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ORIGINAL CONTRIBUTION

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Miscibility, morphology and fracture toughness of epoxy resin/poly(vinyl acetate) blends

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Abstract Diglycidylether of bisphenol A (DGEBA)/poly(vinyl acetate) (PVAc) blends cured with 4,4′-diaminodiphenylmethane (DDM) were prepared. The miscibility and phase behavior were investigated by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). The study results indicate that the epoxy precursor (DGEBA)/PVAc blends are clearly miscible at the entire composition and the Tg values experimentally obtained are in a good agreement with those predicted by Fox equation. Cured at elevated temperature, all the DDM-cured blends underwent phase separation and display two-phase morphology. When PVAc content is more than 10 wt%, the thermoplastics-modified resins began to show a co-continuous phase structure. It is the co-continuous structure that leads to a significantly-improved toughness in K_{IC}. Morphologic investigation of the surfaces of fracture mechanic measurement specimens indicates that the toughening effect of the thermoplastics-modified epoxy resins may arise mainly from the ductile yielding of PVAc.

Key words Epoxy resin – poly(vinyl acetate) – polymer blends – phase separation – morphology – toughness

Introduction

Epoxy resins are a major class of thermosetting polymers, which have extensively been used as the matrices for fiber-reinforced composite materials, adhesives and electronic encapsulating materials [1, 2] due to their thermal stability and chemical resistance. However, not all the properties of the materials are beneficial, and the deficiency in properties is inherent brittleness, i.e., low toughness and crack resistance due to their highly crosslinking densities and the existence of larger internal stress which is mainly caused by volume shrinkage during resin curing [3]. Considerable attention has been paid to modification of epoxy resins. One successful routine is elastomer toughening, e.g., carboxyl-terminated butadiene-acrynoltrile (CTBN) rubber and amine-terminated butadiene-acrynoltrile (ATBN) rubber, and silicone, etc. [9–14] were used to enhance toughness of epoxy resins. As a dispersed phase, the elastomeric actually acts to alleviate crack propagation and improve the toughness of epoxy resins. In these systems, the toughening has been considered mainly to arise from shear-deformation in the matrices [10, 16, 17]. On the other hand, the elastomer can disperse the internal stress of cured systems.

More recently, much effort has been made to modify epoxy resin with high-performance engineering thermoplastics [15–31], especially to improve toughness of highly crosslinked resins, e.g., tetrafunctional epoxy resins. Various types of thermoplastics, such as poly(ether sulfone) (PES) [16, 20, 23–25], poly(ether imide) (PEI)

[17, 22, 23, 28], poly(ether ether ketone) (PEEK) etc. [29–31], have been explored to modify epoxy resins. Some studies indicate that the modifications necessitate a fine phase-separated structure and good interfacial adhesion between the two separated phases. A thermoplastic-dispersed phase structure or a co-continuous phase structure in thermoplastic-modified epoxy resins usually yields better fracture toughness. The enhanced toughness of the system has been suggested to arise from crack pinning and the rupture of the dispersed thermoplastics [16, 32].

In this paper, we present the results of our investigation on the miscibility, morphology and fracture behavior in blends of bisphenol-A-type epoxy resin (ER) and poly(vinyl acetate) (PVAc). PVAc is an important polymer which is predominantly used in the manufacture of vinylon. It is interesting to notice that PVAc has a glass transition temperature (*Tg*) (c.a. 40 °C) just in the neighborhood of room temperature, below which it is a typical thermoplastic and possesses higher modulus of glass state. On the other hand, PVAc is a well-known low-profile polymer additive used to resist the volume shrinkage of thermosets, such as unsaturated resins, during curing process, since the non-uniform shrinkage results in internal stress [3]. Herein we choose PVAc as a modifier of epoxy resin, with an attempt to correlate the miscibility, morphology and fracture behavior of the blends.

