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Miscibility, morphology and fracture toughness of tetrafunctional epoxy resin/poly (styrene-*co*-acrylonitrile) blends

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Poly(styrene-*co*-acrylonitrile) (SAN) was found to be miscible with the tetraglycidylether of 4,4′-diaminodiphenylmethane (TGDDM), as shown by the existence of a single glass transition temperature (T_g) over the whole composition range. However, SAN was found to be immiscible with the 4,4′-diaminodiphenylmethane (DDM)-cured TGDDM. Dynamic mechanical analysis (DMA) shows that the DDM-cured TGDDM/SAN blends have two T_gs. A scanning electron microscopy (SEM) study revealed that all the DDM-cured TGDDM/SAN blends have a two-phase structure. The fracture toughness K_{IC} of the blends increased with SAN content and showed a maximum at 10 wt% SAN content, followed by a dramatic decrease for the cured blends containing 15 wt% SAN or more. The SEM investigation of the K_{IC} fracture surfaces indicated that the toughening effect of the SAN-modified epoxy resin was greatly dependent on the morphological structures. © *2000 Kluwer Academic Publishers*

1. Introduction

Epoxy resins (ER) are one of the most important classes of thermosetting polymers. They are widely used as matrices for fiber-reinforced composite materials and as structural adhesives [1–4] due to their good thermal and chemical resistance, high tensile strength and modulus and dimensional stability. In particular, tetrafunctional epoxy resins have been increasingly used in the applications for advanced composite materials in the aerospace and aircraft industries [5–8]. However, the inherent brittleness of these highly crosslinked networks constrains their use, and thus many studies have been made to improve their toughness and crack resistance. One of the most successful methods of improving the toughness of epoxy resin is to incorporate a second phase of dispersed rubbery particles into the crosslinked polymers [9–15]. As a dispersed phase, the elastomer actually acts to alleviate crack propagation and enhance the toughness of epoxy resins. In these systems, the toughing has been considered mainly to arise from shear-deformation in the matrices. It is also noted that the inclusion of a rubbery component could cause the lowering of the modulus, and thermal stability of materials. Elastomers have successfully been applied to improve the toughness of epoxy resins with low crosslinking density. However, it has been demonstrated to fail to enhance the toughness of highly crosslinked thermosetting polymers [16–19] such as tetrafunctional epoxy resins.

In recent years, high performance thermoplastics have been employed to toughen epoxy resins. Various types of thermoplastics, such as poly(ether sulfone) (PES) [20–24], poly(ether imide) (PEI) [25–29], poly(ether ether ketone) (PEEK) [30–32], etc. have been explored to modify epoxy resins. Some results indicate that a fine phase-separated structure and good interfacial adhesion between the two separated phases usually yield greater fracture toughness. The enhanced toughness of these systems has been suggested to arise from crack pinning and the rupture of the dispersed thermoplastics [20, 33].

A series of studies on the modifications of difunctional ER with thermoplastics have been investigated in this laboratory. It is of not only academic but also practical interest to study the toughening mechanism of tetrafunctional epoxy resin because of their higher crosslinking density and increasing use in aero industries. In the case of the modification of epoxy resins using high performance thermoplastics (especially with higher strength, ductility and higher temperature resistance), the toughening effect should be relative not only to phase structure and interfacial adhesion, etc., but also to the excellent mechanical properties of the thermoplastics used. In order to examine the effect of the morphology in the thermoplastics-modified epoxy resins on toughing and to separate the effect of ductility of the thermoplastics themselves on the toughening effect as far as possible, we had studied the

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bisphenol-A-type epoxy resin modified with poly(styrene-*co*-acrylonitrile) (SAN) [34]. It was found that the cured ER/SAN blends were heterogeneous and had a two-phase structure, and the fracture toughness showed a substantial improvement. As further research, this work concerns the morphology and fracture behaviour of blends of tetrafuntional ER, i.e. the tetraglycidylether of 4,4′-diaminodiphenylmethane (TGDDM) and poly(styrene-*co*-acrylonitrile) (SAN). The SAN used is a commercially available thermoplastic polymer, with 25 wt% acrylonitrile content.

