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

Sixun Zheng, Jian Wang and Qipeng Guo*
Department of Materials Science & Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

and Jun Wei
Department of Mechanics and Mechanical Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

and Jian Li
Laboratory of Internal Friction and Defect in Solids, Academia Sinica, Hefei 230039, People's Republic of China
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Poly(styrene-*co*-acrylonitrile) (SAN) with 25 wt% acrylonitrile (AN) content was found to be miscible with uncured bisphenol-A-type resin, i.e. diglycidylether of bisphenol A (DGEBA), as shown by the existence of a single glass transition temperature within the whole composition range. Miscibility between SAN and DGEBA is considered to be due mainly to entropy contribution. However, SAN was judged to be immiscible with the 4,4′-diaminodiphenylmethane-cured epoxy resin (DDM-cured ER) as revealed by the means of differential scanning calorimetry (d.s.c), dynamic mechanical analysis (d.m.a.) and scanning electron microscopy (SEM). It was observed that the DDM-cured ER/SAN blends have two T_g's, which remain almost invariant with composition and are close to those of the pure components, respectively. SEM study revealed that all the DDM-cured ER/SAN blends have a two-phase structure. The fracture mechanics studies indicate that the DDM-cured ER/SAN blends containing 10 wt% give a substantial improvement of fracture toughness K_{IC}. The fracture toughness K_{IC} increases with SAN content and shows a maximum at 10 wt% SAN content, followed by a dramatic decrease in K_{IC} for the cured blends containing 15 wt% SAN or more. SEM investigation of the K_{IC} fracture surfaces indicates that the toughening effect of the SAN-modified epoxy resin is greatly dependent on the morphological structures. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer miscibility; polymer morphology; fracture toughness)

INTRODUCTION

Epoxy resins are a major class of thermosetting polymers, which are widely used as matrices for fibre-reinforced composite materials, adhesives and coatings as well as other engineering materials[1,2]. However, not all the properties of the materials are beneficial, such as inherent embrittleness, i.e. low toughness and crack resistance due to high crosslinking densities. Considerable attention has been paid to improvements of epoxy resins. One successful modification routine is elastomer toughening, e.g. carboxyl-terminated butadiene-acrylonitrile rubber (CTBN), amine-terminated butadiene-acrylonitrile rubber (ATBN)[3–7], silicone, etc.[8–13] have been employed to toughen epoxy resins. As a dispersed phase, the elastomeric actually acts to alleviate crack propagation and enhance the toughness of epoxy resins. In these systems, the toughening has been considered mainly to arise from shear-deformation in the matrices[9,14,15].

More recently, many attempts have been made to modify epoxy resins with high-performance engineering thermoplastics[16–30], especially to improve toughness of highly crosslinked epoxy resins, e.g. tetrafunctional epoxy resins. Various types of thermoplastics, such as poly(ether sulfone) (PES)[15,19,22–24], poly(ether imide) (PEI)[16,21,26,27], poly(ether ether ketone) (PEEK)[28–30], etc. have been explored to modify epoxy resins. Some results indicate that the modifications necessitate a fine phase-separated structure and a good interfacial adhesion between the two separated phases. A thermoplastic-dispersed phase structure or a co-continuous phase structure in thermoplastic-modified epoxy resin usually yields greater fracture toughness. The enhanced toughness of the system has been suggested to arise from crack pinning and the rupture of the dispersed thermoplastics[15,31].

As a part of a series of our investigations involving

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* To whom correspondence should be addressed

the modifications of epoxy resins with thermoplastics, this work concerns on the morphology and fracture behaviour in blends of bisphenol-A-type epoxy resin (ER) and a poly(styrene-*co*-acrylonitrile) (SAN). The SAN used is a commercially available thermoplastic polymer, with 25 wt% acrylonitrile (AN) contents. In the case of 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 thermoplastics used. The aim of this study is to examine the effect of the morphology in the thermoplastic-modified epoxy resins on toughening, segregating the effect of ductility of thermoplastics itself on toughening effect as far as possible.

EXPERIMENTAL

Materials and preparation of samples

The bisphenol-A-type epoxy resin, diglycidyl ether of bisphenol-A (DGEBA) with epoxide equivalent weight 185–210 was obtained from the Shanghai Resin Factory, 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 melting index of 6.0 g/10 min. The SAN had an intrinsic viscosity $[\eta] = 0.54\,\mathrm{dl\,g^{-1}}$ in butanone solution at 30°C. To calculate the molecular weight, the Mark–Houwink equation was used

$$[\eta] = KM^{\alpha} \tag{1}$$

where M is the viscosity-average molecular weight. The values of K and α for SAN with the present composition are $3.6 \times 10^{-2}\,\mathrm{ml\,g^{-1}}$ and 0.62, respectively[32]. The viscosity-average molecular weight was calculated to be 132 000. The curing agent used was 4,4′-diaminodiphenylmethane (DDM) (chemically pure grade, Shanghai Reagent Co., Inc., Shanghai, China).

