JOURNAL OF MATERIALS SCIENCE 31 (1996) 3523–3533

Multi-phase toughened epoxy with poly(ether sulphone) and carboxyl-terminated butadiene–acrylonitrile rubber

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The structure and properties of ternary blends of epoxy with poly(ether sulphone) (PES) and carboxyl-terminated butadiene–acrylonitrile rubber (CTBN) have been investigated. In these blends, the phase separation occurs in two stages: a macrophase separation during mixing and a microphase separation during curing. At low PES compositions, the PES-rich spherical domains are dispersed. With increasing PES composition, a co-continuous structure develops and, eventually, the phases are inverted. Regardless of structure change, the modulus and yield stress changes with composition just follow the simple rule of mixtures. However, the fracture toughness of these blends exhibits a synergistic effect. Among the various compositions, 5:5 weight ratio of CTBN to PES exhibited the maximum toughness, which was 140% larger than that calculated from the rule of mixtures. The synergism is believed to be due to the bridging by the PES-rich phase followed by a lowering of the yield stress. The lowering of the yield stress can enlarge the process zone size and the amount of plastic dilatation of the matrix.

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 the toughness of brittle epoxies is greatly desired. Toughness of epoxies has often been remarkably enhanced by the incorporation of a rubber phase, but not all epoxies are successfully toughened by rubber [3–8]. Because this 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 crosslinking density can have their toughness greatly increased by the inclusion of rubber, but highly crosslinked epoxies usually cannot. 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. To avoid the loss of the inherent properties of epoxies, rigid particulate inorganic fillers have been used as second phases. Without sacrificing the inherent properties, the inclusion of rigid inorganic particles considerably increases the fracture toughness of epoxies [9, 10]. The improved toughness has been suggested to arise from crack pinning and crack bridging by added rigid inorganic fillers [10, 11]. However, unfortunately, uniform mixing and good dispersion of these particles are rarely obtained because of the higher densities of these inorganic filler particles compared to those of epoxies. Thus, recently, rigid polymers such as poly(ether sulphone) have been used as the rigid second phase for better process and morphology control [12–16]. The enhanced toughness has been suggested to be caused by the rupture and crack pinning by dispersed rigid polymers.

Toughness of epoxies has often been considerably enhanced by the incorporation of a second phase, as mentioned. However, the fracture toughness of both rubber-modified and rigid particle-modified epoxies reaches a maximum at a characteristic volume fraction, i.e. an additional increase in volume fraction does not result in significant improvement in fracture toughness. Therefore, in an effort to develop even tougher epoxies, a multi-phase modified system has been considered. The development of multi-phase modified epoxies considers the occurrence of various toughening mechanisms. Ideally, the mechanisms

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would interact in a positive manner which has been predicted theoretically [17–19]. For example, the interaction of bridging with cavitation/plastic deformation results in multiplicative, not additive, toughening. However, there have been few experimental works on multi-phase toughening [20–22].

In the present study, a new multi-phase toughened epoxy with PES and carboxyl-terminated butadiene–acrylonitrile rubber is investigated, the phase separation behaviours in these blends discussed and the toughening mechanisms induced by multiphase inclusion evaluated.

2. Experimental details

2.1. Materials

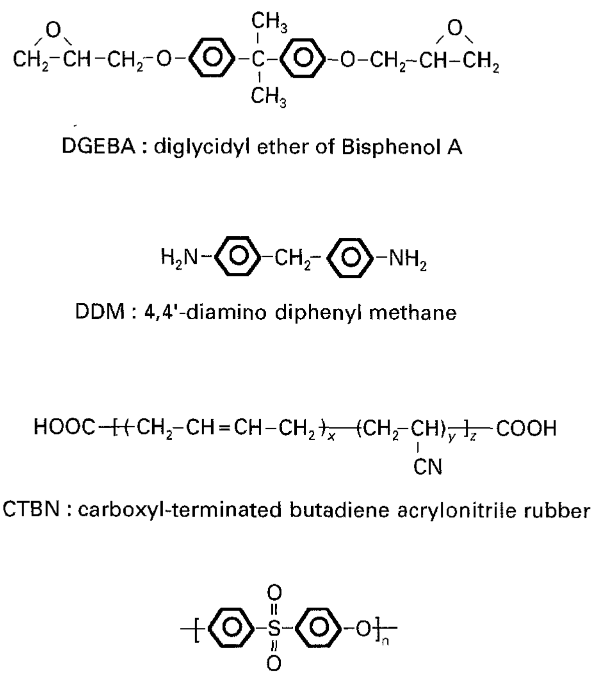
The chemical structures of the materials used in this study are shown in Fig. 1. The epoxy used in this study was diglycidyl ether of bisphenol A, Epon 828, that was cured with 4,4′-diamino diphenyl methane (DDM). The optimum concentration of curing agent, 20 part per hundred resin (phr), was used. The rubber and the rigid thermoplastic used in this study were liquid carboxyl-terminated butadiene–acrylonitrile (CTBN) rubber, Hycar 1300 × 13 (BF Goodrich), and poly(ether sulphone) (PES), Victrex 4100G (I.C.I), respectively.

2.2. Specimen preparation

The binary blends of PES/epoxy and CTBN/epoxy were prepared by a hot-melt, one-step method without a pre-reaction stage. CTBN rubber dissolved well in DGEBA epoxy at 80 °C. However, PES did not dissolve in epoxy without the aid of methylene chloride. After evaporation of methylene chloride, the mixture of PES and epoxy remained as a clear homogeneous mixture. This procedure is known not to affect the structure or properties of the cured epoxy in any way.

The ternary blends of PES/CTBN/epoxy were prepared by a two-step method, because even methylene chloride could not dissolve PES in the presence of CTBN. In the first-step, the homogeneous mixture of PES and epoxy was prepared using methylene chloride through dissolution and evaporation. For the next step, the CTBN/epoxy mixture was added to a homogeneous mixture of PES and epoxy at 80 °C. When the CTBN/epoxy was added to the mixture, a sudden phase separation occurred. In this study, the total modifier content was fixed at 10 wt%.

All the specimens were cured using the following schedule: (i) the mixture of epoxy and the modifiers was heated to approximately 80 °C and degassed while stirring, (ii) the curing agent was added while stirring, (iii) the mixture was again degassed and poured into a preheated mould at 80 °C, (iv) the mixture was cured at 80 °C for 2 h and then postcured at 150 °C for another 2 h.


DGEBA : diglycidyl ether of Bisphenol A

DDM : 4,4'-diamino diphenyl methane

CTBN : carboxyl-terminated butadiene acrylonitrile rubber

PES : poly(ether sulphone)

Figure 1 The chemical structures of the materials.

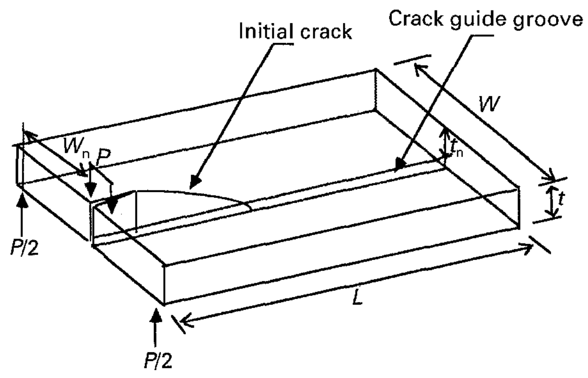


Figure 2 Double torsion (DT) specimen geometry.