Experimental

Materials and preparation of samples

Uncured epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), with epoxide equivalent weight 185 ~ 210, was obtained from Shanghai Resins Factory, Shanghai, China. Poly(vinyl acetate) (PVAc) was supplied by Anhui Vinylon Factory, Chaohu, Anhui, China. It has an intrinsic viscocity $[\eta]$ of 0.93 dL/g in the solution of acetone at 25 °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 PVAc are 2.14×10^{-3} mL/g and 0.68, respectively [33]. The viscosity-average molecular weight was calculated to be 6.66×10^6. The curing agent is 4,4′-diaminodiphenylmethane (DDM), it was chemically pure grade and was purchased from Shanghai Reagent Co., Inc., Shanghai, China.

All the uncured DGEBA/PVAc 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 2 weeks.

To prepare cured epoxy resin/PVAc blends, PVAc was dissolved in the smallest possible acetone, and then DGEBA was mixed with the solution at ambient temperature. The mixture was heated up to 120 °C with continuous stirring to evaporate most of the solvent, and was further degassed under vacuum at 150 °C for 1 h to remove residual solvent. The curing agent DDM was added to the system at 100 °C with continuous stirring until a homogeneous ternary mixture was obtained. The ternary mixture was cured in a mold of Teflon 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 (DSC)

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 DSC cell was kept in the 8 to 12 mg range. The midpoint of the slope change of the heat capacity plot of the second scan was taken as glass transition temperature (*Tg*). A heating rate of 20 °C/min was used.

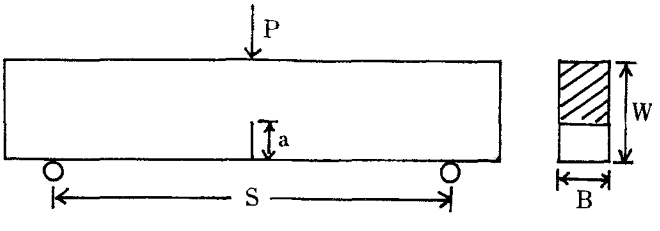
Dynamic mechanical analysis (DMA)

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

Fracture toughness measurements

Fracture toughness was measured by the notched three-point bending test with a crosshead speed of 1.3 mm/s according to ASTM E399. The schematic diagram of three-point bending specimens is shown in Fig. 1. The thickness of the specimens was about 10 mm. The critical stress intensity factors were calculated using the following

Fig. 1 Three-point bending specimen for measuring fracture toughness



Colloid & Polymer Science, Vol. 274, No. 5 (1996)

equation:

$$K_{IC} = PcS/BW^{3/2}f(A/W), \quad (2)$$

where Pc 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 crack length (Fig. 1).

Central Vee-notches were machined into the bars, and extended by pressing a fresh razor blade into the tip of the notches 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 PVAc 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 (SEM) was used for observation, before which the surfaces were coated with thin layers of gold of 200 Å.

Results and discussion

Miscibility of DGEBA/PVAc blends

All the DGEBA/PVAc blends were transparent and no phase separation occurred by heating up to about 300 °C, suggesting that the DGEBA/PVAc blends are homogeneous and have a single amorphous phase. DSC studies showed that each blend has a single composition-dependent Tg, which is indicative of single-phase nature. Thus, PVAc is miscible with DGEBA over the entire composition range.

Figure 2 summarizes the Tg values obtained with DSC as a function of blend composition. It can be seen that the data experimentally obtained are in a quite good agreement with those predicted by Fox equation [34]

$$1/Tg = W_1/Tg_1 + W_2/Tg_2, \quad (3)$$

where Tg is the glass transition temperature of the blends, and Tg_1 and Tg_2 are those of components 1 and 2, respectively; W is the weight fraction.