2. Experimental

2.1. Materials and preparation of samples

Tetrafunctional epoxy resin(ER) AG-80, with epoxy equivalent 115–135, i.e. the tetraglycidylether of 4,4′-diaminodiphenylmethane (TGDDM), was supplied by Shanghai Institute of Synthetic Resins, Shanghai, China. The poly(styrene-*co*-acrylonitrile) (SAN) used was Kibisan PN-127H AS resin with 25 wt% AN content (Chimei Petrochemical Co., Inc., Taiwan) and a meltflow index of 6.0 g/10 min; it has a viscosity-average molecular weight of 132 000 [34]. The curing agent used was 4,4′-diaminodiphenylmethane (DDM) (chemically pure grade, Shanghai Reagent Co., Inc., Shanghai, China) and was used in stoichiometric ratios of epoxide/amine.

TGDDM/SAN blends were prepared by solution casting from acetone. The solvent was evaporated slowly at room temperature. The residual solvent was removed under vacuum at ambient temperature for 2 weeks.

To prepare the DDM-cured TGDDM/SAN blends, SAN was first dissolved in acetone with continuous stirring at 60 °C and then poured into TGDDM. The mixture obtained was first degassed at atmospheric pressure and then under vacuum at 120 °C for half an hour and then cooled to 100 °C. Then, DDM was added to the mixture at 100 °C with continuous stirring until a homogeneous ternary mixture was obtained. The ternary mixture was cured in a Teflon mould that was highly polished. The samples were cured successively at 80 °C for 2 hours, 140 °C for 2 hours, 180 °C for 2 hours, and post-cured at 220 °C for 5 hours.

2.2. Differential scanning calorimetry (DSC)

Calorimetric measurement was performed on a Perkin Elmer DSC-2C thermal analysis apparatus in a dry nitrogen atmosphere. The instrument was calibrated with an indium standard. To remove the thermal history of the samples, a thermal pretreatment was used in which the sample temperature was elevated to 250 °C, kept for 10 minutes and then quenched to −50 °C in a dry nitrogen atmosphere. All the DSC thermograms were recorded at a heating rate of 20 °C/min. The midpoint of the slope change of the heat capacity plot of the second scan was taken as the glass transition temperature (T_g).

2.3. Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements were carried out on a Multifunctional Internal Friction Instrument with a torsion pendulum. The frequency used was 5 Hz and the heating rate was 1.5 °C/min. Specimen dimensions were $20 \times 5 \times 1$ mm^3.

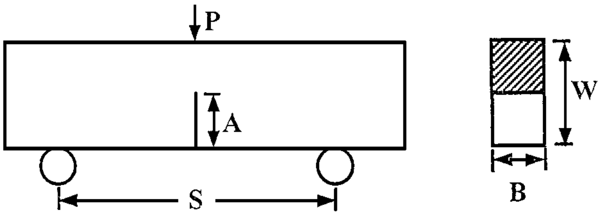

Figure 1 The schematic diagram of three-point bending specimen for measuring fracture toughness.

2.4. Morphological observations

To investigate the phase morphology of the DDM-cured TGDDM/SAN blends, the specimens were fractured under cryogenic conditions using liquid nitrogen. The fractured surfaces thus obtained were etched in chloroform at room temperature for 4 hours. The solvent preferentially etched the SAN phase while the cured ER network remained unaffected. The etched sample was dried to remove the solvent. The K_{IC} fracture surface was also observed. A Hitachi X-650 scanning electron microscope (SEM) was used for these observations, before which the surfaces were coated with thin layers (20 nm) of gold.

2.5. Fracture toughness

Fracture toughness was measured by the notched three-point bending test with an impact velocity of 1.5 m/s according to ASTM E399. The schematic diagram of three-point bending specimens is shown in Fig. 1. The central V-notches were machined into the bars, and extended by pressing a fresh razor blade into the tip of the notch to give a crack length of 3.3 ± 0.3 mm. The thickness of the specimens was about 10 mm and a minimum of five specimens were tested to obtain the average value in all cases.

The critical stress intensity factors, K_{IC}, i.e. fracture toughness, were calculated using the equation

$$K_{IC} = \left[P_C S/BW^{3/2}\right] f\left(\frac{A}{W}\right) \qquad (1)$$

where P_C is the load at crack initiation, B is the thickness of specimen, S is the span width, W is width of the specimen, and A is the crack length (see Fig. 1).

3. Results and discussion

3.1. Miscibility of TGDDM/SAN blends

All the TGDDM/SAN blends were transparent at ambient temperature. on further heating up to 200°C, these blends still remained clear and no phase separation occurred. This observation suggests that the TGDDM/SAN blends possess a single, homogeneous, amorphous phase.

