

Phase behaviour in epoxy resin containing phenolphthalein poly(ether ether sulphone)

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Phenolphthalein poly(ether ether sulphone) (PES-C) was found to be miscible with uncured bisphenol-A-type epoxy resin, i.e. diglycidyl ether of bisphenol A (DGEBA), as shown by the existence of a single glass transition temperature within the whole composition range. Miscibility between PES-C and DGEBA is considered to be due mainly to the entropy contribution. However, dynamic mechanical analysis (d.m.a.) and scanning electron microscopy (SEM) studies revealed that PES-C exhibits different miscibility with four cured epoxy resins (ER). The overall compatibility and the resulting morphology of the cured blends are dependent on the choice of cure agent. For the blends cured with amines (4,4'-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulphone (DDS)), no phase separation occurs as indicated by either d.m.a. or SEM. However, for the blends cured with anhydrides (maleic anhydride (MA) and phthalic anhydride (PA)), both d.m.a. and SEM clearly show evidence of phase separation. SEM study shows that the two phases interact well in the MA-cured blend while the interface between the phases in the PA-cured blend is poorly bonded. The differences in the overall compatibility and the resulting morphology between the amine-cured and anhydride-cured systems have been discussed from the points of view of both thermodynamics and kinetics.

(Keywords: phenolphthalein poly(ether ether sulphone); epoxy resin; phase behaviour; polymer blend; polymer miscibility; polymer morphology)

INTRODUCTION

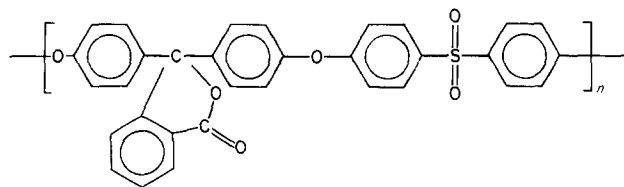
Epoxy resins are a major class of thermosetting polymers, which are widely employed as matrices for composite materials and as structural adhesives¹⁻⁴. They are amorphous, highly crosslinked polymers, and this structure results in these materials possessing a high modulus and fracture strength, low creep and good performance at elevated temperatures. However, it also leads to low toughness and poor crack resistance. One of the most successful methods of increasing their toughness is to incorporate a second phase of dispersed rubbery particles into the crosslinked polymer⁵⁻¹¹. The addition of rubbery materials to epoxy resins has been shown to enhance their fracture toughness while lowering their glass transition temperatures (T_g) and thermal and oxidative stability. Recently, high-performance thermoplastics have also been used to toughen epoxy resins¹²⁻¹⁸. Owing to the high modulus and high T_g of these thermoplastics, the modulus and T_g of the modified epoxy resin can reach or even surpass those of the pure epoxy resin.

However, only a few systematic studies have been done on the overall compatibility and phase behaviour in blends of thermoset resins with elastomers or thermoplastics^{13,19-24}. Since the resulting morphology and extent of phase separation are known to affect the optical and mechanical properties of the cured blends, the need to understand the phase separation processes taking part in thermosetting blends is of great importance.

In the previous work^{23,25}, we have studied the

morphology and phase behaviour of cured epoxy-resin-containing phenolphthalein poly(ether ether ketone) (PEK-C), a novel amorphous high-performance thermoplastic developed in this laboratory²⁶. Since PEK-C proved to be miscible with poly(hydroxy ether of bisphenol A) (phenoxy)^{23,25} and phenoxy may be considered to be a model epoxy resin^{27,28}, PEK-C should be miscible with uncured bisphenol-A-type epoxy resin, i.e. diglycidyl ether of bisphenol A (DGEBA). Indeed, this has been shown, as expected²³. However, our study has revealed that the cured epoxy resin/PEK-C blends are all incompatible and have a two-phase structure^{23,24}.

In this paper, we further report the results of work on the bisphenol-A-type epoxy resin (ER) blends containing phenolphthalein poly(ether ether sulphone) (PES-C), another novel amorphous high-performance thermoplastic also developed in this laboratory²⁹. The repeat unit of PES-C is as follows:



Four cure agents are used in this study. Our attention is particularly paid to the effect of crosslinking and the choice of cure agent on the overall compatibility and the resulting morphology of the cured blends.

