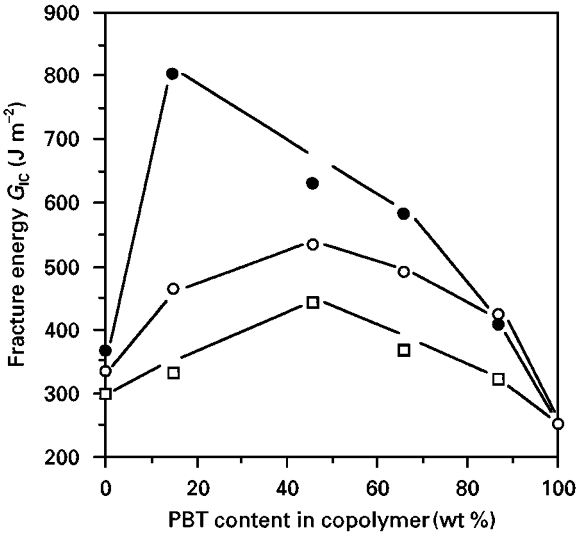

Figure 9 The effects of chemical composition of copolymer on the fracture toughness of modified epoxies showing the synergism. (●) 20% copolymer, (○) 10% copolymer, (□) 5% copolymer.

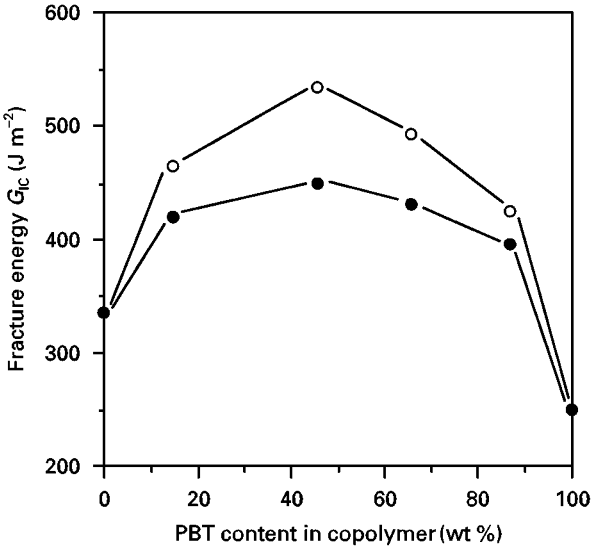

Figure 10 The fracture toughness of modified epoxy with PBT–PTMG copolymer and homopolymers. (○) PBT–PTMG copolymer, (●) PBT and PTMG homopolymer.

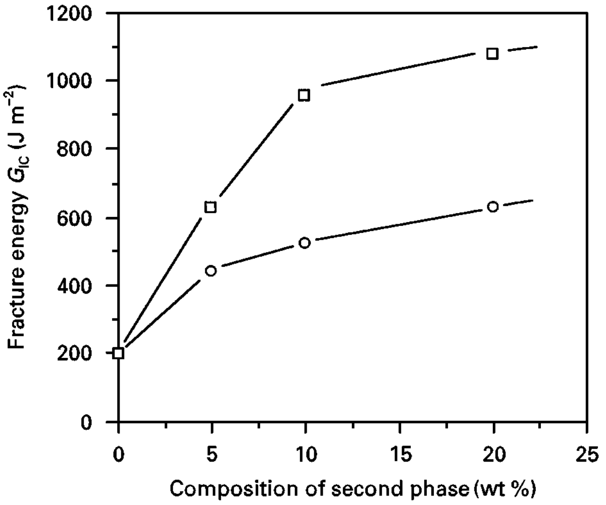

Figure 11 The fracture toughness of PBT–PTMG copolymer modified epoxies prepared by different processes: (□) powder mixing, (○) dissolution and phase separation.

fracture toughness of modified epoxies was highly enhanced by the inclusion of PBT–PTMG copolymer. Fig. 8 shows the effect of the total amount of copolymer with various chemical compositions on the fracture toughness of modified epoxies. The fracture toughness is seen to have increased rapidly up to 5 wt % modifier and then increased, but at a lower rate at higher modifier content. However, only for the epoxy modified with copolymer with 15.7 wt % PBT(H15), did the fracture toughness increase at a higher rate at higher modifier content.