Shown in Fig. 2 are the DSC curves of TGDDM/SAN *blends* at different compositions. All the blends display

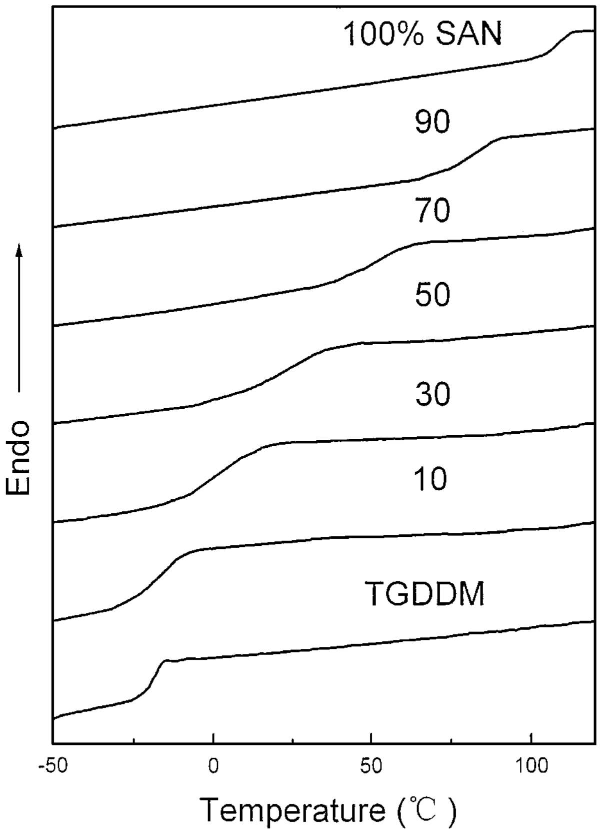

Figure 2 DSC curves of the TGDDM/SAN blends.

a single glass transition temperature (T_g), intermediate between those of the two pure components and changing with the blend composition. In view of the transparency and glass transition behaviour, the TGDDM/SAN blends are judged to be clearly miscible over the entire composition range. Several theoretical and empirical equations have been used to describe the T_g-composition of miscible polymer blends. One of these, the Gordon-Taylor equation [35], is written as

$$T_g = (W_1 T_{g_1} + k W_2 T_{g_2})/(W_1 + k W_2) \qquad (2)$$

where T_g is the glass transition temperature of the blend, T_{g_1} and T_{g_2} are the glass transition temperatures of component 1 and 2, respectively; W is the weight fraction and k is a constant. Fig. 3 summarizes the T_g plot as a function of blend composition. The curve is drawn using the Gordon-Taylor equation, yielding a k value of 0.45, and fitting the experiment data well.

Prud'homme *et al.* [36, 37] have suggested that k can be taken as a semi-quantitative measure of the strength of the interaction between the components of a blend. For instance, in blends of poly(ε-caprolactone) with chlorinated polyethylene, poly(vinyl chloride) (PVC) and chlorinated PVC, k increases from 0.26 to 1.0. When such an approach is used for the TGDDM/SAN blends, we note that the k value (0.45) is small, indicating that the interaction between the two pure components is relatively weak.

3.2. DDM-cured TGDDM/SAN blends

3.2.1. *Dynamic mechanical analysis*

All the DDM-cured TGDDM/SAN blends obtained were opaque, suggesting the occurrence of phase separation. Fig. 4 shows the dynamic mechanical spectrum of the pure DDM-cured TGDDM, and there exists a well-defined relaxation peak centered at 230°C, which is ascribed to the glass transition of the cured