Uncured DGEBA/SAN blends. All the DGEBA/SAN blends were prepared by solution casting from acetone, the solvent was evaporated slowly at ambient temperature. The residual solvent was removed under vacuum at 50°C for two weeks.

Cured epoxy resin/SAN blends. To prepare the DDM-cured ER/SAN blends, SAN was first dissolved in the smallest possible amount of acetone, and the solution mixed with DGEBA at ambient temperature. The mixture obtained were heated up to 120°C with continuous stirring to evaporate the majority of solvent, and degassed under vacuum at 150°C for 1 h to remove residual solvent. Then, the curing agent, DDM was added to the mixture at 100°C with continuous stirring until a homogeneous ternary mixture was obtained. The ternary mixture was poured and cured in a Teflon mould which was highly polished. The samples were cured successively at 80°C for 2 h, 150°C for 2 h, and 200°C for 2 h.

Differential scanning calorimetry (d.s.c.)

The calorimetric measurements were made on a Perkin-Elmer DSC-7 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with indium standard. The sample weight used in the d.s.c. cell was kept in the 8–12 mg range. The midpoint of the slope change of the heat capacity plot of the second scan was taken as glass transition temperature (T_g). A heating rate of $20^{\circ}\mathrm{C\,min^{-1}}$ was used.

Dynamic mechanical analysis (d.m.a.)

Dynamic mechanical measurements were carried out on an Imass Dynastat viscoelastic apparatus in nitrogen atmosphere, with temperature scanned from 0 to 250°C. The frequency used was 5 Hz and heating rate $3.0^{\circ}\mathrm{C\,min^{-1}}$. Specimen dimensions were $6.0 \times 0.4 \times 0.18\,\mathrm{cm^3}$.

Fracture toughness measurements

Fracture toughness was measured by the notched three-point bending test with a crosshead speed of $1.3\,\mathrm{mm\,s^{-1}}$ according to ASTM E399. The schematic diagram of three-point bending specimens is shown in *Figure 1*. The thickness of the specimens was about 10 mm. The critical stress intensity factors were calculated using the following equation:

$$K_{\mathrm{IC}} = P_{\mathrm{c}}S/BW^{3/2}f(A/W) \tag{2}$$

where P_{c} is the load at crack initiation, B is the thickness of the specimen, S is the span width, W is the width of the specimen, and A is the crack length (*Figure 1*).

Central Vee-notches were machined in the bars, and extended by pressing a fresh razor blade into the tip of the notched to give a crack length of 3.3 ± 0.3 mm.

Morphological observations

To investigate the phase structure of the cured ER/SAN blends, the specimens were fractured under cryogenic conditions using liquid nitrogen. The fractured surface so obtained was then immersed in dichloromethane at room temperature for 4 h. The SAN phase was preferentially etched by the solvent while the cured ER phase remained unaffected. The etched samples were dried to remove the solvent. The K_{IC} fracture surfaces were also observed to examine the fracture characters of the cured blends. A Hitachi X-650 scanning electron microscope was used for observation, before which the surfaces were coated with thin layers of gold of 200 Å.

RESULTS AND DISCUSSION

Miscibility of DGEBA/SAN blends

All the DGEBA/SAN blends were transparent and no phase separation occurred by heating up to about 280°C. D.s.c. study showed that each blend has a single composition-dependent T_g, indicating its single-phase nature. Thus, SAN is miscible with DGEBA over the

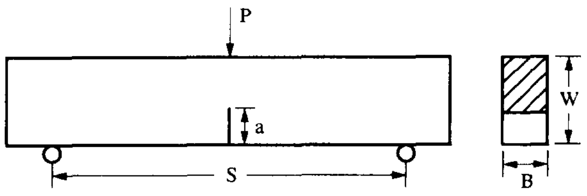

Figure 1 The schematic diagram of three-point bending specimen for measuring fracture toughness