2.3. Mechanical test

The double-torsion (DT) test, which was initially designed for brittle materials, was used to measure the fracture energy. The double torsion specimen can be considered to be a pair of elastic torsion bars, each having a rectangular cross-section, that are joined together. A diagram of the DT specimen and loading configuration is shown in Fig. 2. For small deflections, the fracture toughness K_{IC}, is given by

$$K_{\mathrm{IC}} = P_{\mathrm{crit}} W_{\mathrm{n}} [3(1 + \nu)/W t^3 t_{\mathrm{n}}]^{1/2}$$

where P_{crit} is the maximum load in the stress–strain curve and ν is the Poisson's ratio of the material.

The fracture energy, G_{IC}, is related to the fracture toughness by

$$K_{\mathrm{IC}} = (E G_{\mathrm{IC}})^{1/2}$$

where E is Young's modulus.

The specimens used had a rectangular shape with dimensions 100 mm long, 30 mm wide, and 6 mm thick. A sharp crack was inserted at one end, and a shallow centre groove along one face of the specimen. A sharp crack prevents the formation of a plastic zone in the vicinity of the crack tip and was inserted by tapping with a hammer on a razor blade held against the bottom of a saw cut. The initial crack lengths should be longer than 0.55 times the specimen width to avoid end effects [23]. To guide the propagating crack, a centre groove made by a table saw was inserted along the length of the specimen. The width of the groove was less than 0.5 mm, and the depth was nearly half of the specimen thickness. The specimens were tested on a screw-driven Instron machine at 0.01 mm s^{-1} crosshead speed.

To examine the yield 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 mm s^{-1}. The load from the measured load–displacement curve was converted to stress using the specimen's initial cross-sectional area. Then the compressive modulus, E, and the compressive yield stress, σ_y were also determined.

2.4. 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. Energy dispersive spectroscopy (EDS) (Kevex Instrument Inc.) was used to find the PES phase on the fracture surface. For EDS, carbon was evaporated onto the fracture surface of the samples.

In order to examine a process zone at a crack tip, polarized transmission optical microscopy was used to investigate cavitation zone size and plastic deformation of the matrix near the crack tip. The specimens used for optical microscopy study were broken by employing the double-notched four-point bending method (DN-4PB) [24, 25]. Fig. 3 is a schematic drawing showing details of the test. Due to stress intensification at the crack tips, processing zones are formed at each crack tip upon loading. Because both the cracks can never be identical, one of the cracks propagates in an unstable manner and then the other crack immediately becomes unloaded and stationary. The thin section including this stationary crack was made by using the petrographic polishing technique [21]. The section plane was parallel to the crack propagation direction and normal to the fracture surface.

2.5. Dynamic mechanical thermal analysis

A dynamic mechanical thermal analyser (DMTA) was used with a temperature scan from − 150 to 250 °C. The frequency used was 1 Hz and the heating rate was 5 °C min^{-1}.

3. Results

3.1. Phase separation behaviours

For the binary blend of epoxy and PES, a homogeneous mixture can be obtained with the aid of a solvent such as methylene chloride. The phase separation of PES in epoxy occurs during the curing process. At low PES content, after curing, there is no evidence for phase separation except for the opaqueness of the specimens: there is no detectable primary alpha transition peak of PES, which should be found at 230 °C in the dynamic mechanical thermal analyser (DMTA) spectrum, nor are distinct features of PES domains visible on the fracture surfaces. For 10 wt% PES modified epoxy, no detectable loss peaks of PES are resolved by DMTA, but scanning electron microscopy (SEM) of the fracture surface reveals the presence of nodules whose size is smaller than 0.2 μm, as illustrated in Figs 4 and 5.

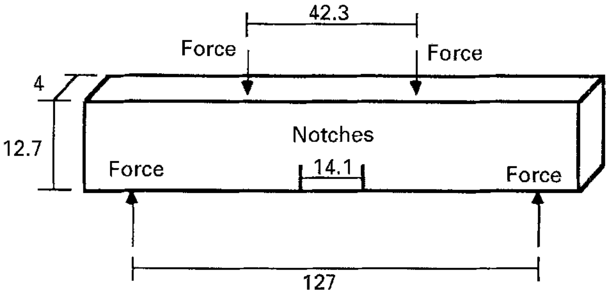


Figure 3 Double notch four-point bending (DN-4PB) specimen geometry.

For the binary blend of epoxy and carboxyl-terminated butadiene–acrylonitrile (CTBN) rubber, a homogeneous mixture can be easily obtained without the aid of a solvent. The phase separation of CTBN in epoxy also occurs during the curing process. Both DMTA and SEM show clear evidence for phase separation, as shown in Figs 6 and 7. The DMTA spectrum of 10 wt% CTBN-modified epoxy shows an alpha relaxation of CTBN, with peak at − 40 °C, and a low temperature beta relaxation of epoxy, with peak at − 60 °C. On the SEM micrograph of the fracture surfaces, the distribution of holes due to extensive cavitation of the rubber particles can be seen.

For the ternary blends of PES/CTBN with epoxy, a homogeneous mixture can not be obtained even with the aid of a solvent. The phase separation of these ternary blends occurs in two stages: macrophase separation during mixing and microphase separation during curing. During mixing of homogeneous binary mixtures of PES/epoxy and CTBN/epoxy, phase separation occurred immediately. The morphology after macrophase separation has been found to be sensitive to the composition. At low PES compositions (the total modifier content is 10 wt%), the spherical domains develop as a dispersed phase, as shown in Fig. 8a. With increasing PES content, the diameter of the spherical domains almost linearly increases up to around 20 μm. When the PES content reaches 7 wt% (i.e. CTBN content is 3 wt%), instead of forming a spherical dispersed phase, a co-continuous structure develops, as shown in Fig. 8b. For blends containing more than 8 wt% PES, the phases are inverted. The macrophase separation morphology after mixing remains unaffected after curing, as shown in Fig. 9a and b, which are SEM micrographs of the fracture surfaces of the ternary blends of CTBN(5)/PES(5) and CTBN(3)/PES(7) in epoxy after curing, respectively. EDS analysis of sulphur indicates that the spherical domains and one of the co-continuous domains are

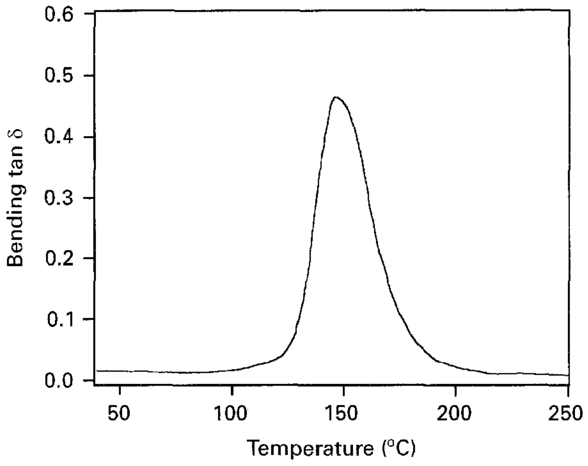


Figure 4 Dynamic mechanical spectrum of the 10 wt % PES-modified epoxy.