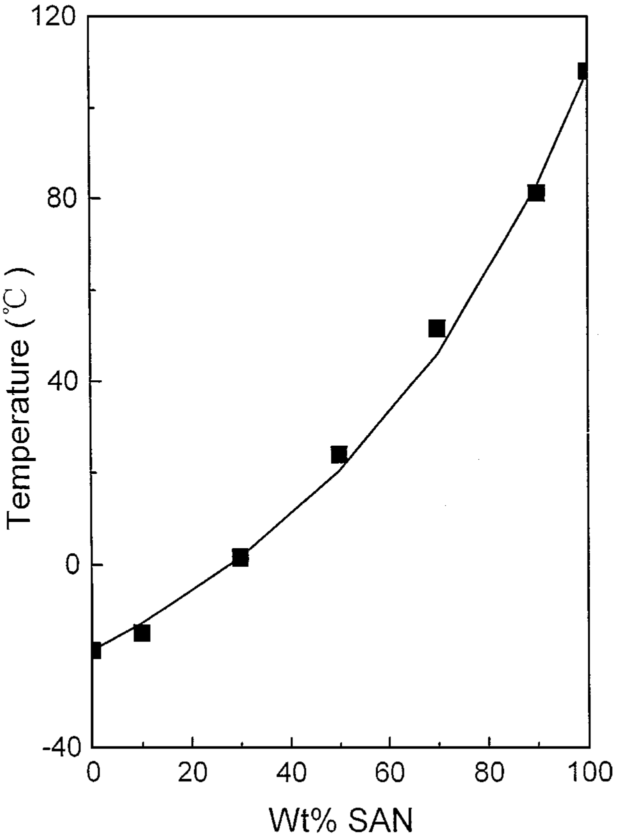

Figure 3 Composition dependence of glass transition temperature of TGDDM/SAN blends. The curve is as predicted by the Gordon-Taylor equation using a k value of 0.45.

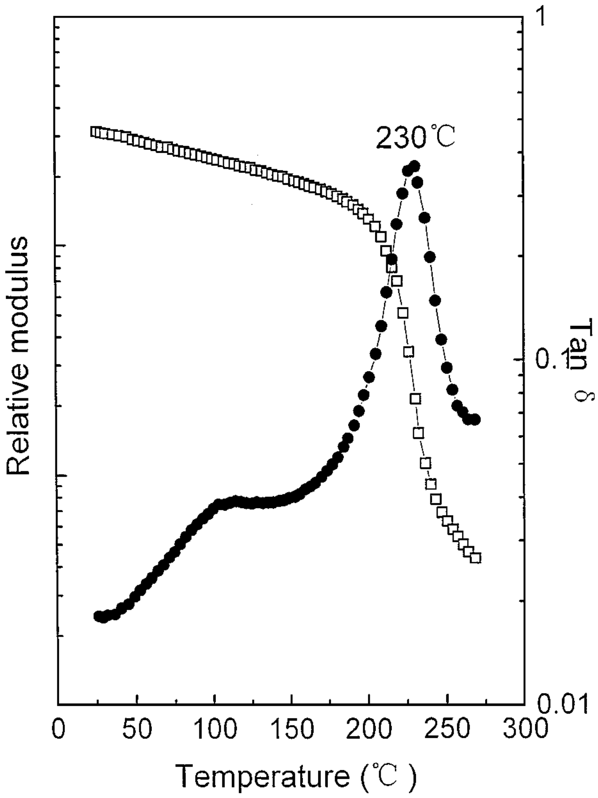

Figure 4 Dynamic mechanical spectra of DDM-cured TGDDM.

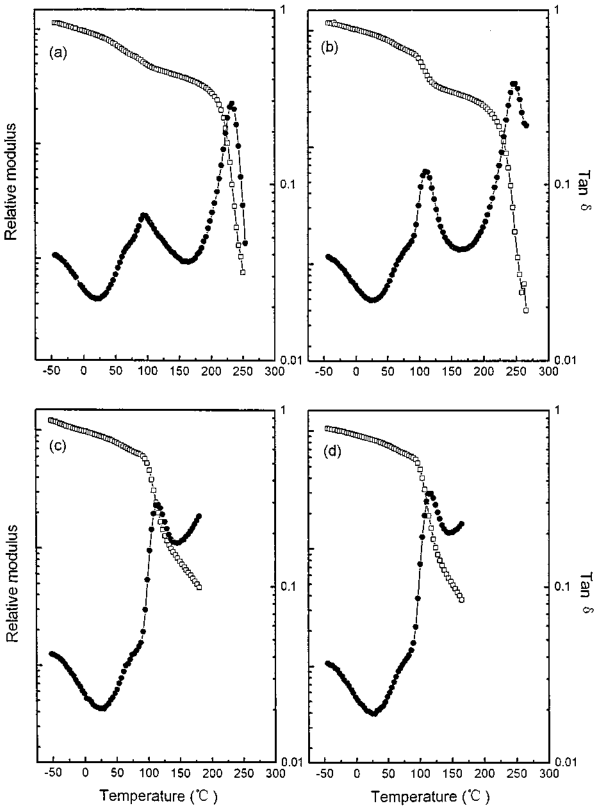

Figure 5 Dynamic mechanical spectra of DDM-cured TGDDM/SAN blends: (a) 95/5, (b) 90/10, (c) 85/15 and (d) 80/20.