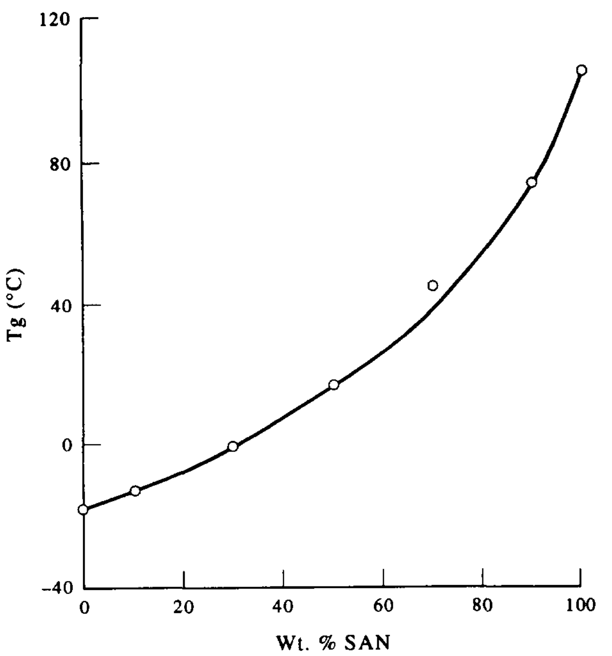

Figure 2 Composition dependence of glass transition temperature of DGEBA/SAN blends. The curve is as predicted by the Gordon–Taylor equation using a k value of 0.44

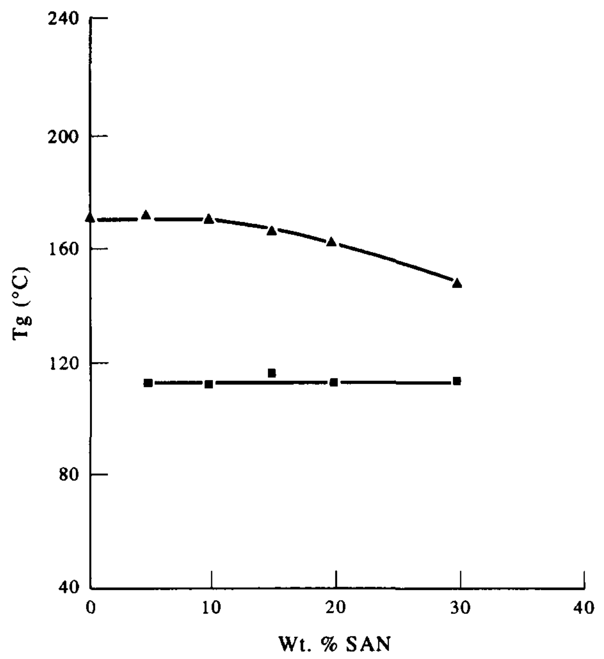

Figure 3 Glass transition behaviour for the DDM-cured ER/SAN blends: (▲) T_g of the ER phase; (■) T_g of the SAN phase

entire composition range. *Figure 2* summarizes the T_g values obtained with d.s.c. as a function of blend composition.

Several theoretical and empirical equations have been used to describe the T_g–composition dependence of miscible blends. One of these, the Gordon–Taylor equation[33], is written as:

$$T_g = (W_1 T_{g_1} + kW_2 T_{g_2})/(W_1 + kW_2) \qquad (3)$$

where T_g is the glass transition temperature of the blend, T_{g_1} and T_{g_2} are the glass transition temperatures of the components 1 and 2, respectively, W is the weight fraction, and k is a constant. The curve in *Figure 2* is drawn using the Gordon–Taylor equation with a k value of 0.44, fitting the experimental data well.

Prud'homme *et al.* have suggested[34,35] that the k value can be taken as a semiquantitative measure of the strength of interaction between the components of the 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 DGEBA/SAB blends, we note that the k value (0.44) is smaller, suggesting that the interaction between DGEBA and SAN is relatively weak. The miscibility of the DGEBA/SAN blends can be considered to be due mainly to the non-negligible entropy contribution as the molecular weight of DGEBA is rather low.

DDM-cured ER/SAN blends

Differential scanning calorimetry. All the DDM-cured DGEBA/SAN blends obtained were opaque, suggesting the occurrence of phase separation. All the d.s.c. thermograms of the cured blends can give two separate T_g, which correspond to those of cured ER phase and SAN-rich phase, respectively, as shown in *Figure 3*. With curing agent adding to DGEBA/SAN mixture and curing at elevated temperature, the curing reaction involving chain extension, branching and crosslinking, took place. As the curing reaction proceeded, the molecular weight of the system greatly increased, and the crosslinking network structure in three-dimension formed. On the other hand, the occurrence of crosslinking causes dramatic changes in the chemical and physical natures of the system. Both the factors give rise to the occurrence of phase separation between SAN component and the crosslinked ER matrix. Of course, there exists a competitive progress between the phase separation and the crosslinking reaction during the cure process.