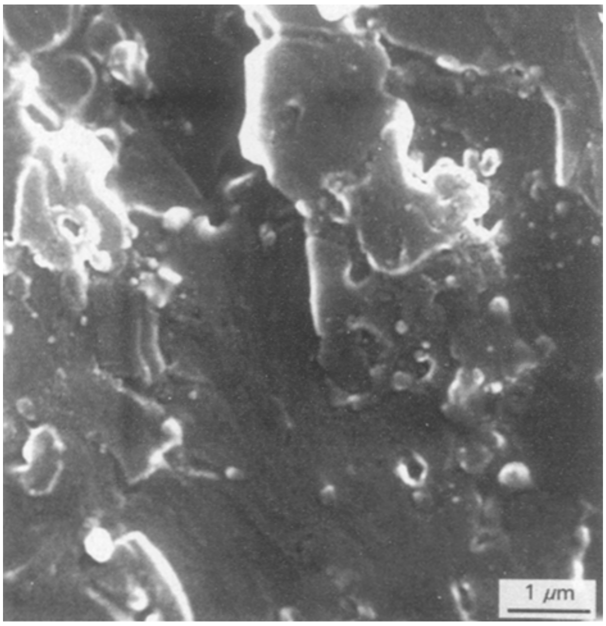


Figure 5 Scanning electron micrograph of the fracture surface of the 10 wt % PES-modified epoxy.

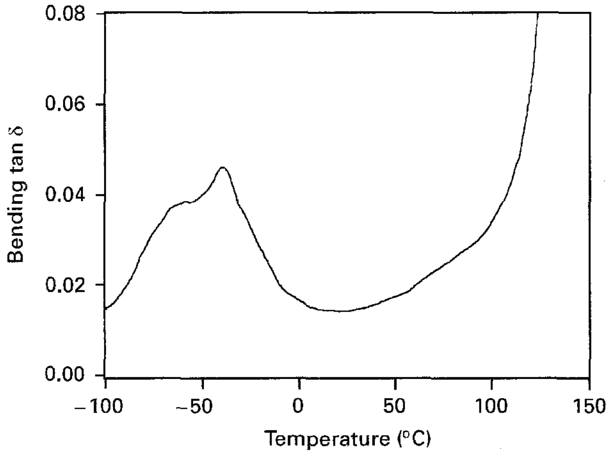


Figure 6 Dynamic mechanical spectrum of 10 wt % CTBN-modified epoxy.

the PES-rich phase, since PES is the only sulphur-containing molecule, as shown in Fig. 9. Consideration of the volume fractions indicates that these domains contain a significant proportion of epoxy.

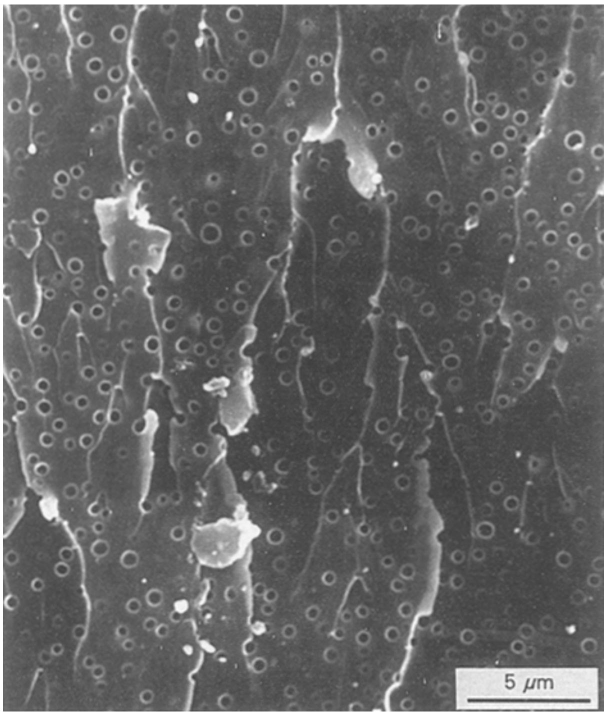


Figure 7 Scanning electron micrograph of the fracture surface of the 10 wt % CTBN-modified epoxy.

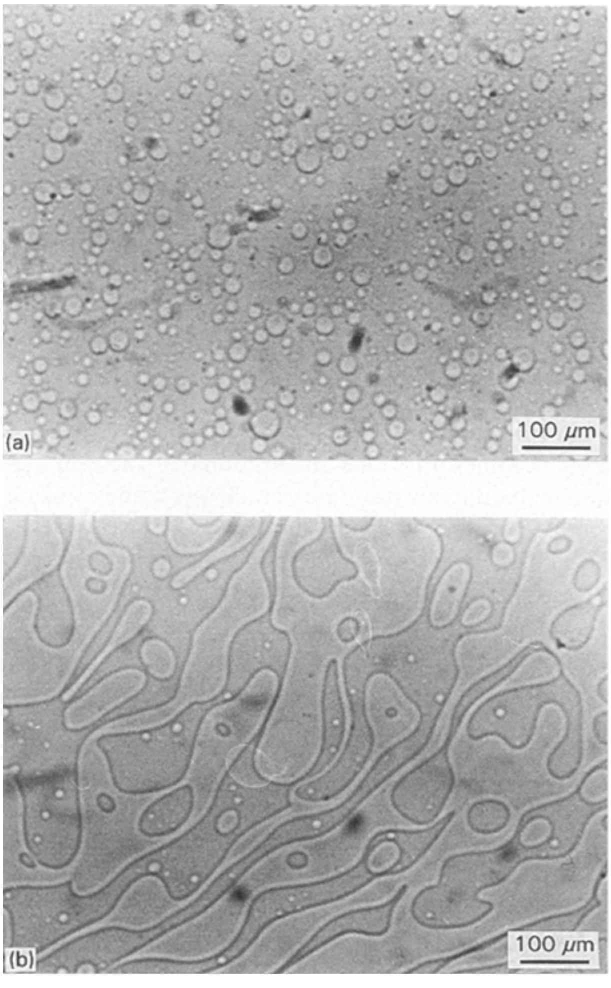


Figure 8 Transmission optical micrographs of the ternary blends after mixing showing the macrophase separation: (a) 5 wt % CTBN/5 wt % PES modified, (b) 3 wt % CTBN/7 wt % PES modified epoxy.