DGEBA/PVAc blends cured with DDM

Differential scanning calorimetry

All the cured DGEBA/PVAc blends were opaque below the degradation temperatures of the blends, suggesting the occurrence of phase separation. The cured blends were subjected to DSC measurement. All the DSC thermogams of the cured blends can give two separate glass transition temperatures (Tg's) which correspond to those of cured epoxy and PVAc-rich phases, respectively, as shown in Fig. 3. With curing agent adding to DGEBA/PVAc mixture and curing at elevated temperature, the curing

Fig. 2 Dependence of glass transition temperatures of DGEBA/PVAc blends on weight percent of PVAc: (----) Prediction of Fox equation, (●) Values experimentally obtained

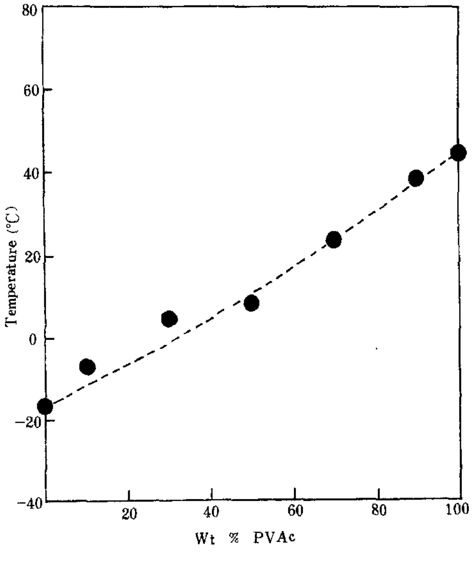
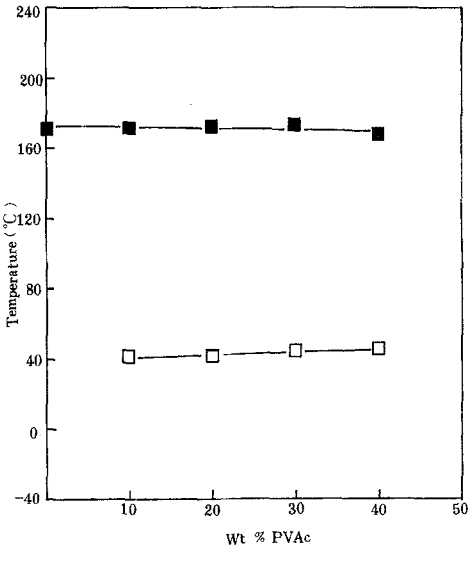


Fig. 3 Dependence of glass transition temperatures of the cured epoxy resin/PVAc blends on weight percent of PVAc: (■) Tg's of the epoxy-rich phase, (□) Tg's of PVAc-rich phase



reaction involving chain extension, branching and crosslinking takes place. As the curing reaction proceeds, the molecular weight of the system greatly increased, and the crosslinking network structure in three dimension is formed. On the another hand, the occurrence of crosslinking causes the dramatic changes of the chemical and physical natures in the system. Both the factors give rise to the occurrence of phase separation between PVAc component and the crosslinked epoxy matrix. Of course, there exists a competitive progress between the phase separation and the crosslinking reaction during the cure process.

From Fig. 3, it can be seen that *Tg* of the cured epoxy-rich phase almost remains constant although PVAc component, which has lower *Tg*, was added to system. This indicates that the phase separation between crosslinked epoxy resin and PVAc is quite complete.

Dynamic mechanical properties

Presented in Fig. 4 are the dynamic mechanical spectra ranging from 0 to 250 °C for the pure epoxy resin and DGEBA/PVAc blends cured with DDM. Figure 4a shows the dynamic mechanical spectrum of DDM-cured DGEBA, and there exist a well defined relaxation peak centered at 178 °C, which is ascribed to the major glass transition of DDM cured-epoxy resin. Figures 4b and 4c show the dynamic mechanical spectra of epoxy resin/PVAc blends cured with DDM containing 10, 20 wt% of PVAc. It was also seen that, except the glass transition of epoxy-rich phase, both the curves show a minor additional peak (~40 °C) corresponding to the glass transition of PVAc-rich phase. The dynamic mechanical behaviors further confirmed the multi-phase structure of the modified network in which the epoxy resin and PVAc are phase-separated. The results obtained from DMA are in a good agreement with that from DSC.