ER. Fig. 5a–d show the dynamic mechanical spectra of the DDM-cured TGDDM/SAN blends containing 5, 10, 15 and 20 wt% SAN, respectively. All DMA spectra of the blends clearly display two transition peaks in the tan δ vs temperature curves in Fig. 5a-b, which corresponds to the T_gs of SAN-rich phase and DDM-cured ER phase, respectively. It is pointed out that Fig. 5c and 5d only showed the glass transition of SAN-rich phase. This is due to the occurrence of phase inversion at this composition (It will be seen below), i.e., SAN-rich phase had become the continuous phase for 85/15 and 80/20 DDM-cured TGDDM/SAN blends and the specimens were too soft to be tested when the testing temperature is higher than the T_g of SAN-rich phase. However, we can say that the trend of a second peak is clear. Dynamic mechanical analysis indicates that the DDM-cured TGDDM/SAN blends have a two-phase structure.

In the early stage of curing, the ternary blends (TGDDM/SAN/DDM) were a single-phase mixture. As the cure reaction proceeded, which involved chain extension, branching and crosslinking, the molecular weight of the system greatly increased, and the crosslinked network structure became three-dimensional. The increase in molecular weight caused a decrease in the configurational entropy of mixing. Therefore curing may cause phase separation in an initially miscible blend. On the other hand, because one component of the blend can crosslink, semi- interpenetrating networks (semi-IPN) may form. In this semi-IPN, the components which are initially immiscible may exhibit some characteristics of miscibility because phase separation was inhibited by crosslinking. Therefore, we can say that there exists a competitive process between the phase separation and the crosslinking reaction during the cure process.

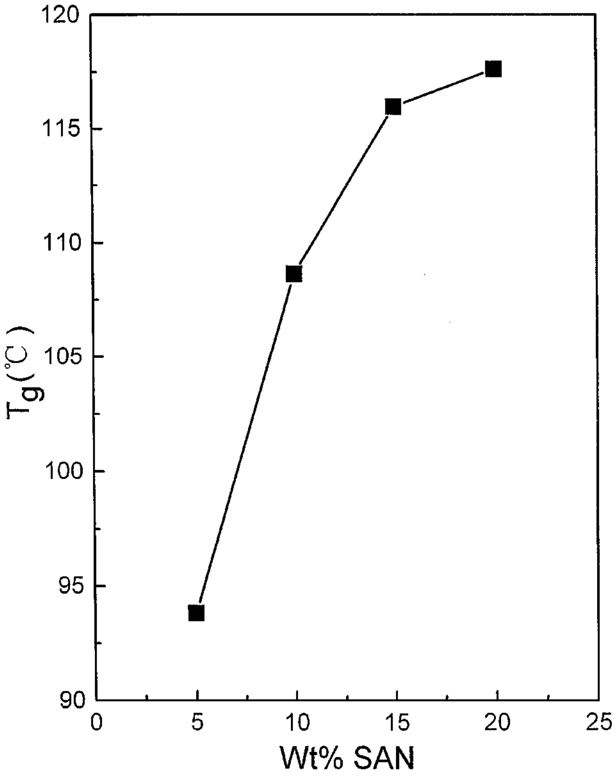

Figure 6 Composition dependence of T_g of SAN-rich phase of TGDDM/SAN blends.

Fig. 6 shows the T_g plot as a function of SAN concentration for the blends studied (DMA results). It can be seen that the T_g increased with increasing SAN content. This phenomenon could be ascribed to the incomplete phase separation between SAN and crosslinked ER.

3.2.2. Morphology

The morphology of the cured blends were investigated by means of SEM. Fig. 7 presents the SEM micrographs of chloroform-etched fracture ends of the 95/5, 90/10, 85/15 and 80/20 DDM-cured TGDDM/SAN blend specimens frozen by liquid nitrogen. The heterogeneous morphology was observed in all the cases, which supports the results of DMA. For the cured blend containing 5 wt% SAN, the discrete thermoplastic particles with average size smaller than 1 μm in diameter were relatively uniformly dispersed in the continuous cured ER matrices (Fig. 7a). With increasing SAN content, the morphology of the modified epoxy resins changed dramatically. Inclusion of 10 wt% of SAN gives rise to an obviously different morphology, i.e., SAN spherical particles begin to coagulate and show SAN vacant holes with irregular shapes and broadly-distributed size after the SAN phase was removed by chloroform. The appearance of epoxy-rich particles suggests that partial phase inversion has occurred. Therefore, this is a combined morphology in which the co-continuous phase begins to appear (Fig. 7b). A similar morphology was reported in trifunctional ER/PEI blends by Hourston *et al.* [26] and difunctional ER/SAN blends