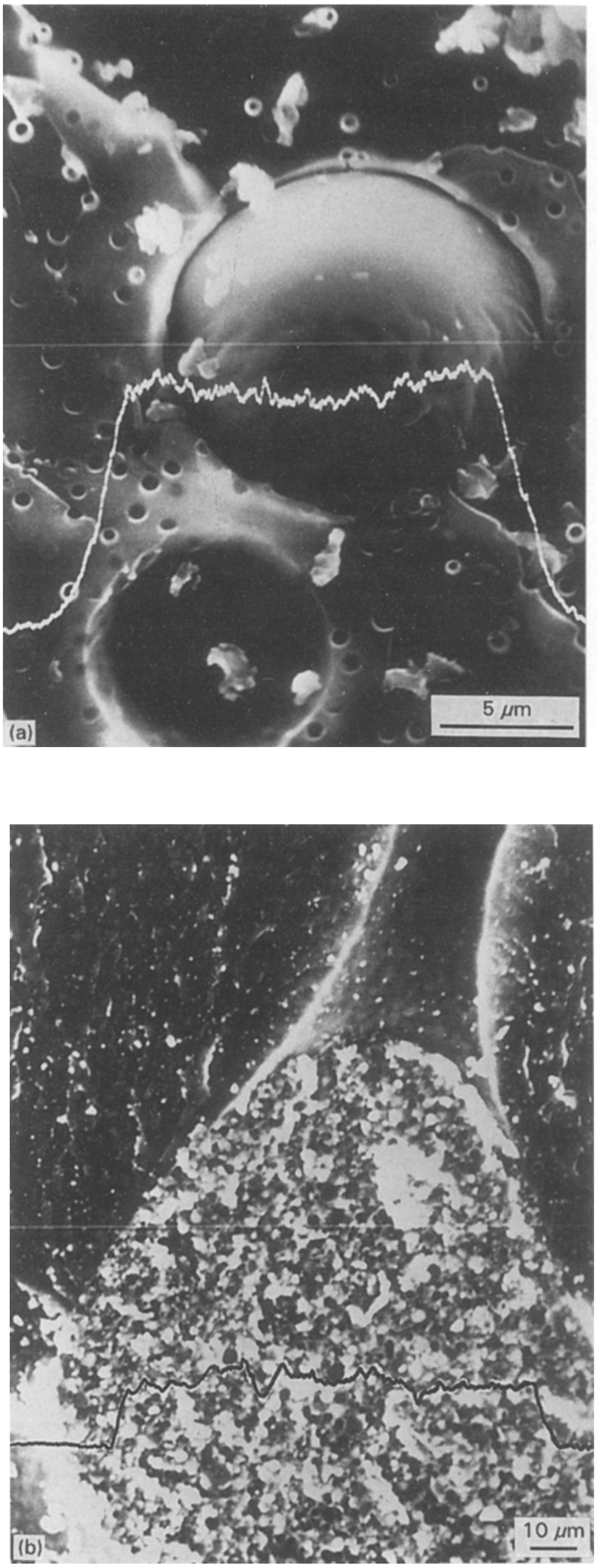


Figure 9 Scanning electron micrographs of the fracture surface of the ternary blends (the line profile on the micrographs indicates the concentration of sulphur measured by energy disperse spectroscopy): (a) 5 wt % CTBN/5 wt % PES modified, (b) 3 wt % CTBN/7 wt % PES modified epoxy.

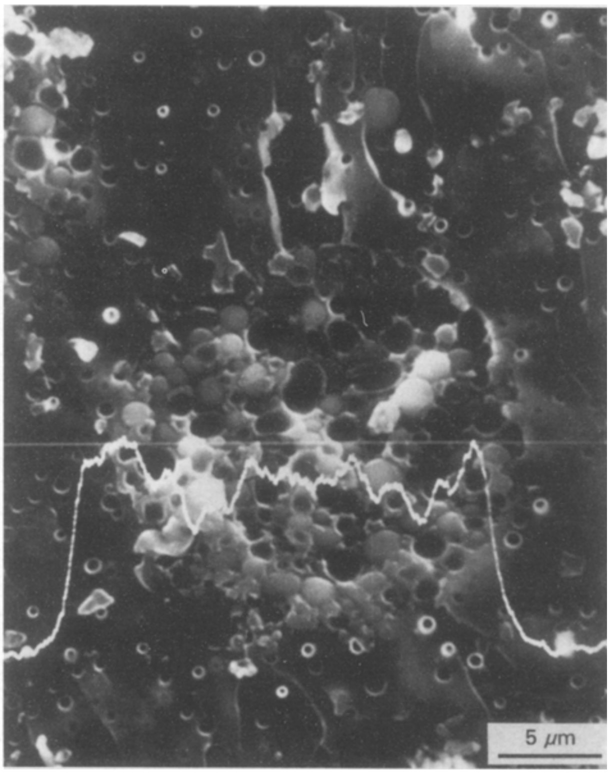


Figure 10 Scanning electron micrograph of the fracture surface of 5 wt % CTBN/5 wt % PES modified epoxy (the line profile on the micrographs indicates the concentration of sulphur measured by energy disperse spectroscopy).

This conclusion is supported by the observation that these domains are unaffected by etching with methylene chloride. During the curing process, a microphase separation occurs inside the PES-rich and the CTBN-rich domains, which developed during mixing. As illustrated in Fig. 10, smaller spherical domains, less than 1 μm, can be seen on the broken surface of PES-rich domains. EDS analysis shows that these smaller spherical domains are also PES-rich domains. On the fracture surface of CTBN-rich domains, holes due to the cavitation of rubber phases can be observed. Cavities cannot be observed inside the PES-rich phases. For ternary blends, in spite of clear evidence for phase separation seen on the fracture surfaces, loss peaks for PES are still not resolved by DMTA.

3.2. Properties of modified epoxies

The modulus and yield stress of the epoxy are essentially not affected by the inclusion of PES. However, with the inclusion of CTBN, a considerable drop in modulus and yield stress of about 25 and 18%, respectively occurs. The toughness enhancement of 10 wt % PES-modified and 10 wt % CTBN-modified epoxy over that of unmodified epoxy are 65 and 217 $\mathrm{J\,m^{-2}}$, respectively. For ternary blends of PES, CTBN, and epoxy, the modulus and yield stress changes with composition just follow the simple rule of mixtures, as seen on the Figs 11 and 12. However, the fracture toughness for 10 wt % modifier content is significantly enhanced over that predicted by the simple rule of mixtures, as shown in Fig. 13. Toughening of the epoxy matrix at 3:7, 5:5, 7:3 weight ratios of CTBN to PES result in fracture toughness greater than the fracture toughness obtainable with 10 wt % CTBN-toughened epoxy. Thus, these ternary blends exhibit synergistic toughening. Among the various compositions, 5:5 weight ratio of CTBN to PES exhibits the maximum toughness, which is 140% larger than that calculated from the rule of mixtures.

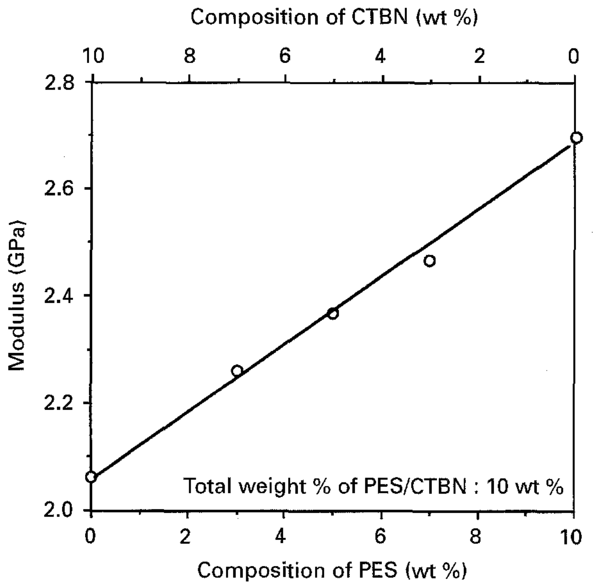


Figure 11 Effect of composition on the modulus of the ternary blends.