It can be seen from *Figure 3* that the T_g of the cured ER phase decreases with a SAN-content of more than 10 wt%. The depression in T_g of the cured ER phase may be considered to be due to the incomplete phase separation between SAN and the crosslinked ER. On the other hand, initially the addition of SAN raises the viscosity of the system, which may result in an incomplete curing reaction due to the steric hindrance under the present curing condition[36]. Furthermore, the dilution effect of SAN is also an important factor giving rise to an incomplete curing reaction, and thus a lower T_g for the ER crosslinked network.

Dynamic mechanical analysis. Figure 4 shows dynamic mechanical properties of the DDM-cured ER as well as the 90/10 and 80/20 DDM-cured ER/SAN blends. The dynamic mechanical spectrum of DDM-cured ER (*Figure 4a*) exhibits a well defined relaxation peak centred at 178°C, which is ascribed to the glass transition of the DDM-cured ER. The dynamic mechanical spectra of the 90/10 (*Figure 4b*) and 80/20 (*Figure 4c*) DDM-cured ER/SAN blends clearly display two maxima on the $\tan\delta$ vs T curves, which corresponds to the T_g's of SAN and DDM cured ER, respectively. The d.m.a. results presented here further indicate that SAN

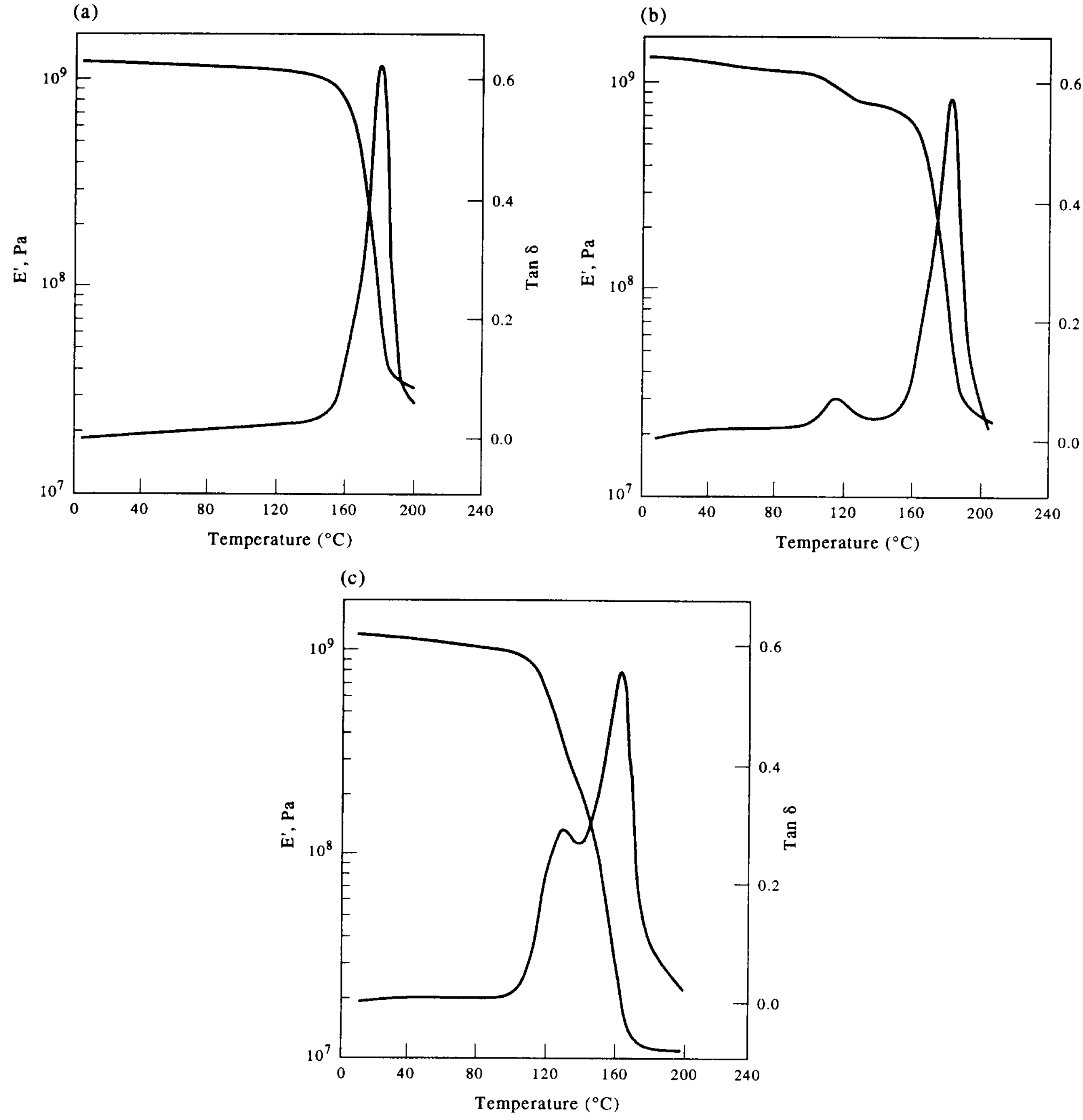

Figure 4 Dynamic mechanical spectra of (a) 100/0, (b) 90/10, and (c) 80/20 DDM-cured ER/SAN blends

and DDM-cured ER are immiscible and the DDM-cured ER/SAN blends had a two-phase structure, which is in a good agreement with that from the d.s.c. study.

Morphology. The morphology of the cured blends were investigated by means of a scanning electronic microscope (SEM). The SEM micrographs of dichloromethane-etched fracture surfaces of the blend specimens freezed by liquid nitrogen are presented in *Figure 5*. The heterogeneous morphology was observed in all the cases, which supports the results of d.s.c and d.m.a. For the cured blend containing 5 wt% SAN, the discrete thermoplastics particles with average size smaller than 1 μm in diameter were uniformly dispersed in the continuous cured ER matrices (*Figure 5a*). With increasing SAN content, the morphology of the modified resin changed dramatically. Inclusion of 10 wt% SAN gives rise to an obviously different morphology for the fracture surface etched with dichloromethane, i.e. SAN spherical particles begin to coagulate and show SAN vacant holes with irregular shapes and broadly distributed size in the resin matrices; at the same time, there appear spherical epoxy-rich particles after the SAN phase was etched by dichloromethane, which suggests the occurrence of partial phase inversion. This could be a combined morphology intermediate between the SAN-dispersed and the co-continuous phase structures (*Figure 5b*). A similar morphology was reported in trifunctional epoxy resin/PEI blends when the PEI concentration was 15 wt% by Hourston *et al.*[21]. When the SAN content rises to 15 wt%, a typical complete co-continuous morphology was formed (*Figure 5c*) and after this, the