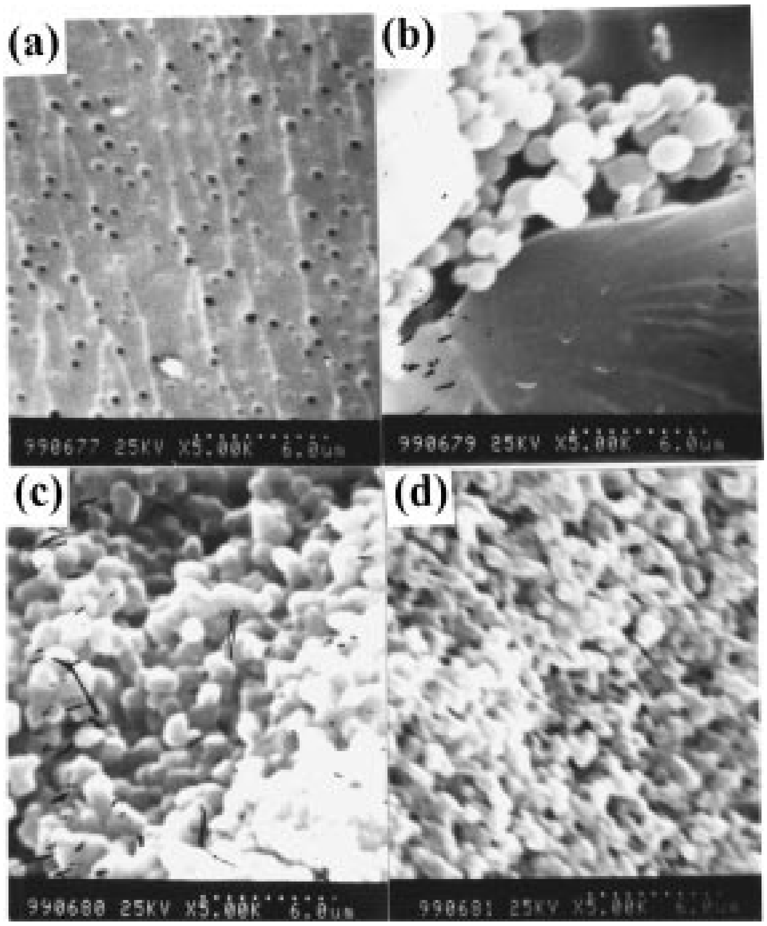

Figure 7 Scanning electron micrographs of fractured surfaces of DDM-cured TGDDM/SAN blends etched with chloroform: (a) 95/5, (b) 90/10, (c) 85/15 and (d) 80/20.

[34] in our previous work. When the SAN content rises to 15 wt%, the cured blends exhibited a phase-inverted morphology which consisted of epoxy domains wrapped in the thermoplastics continuous phase. Fig. 7c–d show the spherical particles of the epoxy-rich phase since the continuous SAN-rich matrices were etched by chloroform, and it can be seen that the epoxy particle size begins to decrease with increasing SAN content in the blends. This phenomenon could be explained by the competition between phase separation and crosslinking reaction. The inclusion of a higher SAN content gives rise to an increase of the viscosity of the mixture, which not only reduces the rate of phase separation, but also decreases the rate of crosslinking reaction, thus resulting in an incomplete curing reaction. Both the factors lead to a smaller size of epoxy particles. A similar morphology can be seen in our previous work both in DDM-cured DGEBA/SAN and in DDM-cured ER/PVAc blends [34, 38].