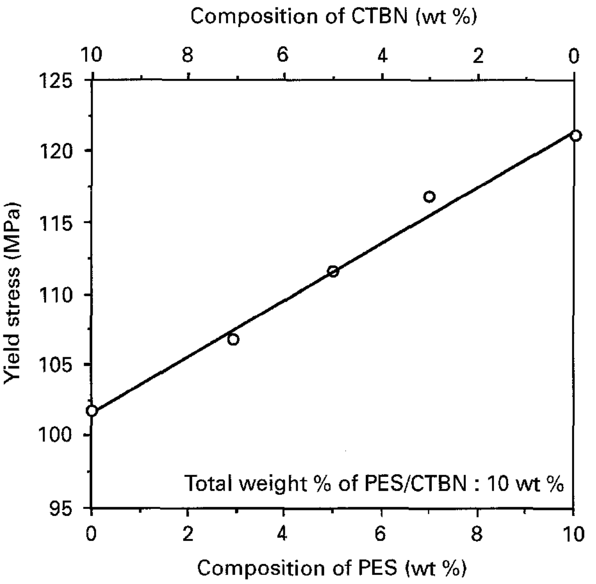


Figure 12 Effect of composition on the yield stress of the ternary blends.

3.3. Microscopic study

Typically in the double-torsion fracture test, crack initiation, propagation, and arrest are induced a number of times before complete fracture of the test specimen occurs. Fig. 14 shows the "stick–slip" mode of fracture which caused several crack arrest/initiation bands to appear on the fracture surface during a double-torsion test. The fracture surface between the crack arrest/initiation bands, which corresponds to the fast crack propagation, is quite smooth and featureless. By contrast, the fracture surfaces in the arrest/initiation bands, which correspond to slow crack propagation, are rough and show a degree of plastic deformation.

For the binary blend of epoxy and PES, there are no distinct features, such as PES domains, visible on the fracture surfaces until PES content reaches 10 wt %.

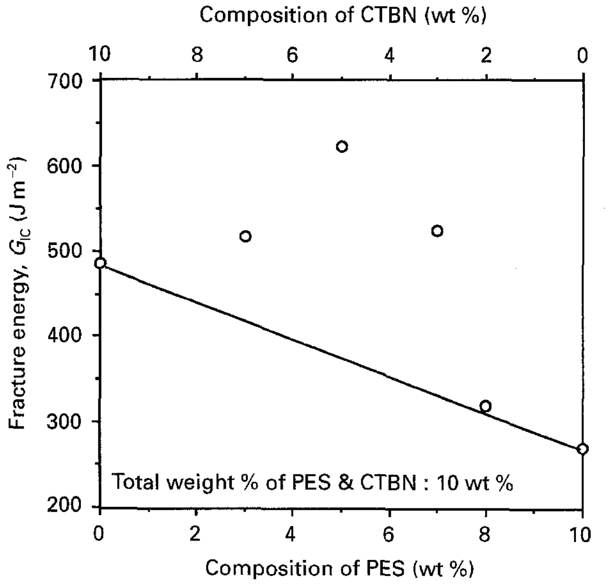


Figure 13 Effect of composition on the toughness of the ternary blends showing the synergystic effect.

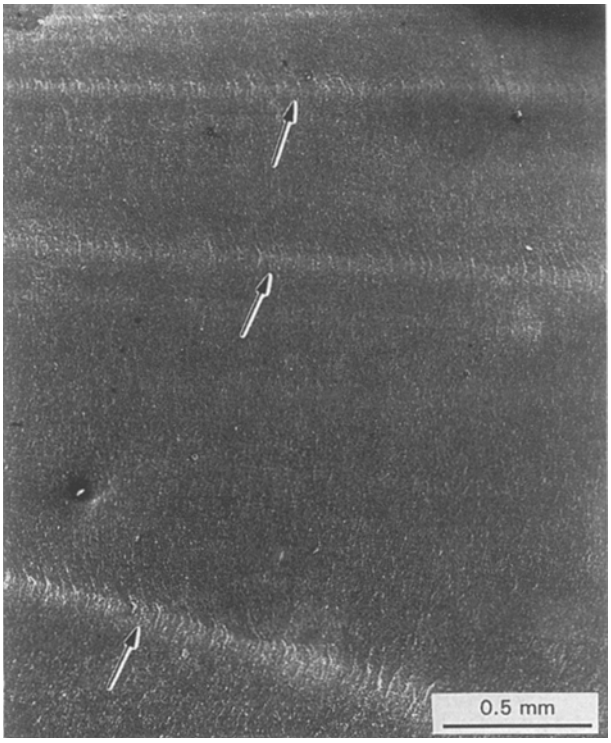


Figure 14 Scanning electron micrograph of the fracture surface of the 10 wt % CTBN-modified epoxy: (The arrows indicate crack arrest bands).

At 10 wt % PES content, scanning electron microscopy of the fracture surface reveals the presence of nodules whose size is smaller than 0.2 μm, as illustrated in Fig. 5. As seen in the micrograph, the nodular-type PES phases seem not to contribute to the toughness enhancement. The only observable effect of PES-rich phases upon fracture behaviour is seen in the deviation of the crack front around the PES nodules. A few shallow tail-like features behind the nodules indicate crack deviation or crack bifurcation is caused by the PES nodules.

The CTBN modified epoxy exhibits microplasticity in terms of permanently dilated cavities which can be

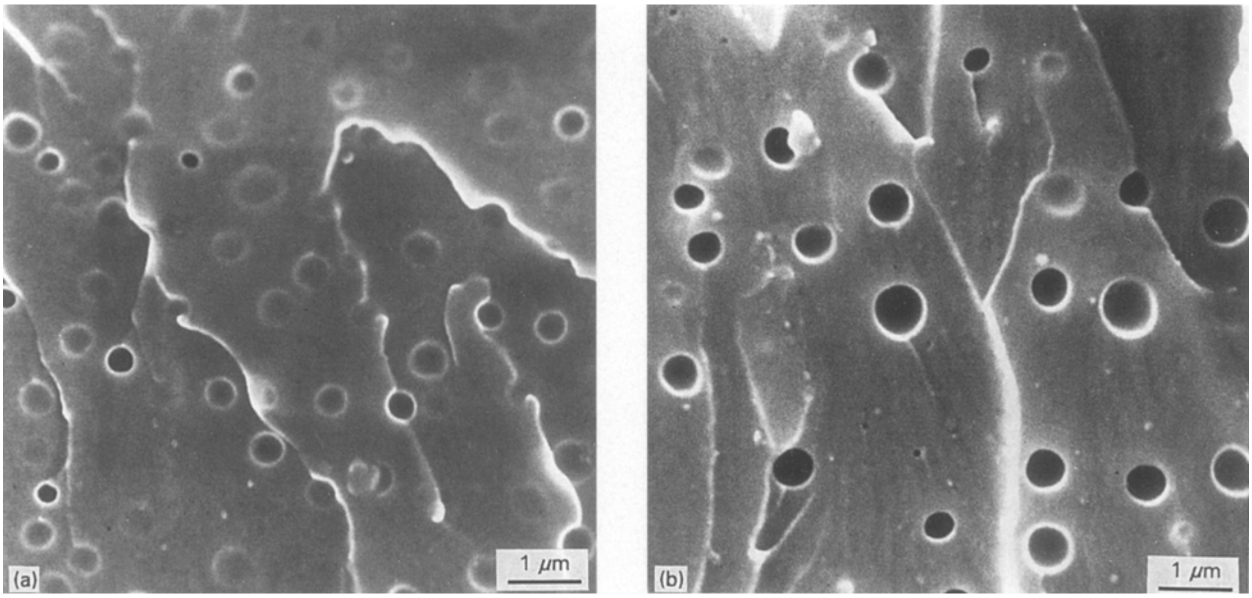


Figure 15 Scanning electron micrographs of the fracture surface of the 10 wt % CTBN-modified epoxy blend: (a) fast crack propagation region; (b) slow crack propagation region.