The effect of the relative composition of PBT/PTMG on the fracture energy of modified epoxy is replotted in Fig. 9. As seen, irrespective of the relative composition of the copolymer, toughening of the epoxy by PBT–PTMG copolymer results in a fracture toughness greater than that obtainable with either component alone. Thus, these modified systems exhibit a synergistic effect. When the amount of copolymer is less than 10 wt %, among the various compositions, the copolymer with 54 wt % PTMG (H46) exhibits the maximum. When the amount of copolymer increases up to 20 wt %, however, the composition with maximum toughness has been moved to 84.3 wt % PTMG(H15). The maximum toughness enhancement is about 650% larger than that calculated from the rule of mixtures.

The dependency of fracture toughness on relative composition of PBT/PTMG is also observed when homopolymers were added separately. However, as seen in Fig. 10, the toughness enhancement is much lower than for the copolymer.

Fig. 11 illustrates the effect of pre-made modifier powders on the fracture toughness of epoxies. As seen in the figure, when using the pre-made powders, the toughness enhancement of modified epoxies is more than twice that of the typical dissolution–precipitation process (see Fig. 8). The fracture toughness of particle-modified epoxy shows a six-fold increase over that of the unmodified epoxy when using 20 wt % modifier.

3.3. Fractographic study

The fracture surface of PBT/PTMG modified epoxies reveals some toughening mechanisms. These include: (1) crack bifurcation, (2) ductile fracture of PBT/PTMG phases, (3) main crack-path alteration, and (4) crack bridging.

Behind every PBT–PTMG phases, several tail or crack bifurcation lines appeared. The effect of relative composition of PBT/PTMG in the copolymer on the crack bifurcation line can be observed in Fig. 12. The size of the bifurcation lines is seen to increase with PTMG composition. The basic longitudinal texture (BLT) on the fracture surface of the epoxy, consisting of a linear pattern of low ridges and shallow grooves that are parallel with the direction of crack propagation, can be used to indicate the role of particles during fracture. As seen in the figure, the BLT is seen to rotate around the particle, which indicates that the PBT/PTMG phases remain unfractured behind the crack tip and can act as a bridge between the two fracture surfaces. After the cracks rotate around the PBT/PTMG phases, due to the loss of coherence, the two parts of the crack path are altered, and end up at two different elevations when they rejoin on the back side of the particle. This results in a pair of steps being formed, the pair being nearly opposite on the two fracture surfaces, with a single welt stretched between them. The welt also acts as the bridge. The greater the loss of coherence, the greater the size of the welt, and the greater is the bridging effect.

The fracture surfaces of the PBT/PTMG phase often exhibit ductile fracture. This is indicated by the fibril and nodular structure on the PBT/PTMG phases. The amount of plastic deformation of PBT/PTMG phases is affected by the relative composition of the copolymer. As seen in the figure, the fracture surface of PBT/PTMG becomes rougher with PTMG composition in the copolymer. The dependency of the roughness of the fracture surface of PBT/PTMG phases on composition is also observed when homopolymers were used.

The occurrence of the plastic deformation of the matrix can be revealed by transmission optical microscopy of thin sections. Micrographs obtained with polarizers of a thin section whose plane was perpendicular to the fracture surface and parallel to the direction of crack propagation, are shown in Fig. 13. Gross plastic deformation of the epoxy matrix should be seen at the tip of the arresting crack.