Morphology

The morphology of the cured blends was investigated by means of electronic scanning microscope (SEM). The SEM micrographs of solvent-etched fracture ends of the blend specimens frozen by liquid nitrogen are presented in Fig. 5. The heterogeneous morphology was observed in all cases, which supports the results of DSC and DMA. When PVAc content is below 10 wt%, the discrete PVAc particles were

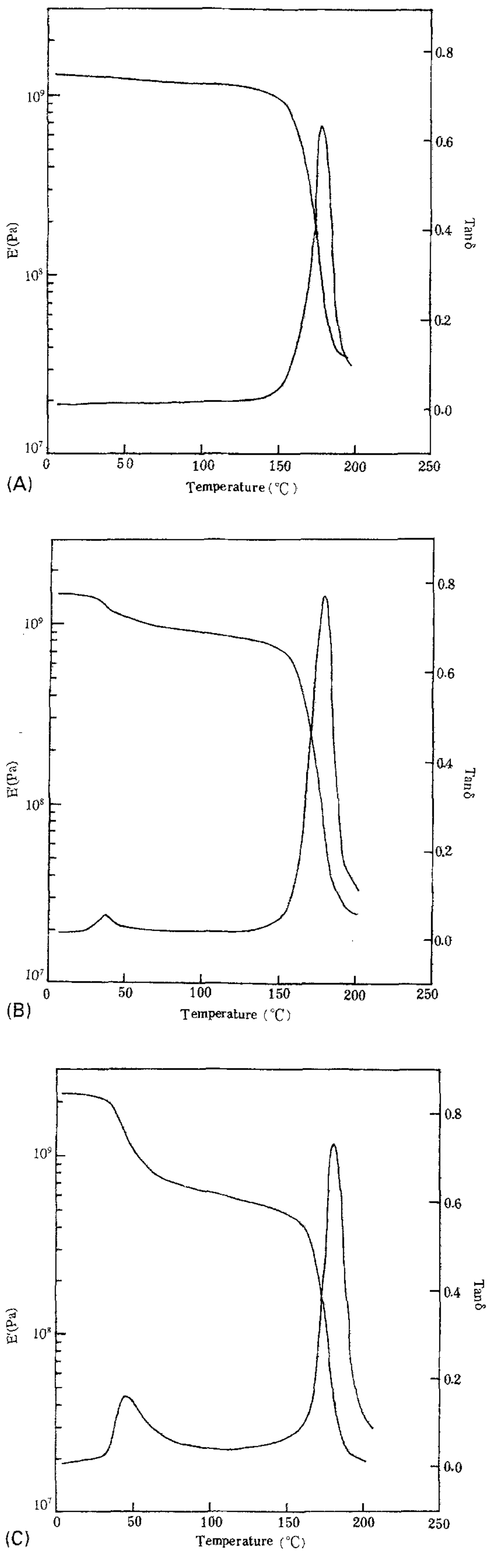


Fig. 4 Dynamic mechanical spectra of DDM-cured ER/PVAc blends: (A) DDM-cured ER, (B) ER/PVAc 90/10 (Wt) blends, (C) ER/PVAc 80/20 (Wt) blends