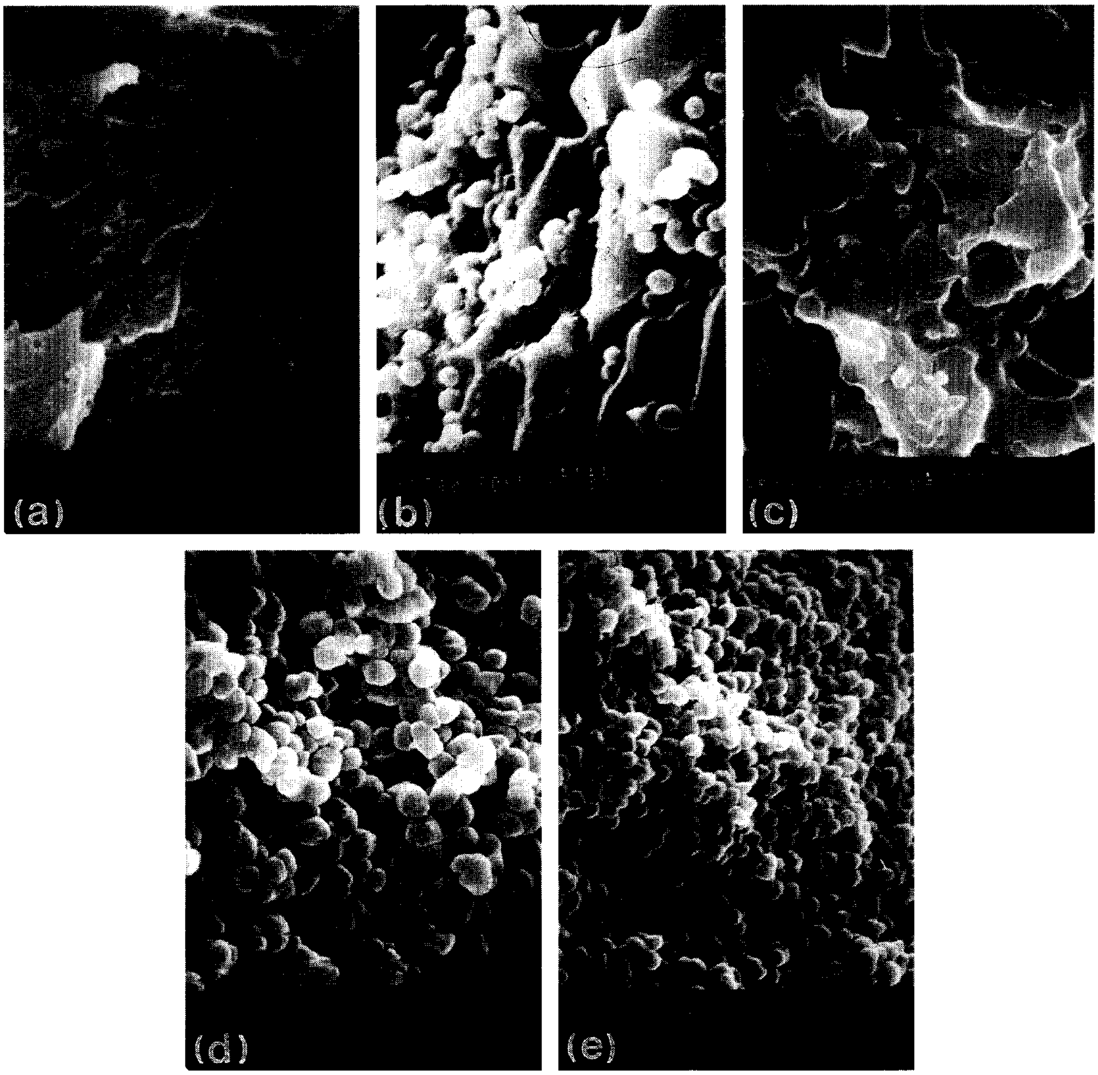

Figure 5 Scanning electron micrographs of fractured surfaces of (a) 95/5, (b) 90/10, (c) 85/15, (d) 80/20, and (e) 70/30 DDM-cured ER/SAN blends etched with dichloromethane

cured blends exhibited a phase-inverted morphology which consists of epoxy domains wrapped in the thermoplastics continuous phase. *Figure 5* (*d* and *e*) shows the micrographs of DDM-cured ER/SAN 80/20 and 70/30 (wt) blends, respectively. It can be seen that there were only spherical particles of epoxy-rich phase (0.5–1.5 μm in diameter) on the fracture surfaces after the continuous SAN-rich matrices were etched by dichloromethane. From *Figure 5* (*d* and *e*), it can be seen that the epoxy particle size begins to decrease with increasing SAN content in the blends. The higher the SAN concentration in the blends is, the smaller the size of epoxy particles. This results is consistent with those reported in epoxy resin/PES blends system by Yamanaka and Inoue[37]. The explanation of the phenomenon could be based on the following: On the one hand, inclusion of a higher SAN content gives rise to an increase of the viscosity of the initial DGEBA/SAN mixture, which reduces the rate of phase separation and coarsening. On the other hand, the rate of crosslinking reaction is also decreased due to the higher viscosity and dilution effect of SAN, and the decrease results in an incomplete curing reaction. Both the factors lead to a smaller size of epoxy particles. Yamanaka and Inoue[37] have proposed that the phase separation in thermoplastics-modified epoxy resins occurs via the spinodal decomposition and is determined by the above competitive processes, i.e. phase separation and crosslinking reaction.

Fracture toughness. The plot of K_{IC} vs SAN content for the cured ER/SAN blends is presented in *Figure 6*. It can be seen that the fracture toughness first increases with the addition of SAN to the system, and then come to the highest value in the vicinity of 10 wt% SAN blends. The blends exhibited an improved fracture toughness by about 50%, which is comparable to those obtained in the epoxy resin systems modified with other high-performance thermoplastics such as PES and PEI[18,23,27] at the same content of thermoplastics. However, when the SAN content is more than 10 wt% there is a dramatic decrease in K_{IC}, and even the K_{IC} value of the blend containing 20 wt% SAN is lower than that of the control epoxy resin. It is noticed that the relatively brittle SAN in comparison with other high performance polymers, can substantially improve toughness in a certain concentration range, and the morphology of the modified epoxy resins could play a very important role in toughening of resins. As stated above, the cured epoxy