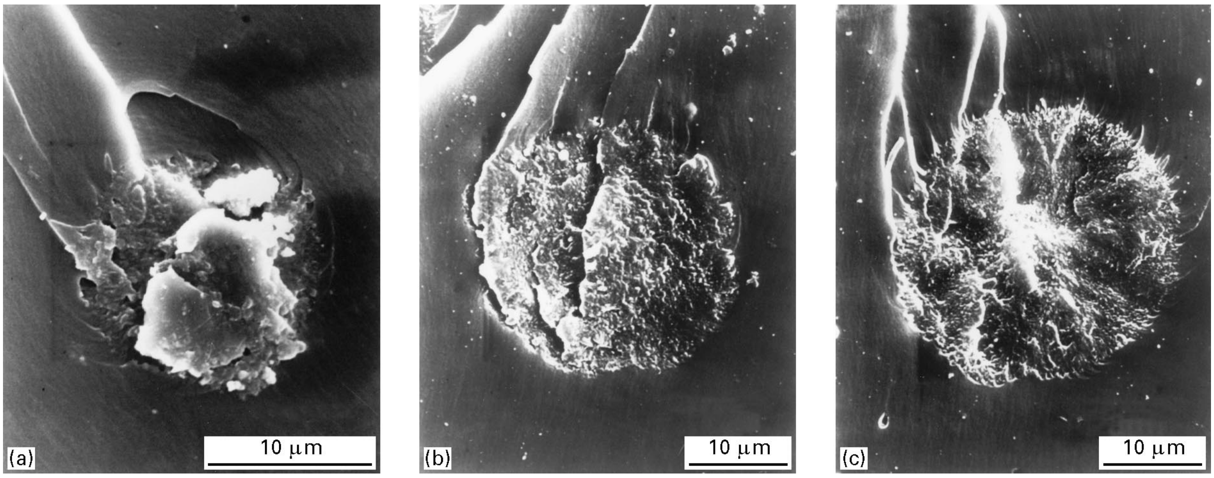

Figure 12 Scanning electron micrographs of the fracture surface of modified epoxies with 10 wt % PBT–PTMG copolymer of various chemical compositions: (a) H46, (b) H66, (c) H87.

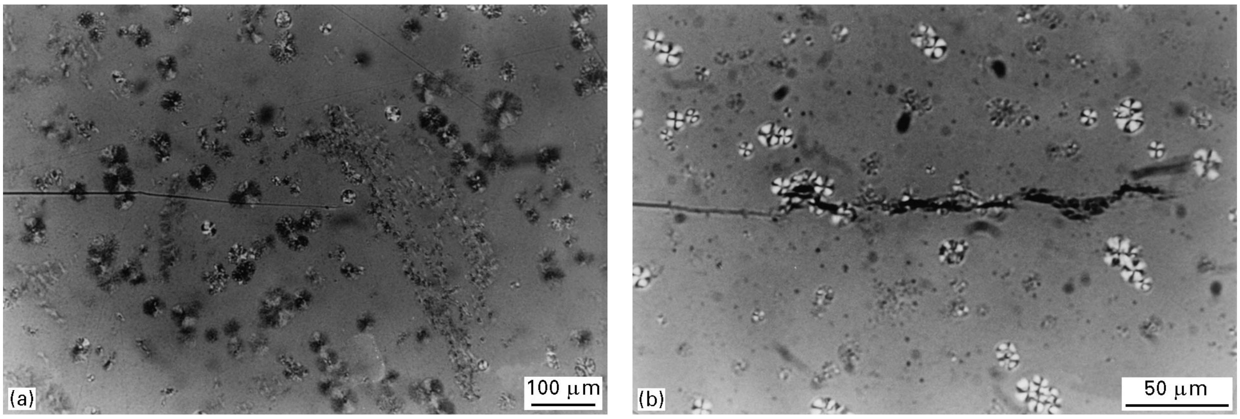

Figure 13 Polarized transmission optical micrographs of a thin section taken mid-plane and near the crack tip of DN-4PB samples of modified epoxies with 10 wt % PBT–PTMG copolymer of various chemical compositions: (a) H87, (b) H46.

However, local plastic deformation, in the vicinity of the PBT/PTMG phases, if present, is obscured by the very bright birefringence of the PBT spherulites. The main crack-path alteration mechanism can also be seen in Fig. 13b. When PBT/PTMG spherulites have a coarse structure, the main crack propagates in a straight line, as seen in Fig. 13a. However, when PBT/PTMG spherulites have perfect structure with a Maltese Cross under crossed polars, the main crack path is altered.

4. Discussion

4.1. Phase separation behaviour and morphology of epoxy/PBT/PTMG blends

An understanding of phase separation behaviour in modified epoxies is highly desired, because the resulting morphology is known to affect the physical and mechanical properties of the blends [12, 13]. However, the phase separation behaviour in blends of reactive thermosets with thermoplastics or elastomers is not yet well understood. Moreover, crystallization of a copolymer in solution represents a most difficult problem which is far from being solved.