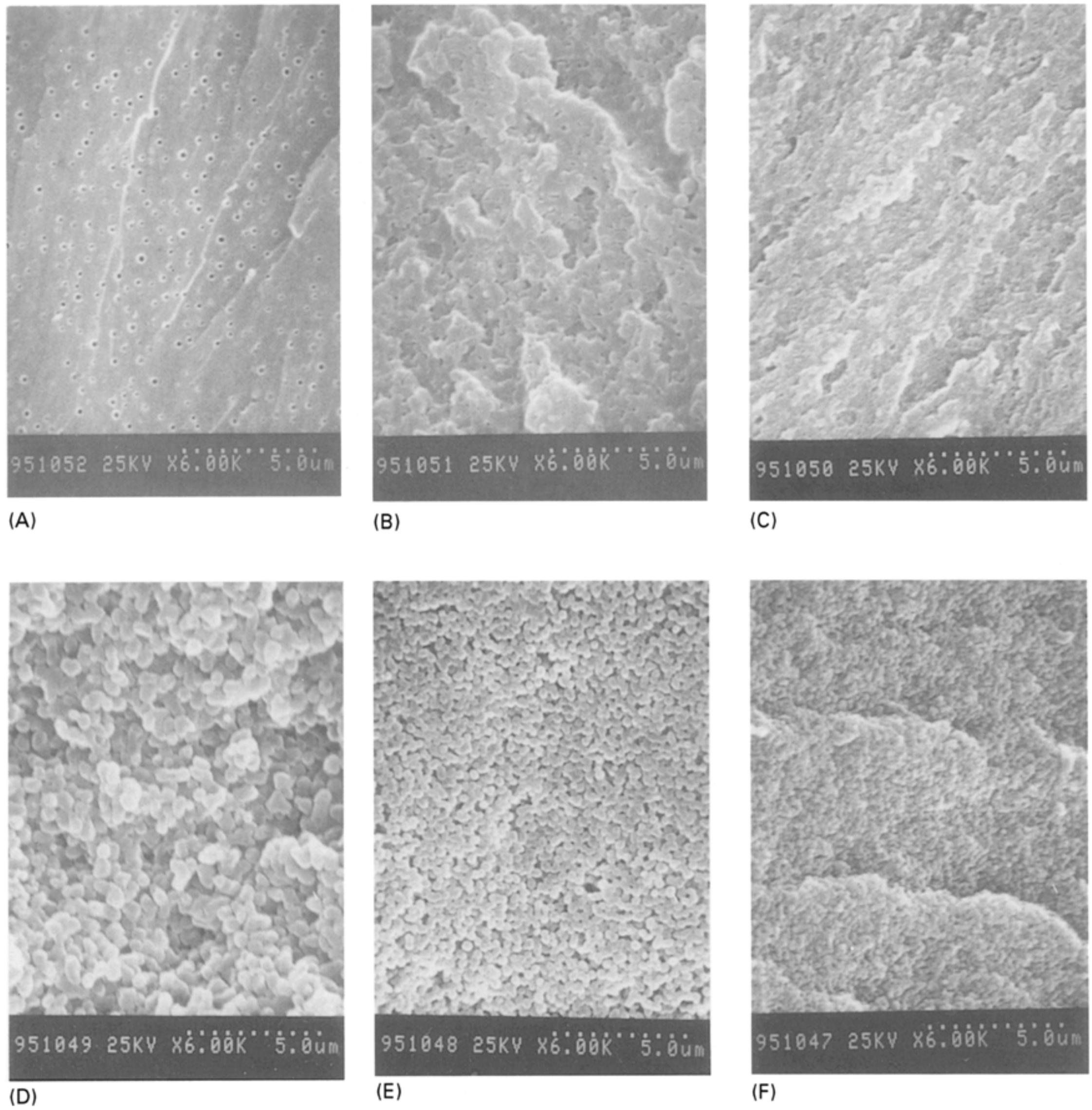


Fig. 5 SEM Micrographs for DDM-cured epoxy resin/PVAc (wt) blends: (A) 95/5 (B) 90/10, (C) 85/15, (D) 80/20, (E) 70/30, (F) 60/40. (Magnification × 6000)