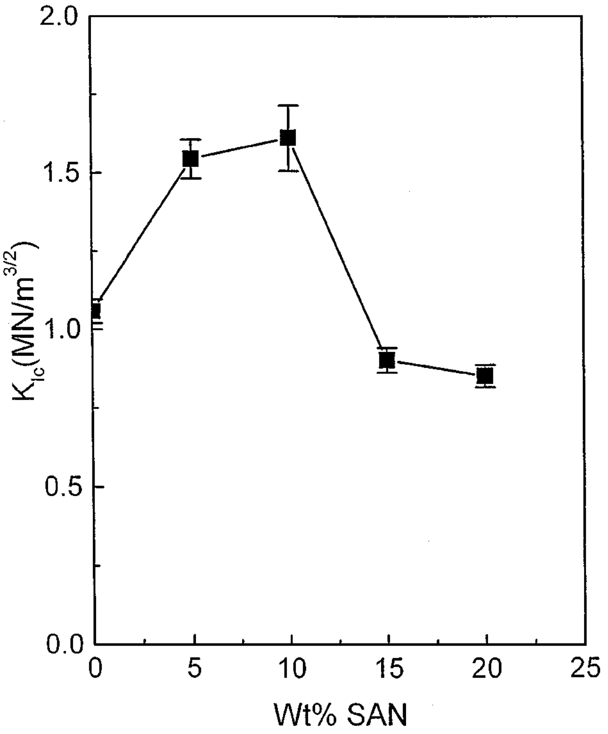

Figure 8 Fracture toughness K_{IC} as a function of SAN content for the DDM-cured TGDDM/SAN blends.

3.2.3. Fracture toughness

The plot of K_{IC} vs. SAN content in the cured blends is presented in Fig. 8. It can be seen that the fracture toughness first increases with the addition of SAN to the system, and then reaches its highest value in the vicinity of 10 wt% SAN blends. The blend exhibited an improved fracture toughness by about 50%. This value is similar to that of DDM-cured DGEBA/SAN system [34], and is also comparable to those obtained in the epoxy resin systems modified with other high performance thermoplastics at the same content of thermoplastics [23, 28]. When the SAN content is more than 10 wt%, there is a dramatic decrease in fracture