For the epoxy/PBT/PTMG blends investigated here, the change in micromorphology of PBT/PTMG phases induced by the different phase separation behaviour is believed to be the most important cause of the dependency of the fracture energy on the processing variables, such as relative PBT/PTMG composition and total amount of modifiers. Thus, an understanding of phase separation behaviour and related morphology of the blends should be sought for further discussion of related properties. The dependency of fracture toughness on the morphology of PBT/PTMG phases will be discussed in Section 4.2.

For epoxy blends with PBT/PTMG homo- and copolymers with various compositions at high temperatures, a homogeneous mixture of the blends can be easily obtained due to their miscibility. The phase separation of the PBT/PTMG as isolated spherulites has been found to occur mainly during cooling of the homogeneous mixture. Unfortunately, it is still not clear whether the phase separation is due to lowering of solubility or the formation of crystalline nuclei. However, the dependency of the final morphology of the PBT/PTMG phases on the crystallization behaviour of PBT reveals that the phase separation process is possibly initiated by the formation of PBT crystal nuclei.

The decrease of crystallization onset temperature, T_{COT}, of PBT–PTMG copolymer in epoxy with an increase of PTMG composition in the copolymer indicates that non-crystallizable PTMG units interrupt or terminate crystal growth of PBT in the molecular chain direction, because their position along the chain is fixed. The interruption by a non-crystallizable unit in the copolymer is not unusual in copolymer crystallization in solution. Frequently the severity of the crystal disruption is not only a fixed property of the nature of the copolymer unit, but also depends on the crystallization conditions.

The lowering of T_{COT} is also observed even when homopolymers are used, even though the degree of lowering is much smaller than for copolymer. In this system, the lowering of T_{COT} of PBT homopolymer may be not due to the interruption by the PTMG homopolymer, but mainly due to the lowering of the PBT composition in the blend. The lowering of T_{COT} with a decrease of PBT composition has already been reported for epoxy/PBT blends [28]. For epoxy/PBT/PTMG blends, the viscosity increase of uncured epoxy in the presence of PTMG might also affect the crystallization of PBT via the suppression of the movement of PBT molecules. Thus, for epoxy blends with copolymer, the lowering of T_{COT} is due to not only the interruption by PTMG segment but also the lowering of PBT composition.

The lowering of the crystallization temperature of PBT in the presence of PTMG has been found to affect the morphology of PBT/PTMG phases, such as the degree of perfection of spherulites, which increases with a decrease of relative PTMG composition in the copolymer. For epoxy blends with PBT–PTMG copolymer, as mentioned, reprecipitation/crystallization of the PBT/PTMG phase as spherulites occurs during cooling of the homogeneous mixture. A macroscopic spherulite crystal symmetry is clearly in violation of homogeneous regular packing of microscopic molecular units. Uniformly space-filling spherulites must be made of crystalline substructures which radiate from a centre, branches with a small angle, and space-filling amorphous phase. Thus, during the reprecipitation stage, inside the spherulites, the PBT crystalline segment is surrounded by a mixture of epoxy and non-crystallizable PTMG. The degree of perfection of the texture of spherulites in solution has been reported to be related to the concentration of solvent and determined by $\delta = D/G$, where D is the diffusion coefficient of solvent and G is the radial growth rate of the spherulites [29, 30]. Higher D/G ratio corresponds to a coarser texture. For epoxy blends with PBT–PTMG copolymer, the epoxy acts as a solvent. Thus, when the T_{COT} of PBT is lowered in the presence of PTMG, the diffusivity of the epoxy decreases and the crystal growth rate of PBT increases. As a result, the D/G ratio decreases and the degree of perfection of the spherulites increases.

The dependency of PBT crystal structure in the presence of PTMG is not only due to lowering of T_{COT} but also due to $\Delta\chi$ effect. The $\Delta\chi$ effect in this system is a result of the much higher compatibility of epoxy with PTMG than PBT.