uniformly dispersed in the continuous epoxy matrices and below 1 μm in diameter (Fig. 5a). With increasing PVAc content, the morphology of the modified epoxy resins changed dramatically. Inclusion of 10 wt% of PVAc gives rise to an obviously different morphology, i.e., PVAc spherical particles begin to coagulate and show PVAc vacant holes with irregular shapes and broadly-distributed size after PVAc phase was rinsed by methylene dichloride. This is a combined morphology in which the co-continuous phase began to appear (Fig. 5b). When PVAc content is 15 wt%, a complete co-continuous morphology have been formed (Fig. 5c). After this, the cured blends exhibited a phase-inverted morphology which consisted of epoxy domains wrapped in the thermoplastics continuous phase. Figures 5d and 5f only show the spherical particles of epoxy-rich phases (0.6–1.4 μm in diameter) since the continuous PVAc-rich matrices were etched by methylene chloride. It is noticed that the epoxy particle size decreases with increase of PVAc content in the blends as shown in Figs. 5d and 5f. The higher PVAc content gives rise to the higher viscosity of epoxy precursor/PVAc mixture, which reduces the rate of phase separation and coarsening of the system. At the same time, the rate of crosslinking reaction is also reduced due to the higher viscosity and dilution effect of PVAc. These factors lead to a smaller size of epoxy particles. Inoue et al. [37] have proposed that the phase separation in thermoplastics-modified epoxy resins occurs via the spinodal decomposition and is determined by the balance of two competitive process, i.e., phase separation and crosslinking reaction. In this case, the co-continuous structure was obtained for the cured blends containing 10 ~ 15 wt% of PVAc.

Fracture toughness

The plot of K_{IC} versus PVAc content in the cured blends is presented in Fig. 6. As observed, the fracture toughness was dramatically increased by the addition of PVAc to the system and exhibits a significant increase with increase of

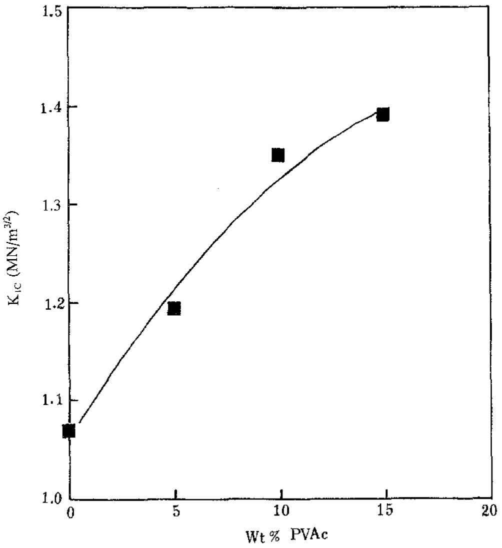
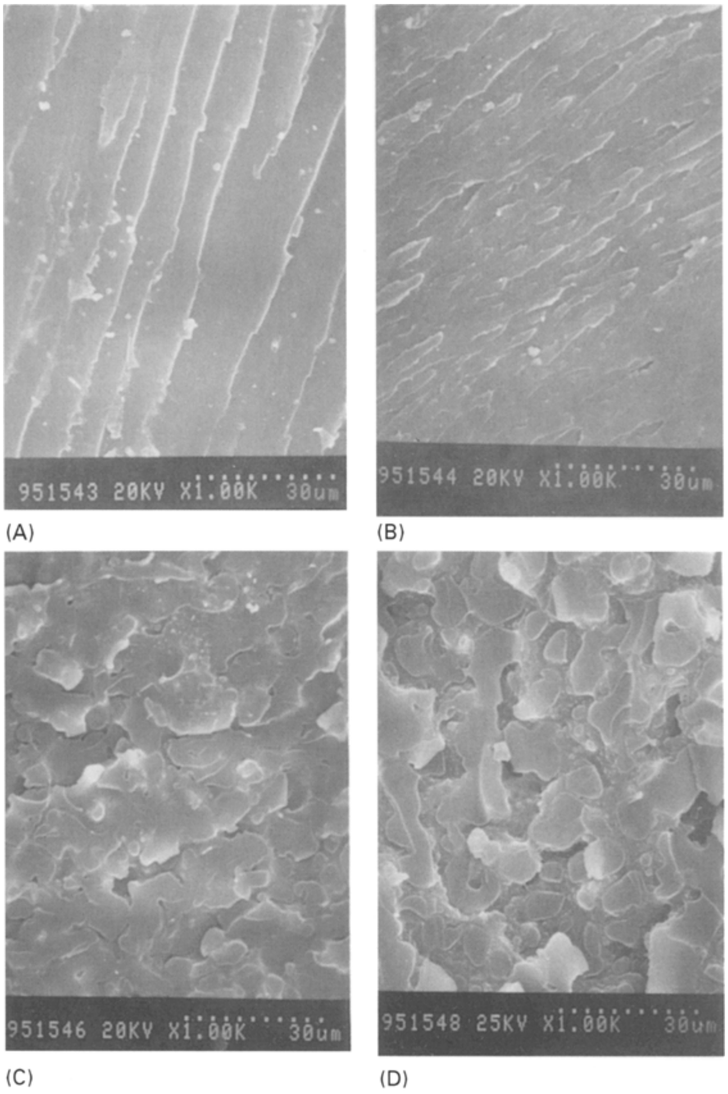