seen on the fracture surfaces. The hole diameters of cavities observed in the fast fracture region are in the range 0.3 to 0.5 μm, which are essentially the same size as the undeformed rubber particles, as illustrated in Fig. 15a. In contrast, the amount of plastic dilatation of the cavities in the slow crack propagation region are greater than that in the fast crack propagation region, as seen in Fig. 15b. Fig. 16 shows an optical micrograph of a thin section perpendicular to the fracture surface of a DN-4PB specimen which elucidated the nature of the sub-surface damage zone. As seen in the micrograph, ahead of the sub-critical loaded crack tip, there exists a dark region which corresponds to the rubber cavitation zone. The light diffracting properties are caused by internal cavitation. However, the limited resolution of the optical microscope make it impossible to ascertain the exact size of the cavities, nor is it possible to determine if cavitation has occurred. But cavitation of the rubber particles must have occurred, judging by the intense stress whitening.

For ternary blends of PES/CTBN with epoxy, fracture behaviour is highly affected by the composition. As mentioned above, in the ternary blends with CTBN(7)/PES(3) and CTBN(5)/PES(5) in epoxy, the spherical PES-rich domains are a dispersed phase. As shown in Fig. 17, in the slow crack growth region, the spherical PES-rich domains remained unfractured, while, in the fast crack growth region, most of the spherical PES-rich domains were fractured. Behind the PES-rich domains, whether fractured or not, crack bifurcation lines exist, indicative of crack shielding/deflection by the PES-rich spheres. The crack bifurcation can also be observed at the interface of the co-continuous structure of a ternary blend with CTBN(3)/PES(7) in epoxy. The diameters of the cavities in the CTBN-rich phase correlate well to the fracture toughness, as illustrated in Figs 18 and 19. The plastic dilatation in 5:5 weight ratio of PES to CTBN is larger than that for the other compositions.

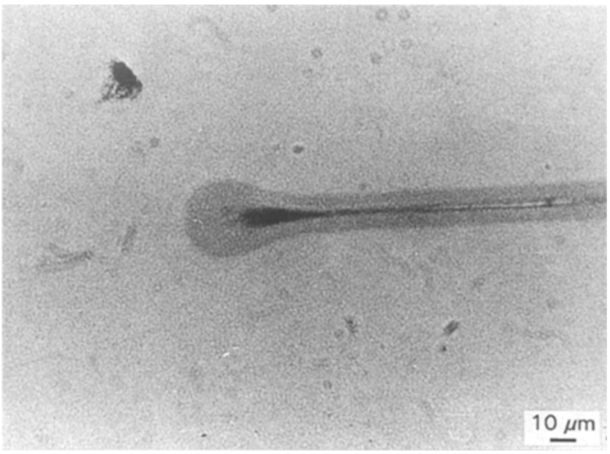


Figure 16 Transmission optical micrograph of thin sections taken mid-plane and near the crack tip of a DN-4PB sample of 10 wt % CTBN-modified epoxy.

Optical micrographs of a thin section perpendicular to the fracture surface of a DN-4PB specimen are shown in Fig. 20. As seen in the micrographs, the dark region corresponding to the rubber cavitation increases with PES composition. The size of the cavitation zone also correlates well with the fracture toughness. The crack bifurcation at the interface of the co-continuous structure can be clearly seen.

4. Discussion

4.1. Phase separation behaviours

The phase separation behaviour in blends of reactive thermosets with thermoplastics or elastomers is not well understood yet. Nevertheless, understanding the phase separation behaviours is highly desirable, since the resulting morphology is known to affect the physical and mechanical properties of the cured blends. An attempt to understand phase separation in modified thermosets has been made using the concept of the

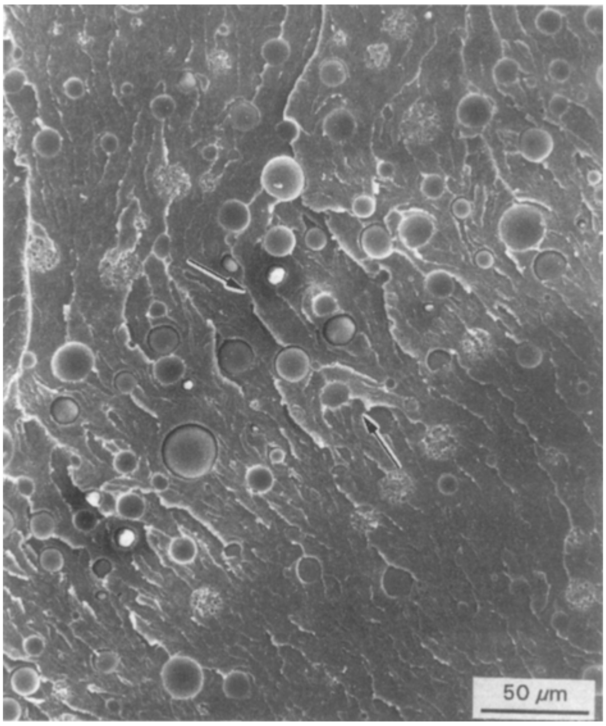


Figure 17 Scanning electron micrograph of the fracture surface of the ternary blend of 5 wt % CTBN/5 wt % PES modified epoxy (the arrows indicate the crack arrest band).

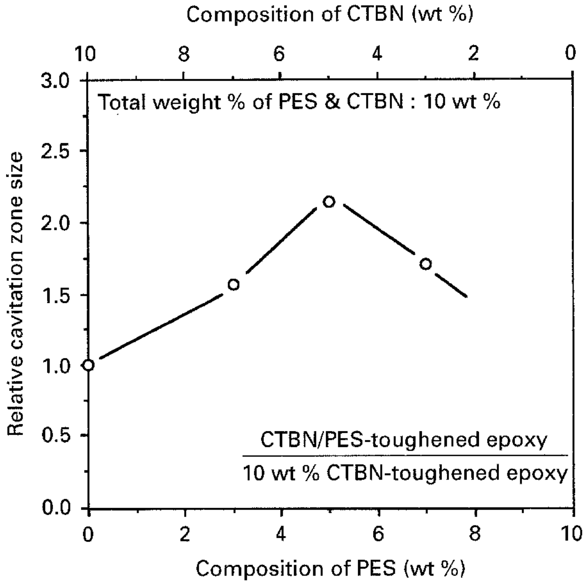


Figure 18 Effect of composition on the relative cavitation zone size of the ternary blends.

solubility parameter, δ, developed by Hildebrand [26], even though it has obvious deficiencies, particularly when dealing with specific interactions between molecules. The solubility parameters of DGEBA epoxy, PES, and CTBN have been reported as 10.0, 11.3, and 9.9, respectively [26]. Thus, for the ternary blends investigated in this study, the compatibility between epoxy and CTBN was expected to be much better than that between epoxy and PES. In fact, DGEBA epoxy and CTBN can easily form a homogeneous mixture. However, to obtain homogeneous mixture of epoxy and PES, the aid of a solvent, such as methylene chloride, is needed.