4.2. Toughening mechanisms and the synergistic effect

The fracture surface morphology of toughened epoxies reveals some toughening mechanisms. For epoxy blends with PBT–PTMG copolymer, as mentioned in Section 3.3, the toughening mechanisms shown in the fracture surface are (1) crack bifurcation by PBT/PTMG phases, (2) ductile fracture of precipitated phases, (3) crack bridging, and (4) main crack-path alteration. However, the considerable increase in toughness and synergism of PBT/PTMG toughened epoxies reveals the possibility of another toughening mechanism operating dominantly in this system. This might be the so-called phase transformation toughening, which has exhibited a dramatic toughening of the brittle matrix in zirconia-containing ceramics. The metastable tetragonal phase of zirconia, incorporated into a brittle ceramic, transforms to the stable monoclinic phase with volume expansion under the influence of the stress field ahead of the crack tip. A compressive stress due to transformation is superimposed on the tensile stress field ahead of the crack tip, which slows or stops the growing crack and has the effect of increasing the critical fracture energy.

Among the crystalline polymers, as with zirconia, it has been reported that only PBT exhibits a stress-induced transformation with volume expansion, from the normal α-structure to a more extended β-structure along the chain axis [28]. As expected, PBT powder has been found to be remarkably effective for toughening of brittle epoxies [28]. But owing to a reverse phase transformation on release of the applied stress, a direct confirmation of phase transformation of the PBT in the epoxy has been difficult to obtain. However, it has been reported that several phenomena strongly support the possibility of the phase transformation toughening mechanism in PBT/epoxy blend: (1) the suppression of the cavitation of rubber in the presence of the PBT due to the volume expansion of PBT phases accompanying the phase transformation in epoxy/PBT/rubber system; (2) the dependency of the fracture toughness on micro-morphology of PBT spherulites, such as the degree of perfection; (3) the dependency of the fracture toughness on crack growth rate [28].

In terms of toughness enhancement for brittle epoxies, PBT/PTMG has been found to be more effective than PBT alone. The remarkable enhancement and the synergism in fracture toughness of PBT/PTMG-modified epoxies is believed to be due to the enhancement of degree of phase transformation toughening, which is a result of the enhancement of the degree of perfection of PBT spherulites in the presence of a PTMG segment. As mentioned, the degree of perfection increases with an increase of PTMG composition, which is the result of the lowering of T_{COT} and the $\Delta\chi$ effect.

The phase transformation toughening mechanism, if it is operative in the PBT/PTMG/epoxy system, is expected to be affected by the degree of perfection of the PBT spherulite. To transform the α-structure of PBT, a tensile load should be applied along the chain axis. Thus, for the PBT crystal in the spherulite to transform, the crystal should be oriented with the axis of the applied load along the PBT chain axis. The PBT crystals all have orientations in a spherulite, however, and the transformation is less likely when the chain axis is tilted away from the axis of the applied tensile stress. To obtain phase transformation of whole PBT spherulites, the axis of these crystals must rotate to align the PBT chain axis with the direction of applied stress. But when PBT spherulites develop during cooling of the epoxy/PBT/PTMG mixture, inside the amorphous region of the spherulite, an epoxy with dissolved PTMG exists, and this tends to isolate the PBT crystalline segment. When the PBT crystals are isolated and surrounded by a rigid mixture of epoxy and PTMG, however, the rotation is restricted by the three-dimensional cross-link epoxy. As a result, the amount of phase transformation is expected to decrease with an increase in the degree of isolation of the PBT crystals, an increase of the amount of epoxy inside the spherulites, and a decrease of the degree of perfection of PBT spherulites.

As expected, the epoxy with PBT spherulite showing a clear Maltese cross under crossed polars exhibits the highest G_{IC} value (see Figs 6 and 9). Also, all of the fracture energy values of PBT/PTMG-modified epoxies correspond well with the morphology of PBT spherulites, such as the degree of perfection. This coincidence with expectation indicates that the remarkable enhancement of fracture toughness and the synergism are results of the dependency of fracture energy on the morphology of PBT spherulites, and that the phase transformation toughening is dominantly operative in PBT/PTMG modified epoxies.