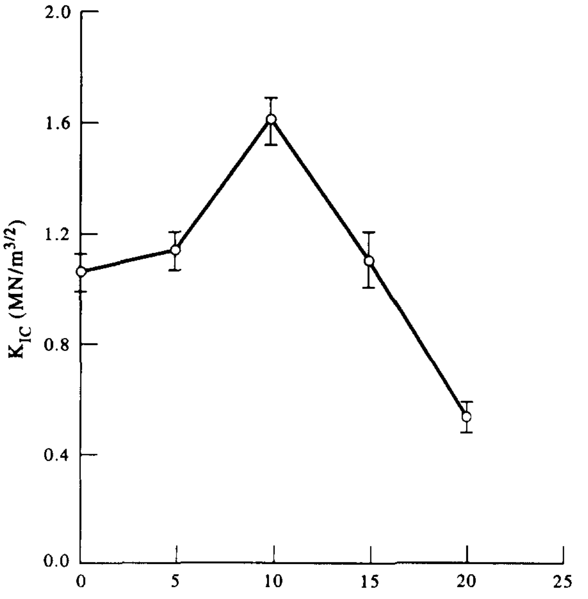

Figure 6 Fracture toughness K_{IC} as a function of SAN content for the DDM-cured ER/SAN blends

blends with 10 wt% SAN contents exhibit a combined morphology, and it is this phase structure that seems to yield a better fracture toughness. In the previous reports, the better toughness is also obtained for blends with co-continuous phase structures as reported in other high performance thermoplastic-modified systems[16,19,25]. However, the co-continuous phase structures for the blends containing 15 wt% SAN did not exhibit an improved toughness in the present system. When the SAN content exceeds 15 wt%, phase inversion of the cured blend occurred and thus the fracture properties of the phase-inverted blends seem to depend predominantly on the ductile tearing of the thermoplastics and thus give lower the values of K_{IC} since SAN polymer used in the blends system characteristically possesses lower ductility.

The SEM micrographs of the K_{IC} fracture surfaces of the control epoxy resin and the DDM-cured ER/SAN blends are shown in *Figure 7*. For the control epoxy resin, the cracks spread freely and regularly, and oriented in the direction of loading, suggesting a typical characteristics of brittle fracture (*Figure 7a*). However, the SEM micrograph of the cured blend containing 5 wt% SAN apparently displays tortuous and trivial cracks, which could be held back or delayed due to the