Fig. 6 Effects of PVAc content on K_{IC} of cured epoxy resin/PVAc blends

Fig. 7 SEM micrographs of the surfaces of fracture mechanics test ends for the cured epoxy resin/PVAc blends: (A) 95/5, (B) 90/10, (C) 85/15, (D) 80/20. (Magnification × 1000)



PVAc content, enhancing the fracture toughness by 50% at the PVAc content of 15 wt%. The results obtained in the present work is approximately close to those obtained in other high-performance thermoplastics (such as PES, PEI [19, 24, 28])-modified epoxy resin systems with the same amount of thermoplastics. The effect of morphology could play a significant role in the fracture toughness of thermoplastics-modified epoxy resins. It has been observed that the cured blends with the 10 ~ 15 wt% of PVAc exhibited co-continuous morphology. The co-continuous structure can yield better fracture toughness as reported in other thermoplastics-modified systems [17, 20, 26]. When the PVAc content exceeds 15% wt, the phase inversion phenomenon have occurred. Therefore the fracture properties of the phase-inverted blends seems to depend predominantly on the ductile tearing of the thermoplastics.

The SEM micrographs of the surfaces of fracture mechanics test ends can give some information about the toughening mechanism. Shown in Figs. 7a through 7d are the SEM micrographs with lower magnification of the fracture surfaces unetched. For the plain cured epoxy resins, the cracks spread freely and regularly, and oriented in the direction of loading, suggesting typical characteristics of brittle fracture (Fig. 7a). However the SEM micrograph of the modified resins containing PVAc of 5% wt apparently displays tortuous and trivial cracks, which could be held back or delayed due to the existence of the second dispersed PVAc phase (Fig. 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 alteration. Close examination of the unetched specimens containing PVAc of 10 ~ 15 wt% shows a clear evidence of ductile drawing on the fracture surfaces, which mainly occurs in the PVAc phase, since there are obvious crevices produced by the fracture process on the interfaces of the two phases are presented in Figs. 7c through 7e. It is the plastic deformation of PVAc that results in the energy absorption. As stated above, in fact the enhancement in toughness in the thermoplastic-modified epoxy resins seems to arise from a synergistic combination of several toughening mechanisms.

Conclusions

The results presented here show that the uncured epoxy precursor, DGEBA is miscible with PVAc over the entire composition. The *Tg* values experimentally obtained are in good agreement with those predicted by Fox equation. The miscibility between PVAc and DGEBA is mainly attributed to entropy contribution since DGEBA possesses lower molecular weight. Cured at elevated temperature, all the DDM-cured blends underwent phase separation and displayed two-phase morphology as revealed by DSC, DMA and SEM studies. At low concentration of PVAc (5% wt), PVAc domain was spherically dispersed in the continuous epoxy matrix and possesses uniform size of 0.4 μm in diameter. When PVAc content is more than 10, the co-continuous phase structure began to appear in the cured blends. It is the co-continuous structure that leads to the significant modification of the cured epoxy resins. With inclusion of PVAc more than 15 wt%, the cured blends exhibit an obvious phase-inverted structure. Morphologic investigation of the surfaces of fracture mechanic measurement specimens indicates that the toughening effect of the thermoplastics-modified epoxy resins may arise from the crack bifurcation including crack path alteration and the ductile yielding of PVAc, depending on the blend composition.

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