For the binary blends of PES/epoxy and CTBN/epoxy, phase separation occurs during the curing process. It is known that the phase separation mechanism for both systems is nucleation and growth [26]. For binary blends of epoxy and CTBN, copolymerization occurs between epoxy and CTBN, and, with increasing molecular weight, the copolymer phase separates from the homopolymers. For binary blends of epoxy and PES, during the curing process, the solubility parameters changed continuously due to the reaction. Because of the solubility parameter change and the molecular weight increase of epoxy, the PES phase separated from the homogeneous mixture.

For ternary blends of CTBN/PES with epoxy, it is clear that the phase separation occurred in two stages: macrophase separation during mixing and microphase separation during curing. For the ternary system, although each binary pair was miscible or partially miscible, asymmetry in the molecular interaction, the so-called $\Delta\chi$ effect, can cause a region of the

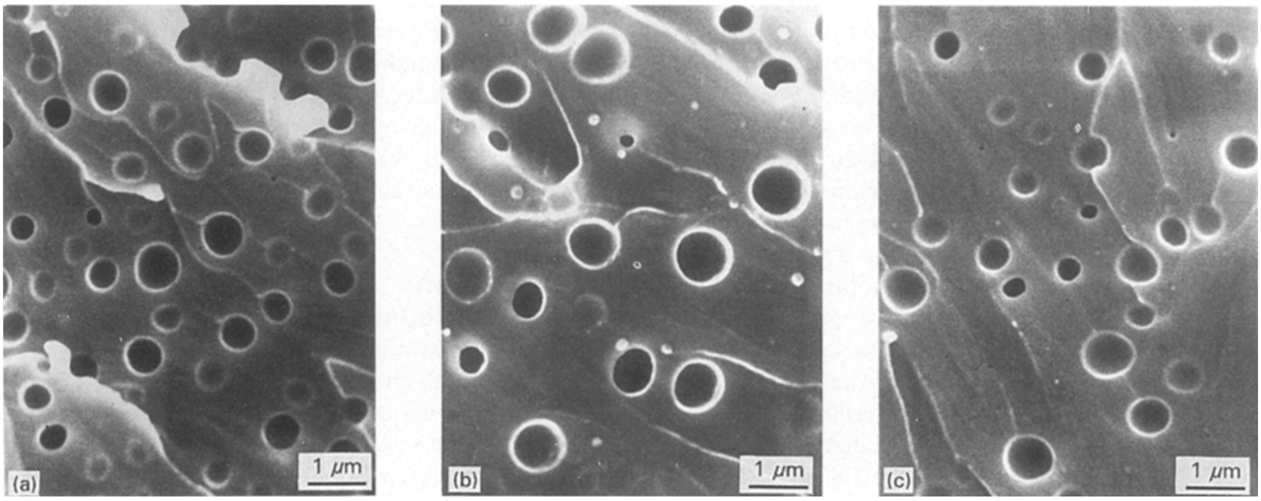


Figure 19 Scanning electron micrographs of the fracture surface of the ternary blends showing the dilatation of cavities: (a) 7 wt % CTBN/3 wt % PES modified, (b) 5 wt % CTBN/5 wt % PES modified, (c) 3 wt % CTBN/7 wt % PES modified epoxy.

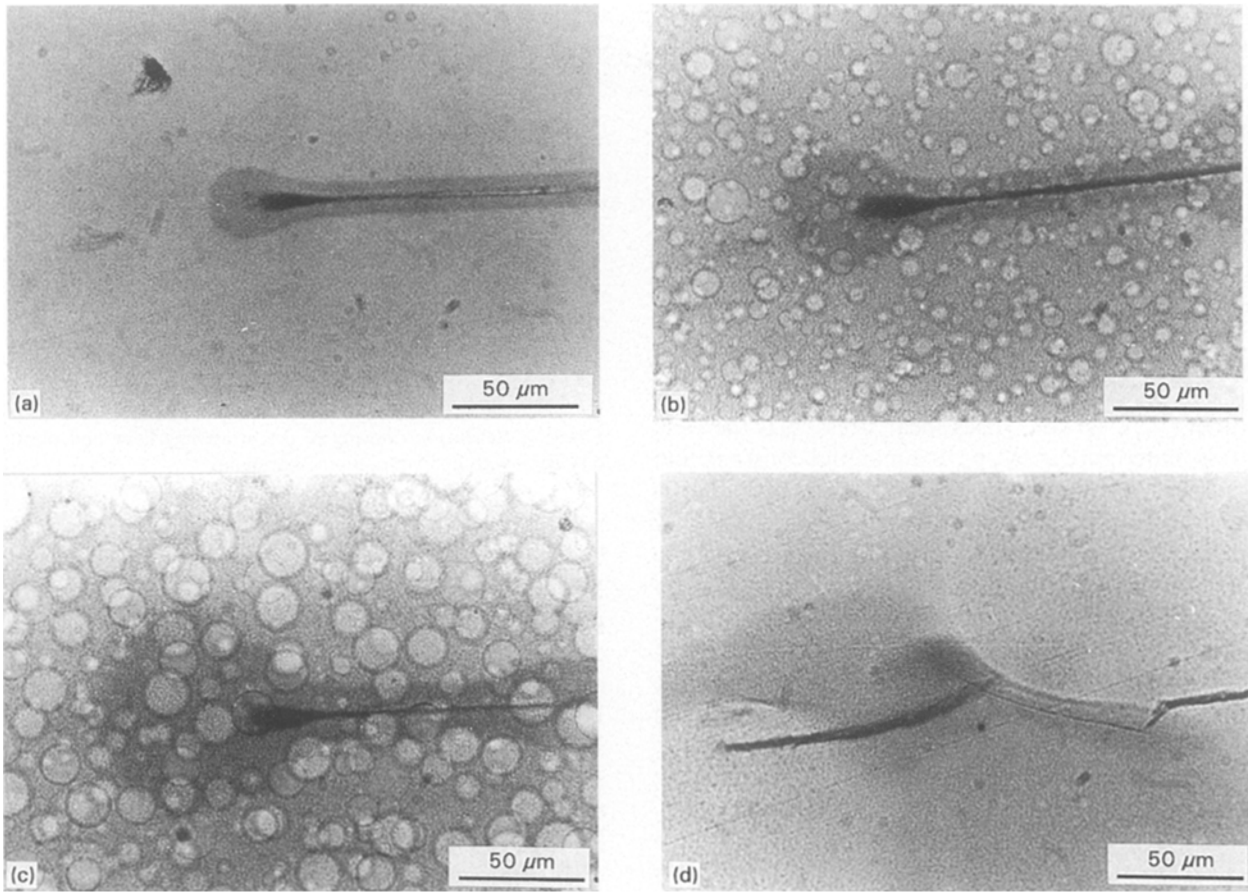


Figure 20 Transmission optical micrographs of thin sections taken mid-plane and near the crack tip of DN-4PB samples showing the size of the cavitation zone: (a) 10 wt % CTBN modified, (b) 7 wt % CTBN/3 wt % PES modified, (c) 5 wt % CTBN/5 wt % PES modified, (d) 3 wt % CTBN/7 wt % PES modified epoxy.