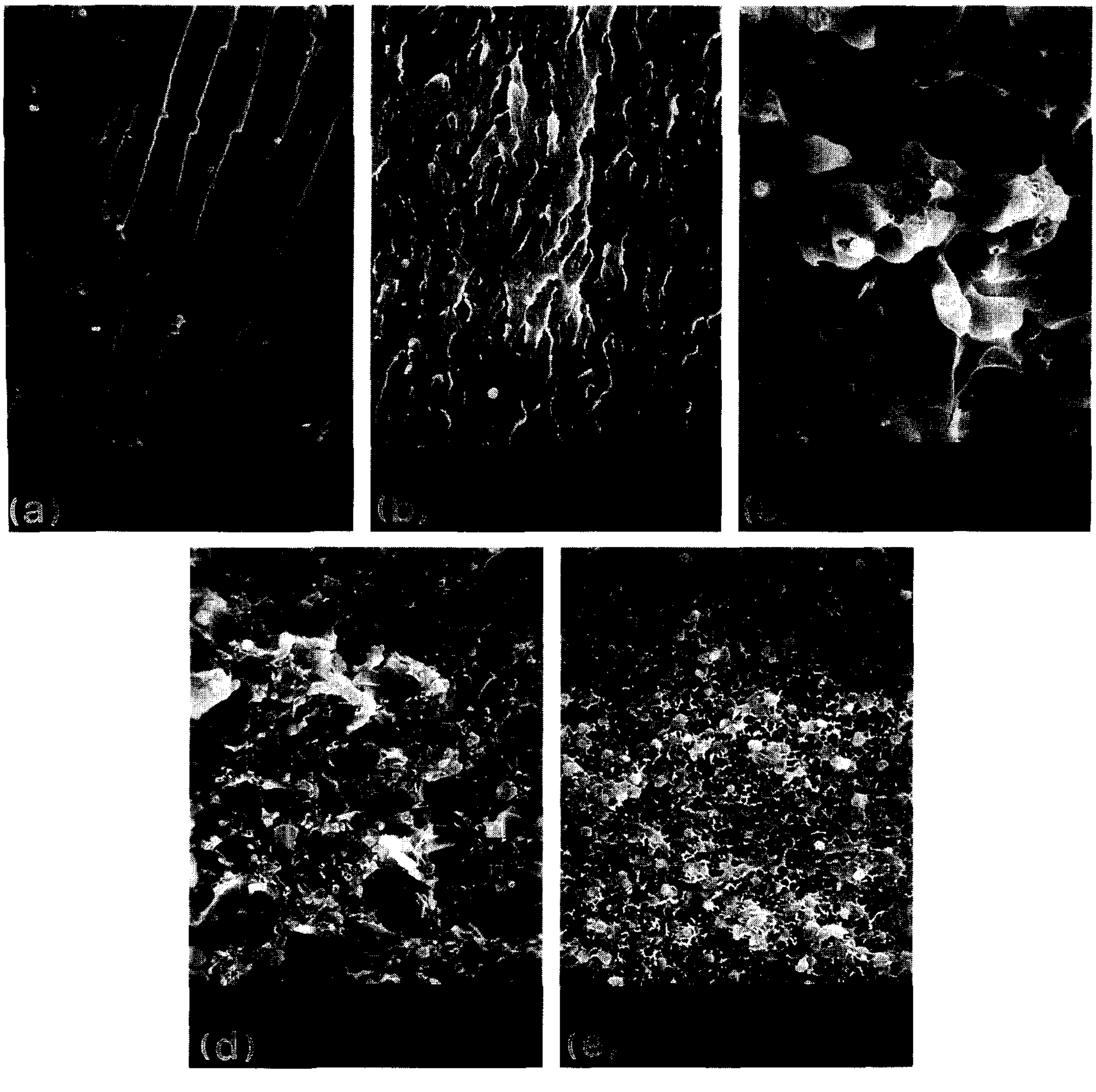

Figure 7 Scanning electron micrographs of K_{IC} fracture surfaces of (a) 100/0, (b) 95/5, (c) 90/10, (d) 85/15, and (e) 80/20 DDM-cured ER/SAN blends

existence of the second dispersed SAN phase (*Figure 7b*). In this case, the dissipation (or absorption) of relatively large part of the fracture energy may be attributed to crack bifurcation and crack path alternation. Kim and Brown have proposed that the yielding in the continuous resin matrices was the principle mechanism of toughening when the concentration of thermoplastic is up to about 10 wt% for the less highly crosslinked epoxy resin[38]. The SEM micrographs of the K_{IC} fracture surfaces of the cured blends containing 10 and 15 wt% SAN clearly shows to some extent ductile 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 (*Figures 7c* and *d*). The plastic deformation of SAN might cause the energy absorption. However, as mentioned above, the 10 wt% SAN blends possess a combined phase structure, which gives an improved toughness, whereas the cured blends containing 15 wt% SAN which possesses a co-continuous phase structure is relatively brittle. In view of the above observations, the ductile yielding may play a lesser role in the improvement of toughness for the SAN-modified epoxy system in comparison with the modification systems using high performance polymers. It is interesting to note that the 10 wt% SAN blends possess a remarkably improved toughness, and further study is required to understand the toughening mechanism. After this, the cured blends exhibited a phase-inverted morphology which consists of epoxy domains wrapped in the thermoplastics continuous phase (*Figure 7e*). Therefore, the fracture properties of the phase-inverted blends may dominantly depend on the toughness of the thermoplastic.