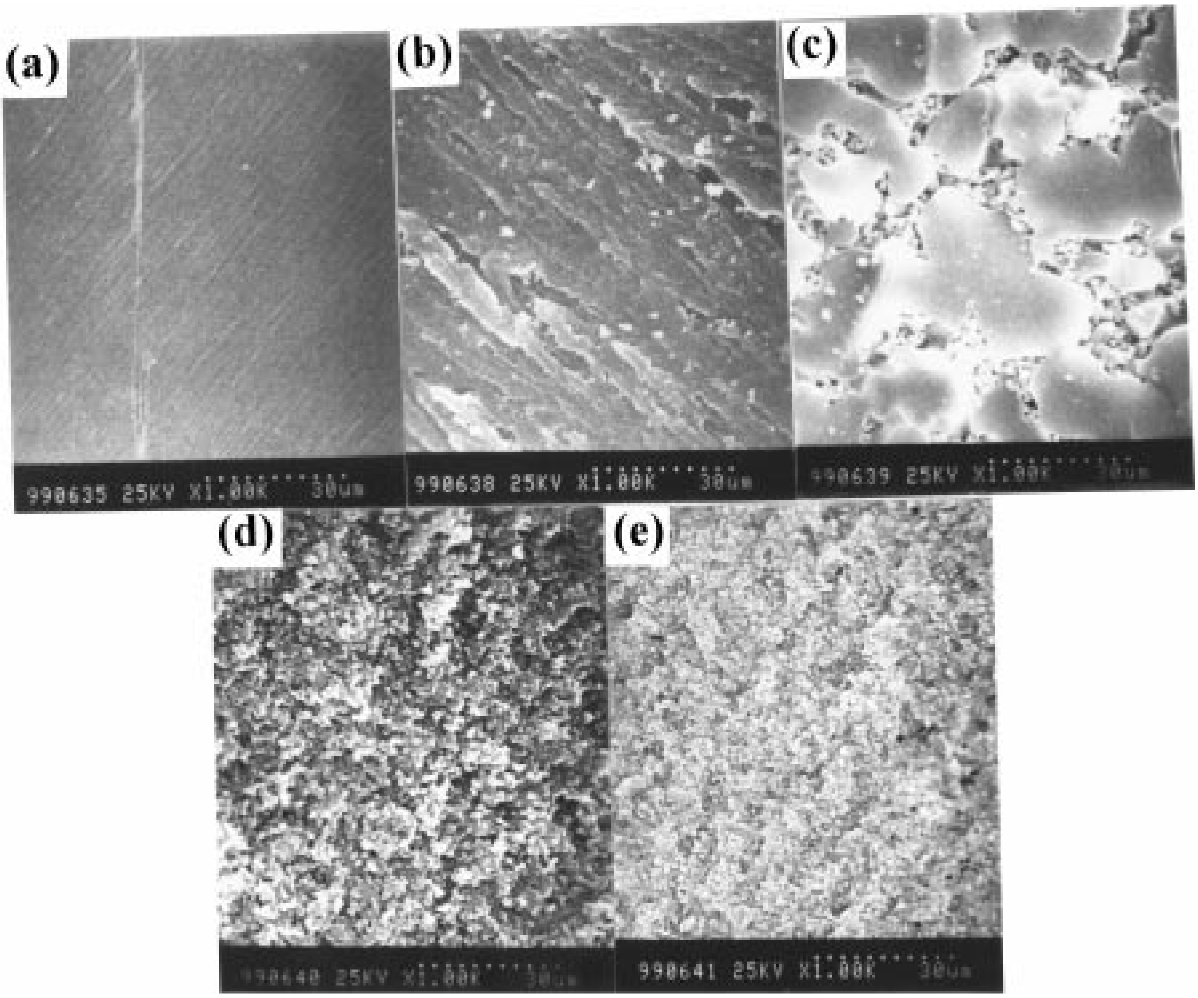

Figure 9 Scanning electron micrographs of K_{IC} fracture surfaces of DDM-cured TGDDM/SAN blends: (a) 100/0, (b) 95/5, (c) 90/10, (d) 85/15 and (e) 80/20.

toughness. As previously reported, better toughness is obtained with co-continuous phase structures in other high performance thermoplastic modified systems. In this case, the co-continuous structure was obtained for the cured blends containing 10–15 wt% of SAN. The cured blends with 10 wt% SAN content exhibit a combined morphology and yield a better fracture toughness. Phase inversion of the cured blend occurred when the SAN content was more than 15 wt%, thus the fracture toughness of the phase-inverted blends seem to depend predominantly on the ductile tearing of the thermoplastics. As is known, SAN is a relatively brittle polymer in comparison with other high performance polymers, and low values of fracture toughness were obtained. Although SAN polymers are brittle, they can substantially improve toughness in a certain concentration, and the morphology of the modified epoxy resins could play a very important role in toughening of resins.

The SEM micrographs of the K_{IC} fracture surfaces of the pure ER and the ER/SAN blends are shown in Fig. 9. For the pure ER, the cracks spread freely and regularly, and are oriented in the direction of loading, suggesting a typical characteristic of brittle fracture (Fig. 9a). However, the SEM micrograph of the cured 95/5 ER/SAN blend apparently displays tortuous and trivial cracks, which could be held back or delayed due to the existence of the second dispersed SAN phase (Fig. 9b). The absorption of a relatively large part of the fracture energy may be attributed to crack bifurcation and crack path alternation. The yielding in the continuous resin matrices is the principal mechanism of toughening [39]. For 90/10 ER/SAN blends, the SEM micrograph shows that ducting drawing phenomenon on the fracture surfaces, which appears mainly in the SAN phase, since there is some plastic deformation on the interfaces of the two phases (Fig. 9c). The plastic deformation of SAN might cause energy absorption and the blend fracture toughness increases. After this, the cured blends exhibited a phase-inverted morphology which consists of epoxy domains surrounded by the thermoplastics continuous phase (Fig. 9d-e). The fracture toughness may predominantly depend on the toughness of the thermoplastic.

4. Conclusions

The results presented here show that TGDDM/SAN blends are completely miscible over the entire composition range. DMA and SEM studies revealed that the DDM-cured TGDDM/SAN blends obtained were heterogeneous and had a two-phase structure. At low concentrations of SAN (5 wt%), SAN particles were spherically dispersed in the continuous epoxy matrix. When the SAN content was more than 10 wt%, a co-continuous phase structure began to appear in the cured blends. With inclusion of SAN 15 wt% or more, the cured blends exhibited an obvious phase-inverted structure. The fracture toughness of DDM-cured TGDDM/SAN blends increased with SAN content and reached a maximum at 10 wt% SAN content, followed by a dramatic decreases of K_{IC} for the cured blends containing 15 wt% SAN or more. Morphological investigation of the K_{IC} fracture surfaces indicated that the toughening effect of the SAN-modified epoxy resin greatly depended on the phase structures. Both the SAN-dispersed and the combined phase structures of SAN and epoxy particles can give improved values of K_{IC}, whereas the cured blend with the phase-inverted structures possessed a lower toughness.

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