ternary blend to become immiscible [27, 28]. For the ternary blends investigated in this study, probably due to the larger interaction of CTBN/epoxy than PES/epoxy, macrophase separation of the PES-rich phase and the CTBN-rich phase occurs. Neither phase contains the other component, and this is confirmed by SEM and EDS. At low PES composition, PES-rich phases are separated out as dispersed spherical domains, whose diameters increase with increasing PES composition. At higher compositions, by interconnection of the larger spherical domains, a co-continuous structure develops and, finally, the phases are inverted. As mentioned above, the PES-rich domains contain a significant proportion of epoxy when considered in terms of the volume fraction. During curing, microphase separation occurs in both the PES-rich and the CTBN-rich domains which formed during the macrophase separation. The phase separation behaviours in both phases probably occur in the same manner as that in binary blends of PES/epoxy and CTBN/epoxy. After curing, inside PES-rich domains, the smaller spherical domains, less than 1 μm, developed instead of forming nodular structures. This might be due to the concentration effect. These small spherical particles can not be etched by methylene chloride, which indicates that these small domains also contain a significant amount of epoxy.

4.2. Synergistic effect

Many investigators [20–22] have studied the "synergistic effect" in toughening of epoxy. Among them, the model proposed by Evans *et al.* [17] seems the most systematic for understanding the synergistic effect. According to this, the bridging particles will increase the fundamental toughness of the matrix. Bridging with cavitated rubber particles that induced plastic deformation should result in multiplicative, not additive, toughening, because the toughness enhancement by the plastic deformation of the epoxy matrix is a function of the fundamental toughness. However, Pearson and Yee [21] did not observe the synergistic effect for epoxy toughened by CTBN which had a bimodal size distribution. Nevertheless, their results has clearly shown the interaction between the two toughening mechanisms. The synergistic effect was observed experimentally in a hybrid system, by Smith *et al.* [20]. Positive interaction between glass particles and rubber particles in a hybrid epoxy was observed [20].

The toughness of ternary blends of PES/CTBN with epoxy investigated in this study exhibits this synergistic effect. As mentioned, toughening of the epoxy matrix at 3:7, 5:5, 7:3 weight ratios of CTBN to PES result in fracture toughness greater than the fracture toughness obtainable with either modifier alone. In this system, the rigid PES-rich phases can act as bridging particles just like the glass beads in the hybrid system. When bridging occurs, the hydrostatic stress component continuously increases before the complete fracture of the bridging particle. It is known that the yielding of glassy polymers usually depends on the hydrostatic stress component, and that the simple von Mises criterion is not strictly satisfied [29]. Instead, the von Mises criterion should be modified by

$$\tau_{vm} = \tau_y - \mu_m P$$

$$P = 1/3(\sigma_1 + \sigma_2 + \sigma_3)$$

where τ_{vm} is the von Mises shear stress, τ_y is the yield stress under pure shear, μ_m is a material constant, and p is the hydrostatic stress [30]. Thus, due to the increased hydrostatic stress component caused by bridging, it is obvious that the stress required for the material to shear yield under tensile loading is reduced. The lowering of the yield stress might be related to the increase of the fundamental toughness of the matrix mentioned by Evans *et al.* [17], because the fundamental toughness of the epoxy is directly related to the deformability of the epoxy.

The lowering of the yield stress due to bridging strongly affects the radii of the plastic zone and maximum stress concentration factor. From the concepts of linear elastic fracture mechanics (LEFM), the radius of the plastic zone, or process zone, is inversely proportional to the square of the yield stress by

$$(\sigma_{yu}/\sigma_{ym})^2 = r_{ym}/r_{yu} = K_{vm}^2$$

where σ_{yu} and σ_{ym} are the yield stress for the unmodified and modified epoxy, respectively, r_{yu} and r_{ym} are the plastic zone radii for the unmodified and modified epoxy, respectively, and K_{vm} is the maximum stress concentration factor of the von Mises stress in the matrix. The value of K_{vm} represents the reduction of the effective yield stress. It is known that the stress concentration factor increases with the volume fraction of the rubber particles or voids [31]. When the lowering of the yield stress caused by bridging occurs, the plastic dilatation of cavities, i.e. the void growth process, would be enhanced. As a result, the stress concentration in the epoxy matrix will be enlarged by the void growth process. For the ternary blends investigated here, as expected, the radii of the cavities and the size of the cavitation zone related well to the fracture toughness. Obviously, the radii of the cavities and the size of the cavitation zone are related to the bridging effect, and the bridging effect produced by PES is sensitive to a morphology change. The bridging effect of the co-continuous structure seems to be lower than that of the dispersed structure. When comparing the ternary blend of CTBN(3)/PES(7) with CTBN(2)/PES(8), it is clear that the phase inverted structure can not contribute to the bridging, which is another indication that the synergistic effect in these systems is due to the change in plastic deformation followed by bridging. A schematic drawing of the interaction between bridging and plastic deformation is shown in Fig. 21.

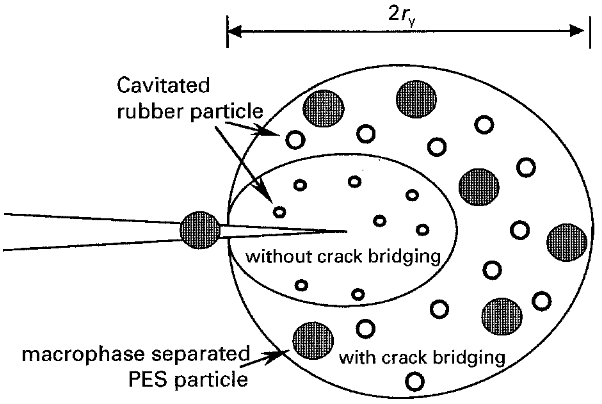


Figure 21 Schematic drawing of the processing zone and plastic dilatation with and without crack bridging.

5. Conclusions

For ternary blends of CTBN/PES with epoxy, the phase separation occurs in two stages: macrophase separation during mixing and microphase separation during curing. The macrophase separation of the PES-rich and the CTBN-rich phases is possibly due to asymmetry in the interaction of CTBN and PES with epoxy, the so-called $\Delta\chi$ effect. At low PES compositions, during mixing, PES-rich phases separate out as dispersed spherical domains whose diameters increase with PES composition. At higher PES compositions, by interconnection of the larger spherical domains, a co-continuous structure develops and, finally, the phases are inverted. The microphase separation during curing occurs in the same manner as in the binary blends for both the PES-rich and the CTBN-rich domains which developed during the macrophase separation.

For ternary blends of PES/CTBN with epoxy, the modulus and yield stress changes with composition follow the simple rule of mixtures. However, the fracture toughness of these blends exhibits a synergistic effect. The synergism is believed to be due to bridging by the PES-rich phase followed by a lowering of the yield stress. When bridging occurs, the hydrostatic stress component continuously increases before the complete fracture of a bridging particle. Thus, because of the increased hydrostatic stress component, it is obvious that the stress required for the material to shear yield under tensile loading is reduced. The lowering of the yield stress can enlarge the size of the process zone and the amount of plastic dilatation of the matrix. The bridging effect by PES was found to be sensitive to the morphology of the ternary blends.

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Received 6 March
and accepted 1 December 1995