CONCLUSIONS

The results presented here show that uncured epoxy resin, DGEBA, is miscible with SAN copolymer over the entire blend composition range. The miscibility between SAN and DGEBA is mainly attributed to entropy contribution. However, SAN is not miscible with the DDM-cured ER. The DDM-cured ER/SAN blends have two T_g's, which remain almost invariant with composition and are close to those of the pure components. SEM studies revealed that all the DDM-cured ER/SAN blends have a two-phase structure. In the blend with low SAN content (5 wt%), SAN domains were spherically dispersed in the continuous epoxy matrix and possess uniform size smaller than 1.0 μm in diameter. The cured blend containing 10 wt% SAN shows a kind of combined phase structure, whereas the 15 wt% SAN blends exhibited a typical co-continuous phase structure. After this, the blends possess the phase-inverted structure, i.e. epoxy particles were wrapped in the continuous SAN matrix. The fracture toughness of DDM-cured blends increases with SAN content and comes to a maximum at 10 wt% SAN content, followed by a dramatic deceases of K_{IC} for the cured blends containing 15 wt% SAN or more. Morphological investigation of the K_{IC} fracture surfaces indicates that the toughening effect of the SAN-modified epoxy resin greatly depends 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 blends with both the co-continuous and the phase-inverted structures possess a lower toughness.

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