The high effectiveness of pre-made powder in fracture toughness also strongly supports the possibility of the phase transformation toughening mechanism in PBT/PTMG-modified epoxies (see Fig. 11). For modified epoxies prepared by the typical dissolution/precipitation process, even though the PBT spherulites become relatively perfect due to lowering of crystallization temperature, some amount of epoxy still exists inside the spherulite. However, for pre-made powders, no epoxy exists inside. Thus, the amount of phase transformation toughening in pre-made powder-modified epoxy should be higher than epoxies made by the typical dissolution/precipitation process, if the phase transformation toughening mechanism is operative in this system. The great effectiveness of pre-made powder for toughening has also been reported for PBT/epoxy blends [28].

A phase transformation of PBT in the PBT/PTMG/epoxy blends is potentially able to enhance toughness in several ways. Like that occurring in ceramics, the transformed particles could superimpose a compressive stress field on the surrounding matrix in the critical tensile stress region just ahead of the crack tip. Because the transformed PBT phase acts like pressurized cavities, the superimposed stress field on the matrix surrounding the cavities would actually be both tensile and compressive, tensile in the tangential directions and compressive in the radial directions. If the transformation is triggered by shear, however, as seems to occur in ceramics and is likely to occur in polymers also, the compressive stress is developed in the most critical tensile stress region ahead of the crack. Beside diminishing the crack-driving quality of the triaxially tensile stress field associated with the crack, the superimposed stress field may also alter the ductile/brittle behaviour of the epoxy. Confirmation of the observation of plastic deformation due to a ductile/brittle transition in the immediate vicinity of the PBT particles, has not been possible. The region has been obscured by the very bright birefringence of the PBT particles under polarized light.

A second way in which phase transformation can enhance the toughness is through crack-path alteration and secondary crack bridging by welts, which results from the loss of symmetry in stress fields at the crack front and the loss of coherence of the crack when it splits and passes around the particle, respectively. The phase transformation of the particle induces or strongly contributes to stress field asymmetry and crack incoherence if the particle distorts asymmetrically during the transformation. For epoxy blends with PBT/PTMG, the main crack-path alteration can be observed only in specimens with perfect PBT spherulites showing the Maltese cross (see Fig. 13b).

For epoxy blends investigated here, as mentioned, it has been observed that the size of the PBT/PTMG phases depends on the relative composition of PBT/PTMG and the whole composition of the copolymer. The dependency of size on composition has also been observed in PBT-modified epoxies [16]. However, in the PBT/epoxy system, the size effect on fracture toughness cannot be observed. Thus, for this system, the size effect on fracture toughness has been ignored.

5. Conclusion

The fracture toughness of brittle epoxy is successively enhanced by the inclusion of PBT–PTMG copolymer without loss of intrinsic mechanical properties of the epoxy, such as modulus and yield stress. Toughening of the epoxy by the PBT–PTMG copolymer also results in a fracture toughness greater than that obtainable with either component alone. Thus, these modified systems exhibit a synergistic effect.

The remarkable enhancement and the synergism in fracture toughness of PBT/PTMG-modified epoxies is believed to be due to the enhancement of the degree of phase transformation toughening, which is a result of the enhancement of the degree of perfection of PBT spherulites in the presence of a PTMG segment. For these blends, the phase separation behaviour and resulting morphology are sensitive to the relative composition of PBT/PTMG in the copolymer. The crystallization onset temperature, T_{COT}, of PBT in the epoxy decreases almost linearly with an increase of PTMG composition in the copolymer, due to not only the interruption by the PTMG segment but also the lowering of the PBT composition. Thus, the degree of perfection was increased with an increase of PTMG composition, as a result of the lowering of T_{COT} and $\Delta\chi$ effect. The change in micro-morphology of PBT/PTMG phases induced by the different phase separation behaviour is believed to be the most important cause of the dependency of the fracture energy on the processing variables, such as relative PBT/PTMG composition and total amount of modifiers.

The high effectiveness of pre-made powder in fracture toughness also strongly supports the possibility of the phase transformation toughening mechanism in PBT/PTMG-modified epoxies. When using the pre-made powders, the toughness enhancement of modified epoxies is more than twice that of the typical dissolution–precipitation process because the amount of epoxy inside the PBT/PTMG phases is much lower.

The fracture surface of PBT/PTMG-modified epoxies reveals some other toughening mechanisms, such as crack bifurcation, ductile fracture of PBT/PTMG phases, main crack-path alteration, and crack bridging.

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