EXPERIMENTAL

Materials

The PES-C resin was supplied by Xuzhou Chemical Factory, Xuzhou, Jiangsu, China. It has a reduced viscosity of 0.68 dl g^{-1} when measured in 0.5 wt% chloroform at 25°C . The diglycidyl ether of bisphenol A (DGEBA), E-51, with epoxy equivalent 185–210, was supplied by Wuxi Resin Works, Wuxi, Jiangsu, China. The hardeners used were 4,4'-diaminodiphenylmethane (DDM) (purity >98%), 4,4'-diaminodiphenylsulphone (DDS) (purity >98%), maleic anhydride (MA) (purity >98%) and phthalic anhydride (PA) (purity >98%). The solvents used were AR-grade chloroform and tetrahydrofuran (THF).

Preparation of samples

Blends of PES-C with DGEBA were prepared by solution casting from chloroform. Solvent was allowed to evaporate slowly at room temperature. To remove the residual solvent, the blends were then dried in a vacuum oven at 50°C for two weeks.

The ER/PES-C blends were prepared by mixing preweighed PES-C, DGEBA and hardener in the smallest possible amount of THF. The solution was cast onto an aluminium plate to form film specimens. The residual solvent was removed under vacuum at room temperature. The blend films thus obtained were then cured successively at 150°C for 8 h, 200°C for 4 h and 250°C for 4 h.

Differential scanning calorimetry

The glass transition temperature (T_g) of the PES-C/DGEBA blends was determined with a Perkin-Elmer DSC-2C differential scanning calorimeter at a heating rate $20^\circ\text{C min}^{-1}$. The midpoint of the slope change of the heat capacity plot of the second scan was taken as T_g .

Dynamic mechanical measurements

Dynamic mechanical measurements were carried out on a Rheovibron model DDV II dynamic viscoelastometer (Toyo Baldwin Co., Japan). The frequency used was 3.5 Hz and heating rate $3.0^\circ\text{C min}^{-1}$. Sample dimensions were $4.0 \times 0.4 \times 0.04 \text{ cm}^3$.

Morphological observations

The specimens were fractured under cryogenic conditions using liquid nitrogen. The fractured surface was then immersed in chloroform at room temperature for 15 h. The PES-C phase and/or the sol fraction of the epoxy network were preferentially etched by the solvent while the crosslinked ER phase remained relatively little affected. The etched samples were dried to remove the solvent. A JEOL JXA-840 scanning electron microscope (SEM) was used for observation, before which the surfaces were coated with a thin layer of platinum of about 200 Å.

RESULTS

PES-C has been found to be miscible with poly(*N*-vinyl-2-pyrrolidone)³⁰. All the PES-C/DGEBA 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, PES-C is miscible with

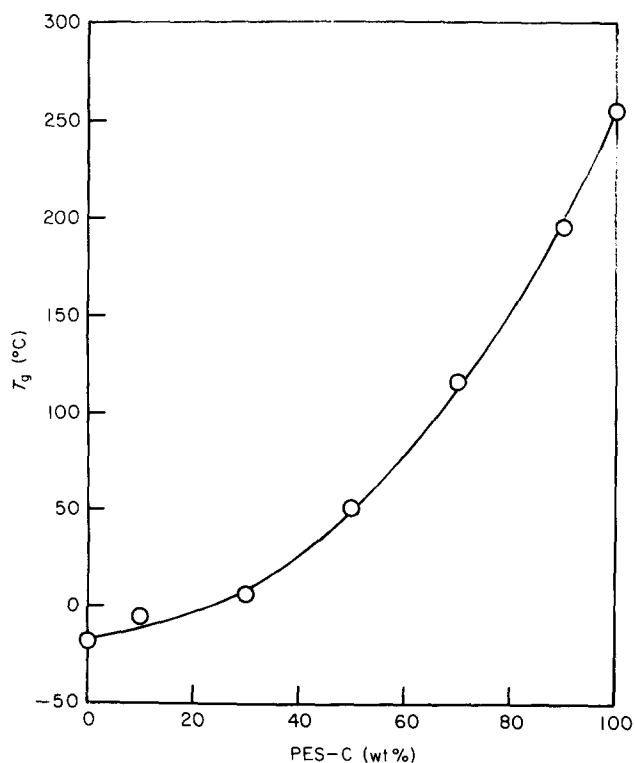


Figure 1 Composition dependence of glass transition temperature of DGEBA/PES-C blends. The curve is as predicted by the Gordon-Taylor equation using a k value of 0.31

DGEBA over the entire composition range. Figure 1 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 equation³¹, is written as:

$$T_g = (W_1 T_{g1} + k W_2 T_{g2}) / (W_1 + k W_2) \quad (1)$$

where T_g is the glass transition temperature of the blend, whereas T_{g1} and T_{g2} are the glass transition temperatures of components 1 and 2, respectively, W is the weight fraction and k is a constant. The curve in Figure 1 is drawn using the Gordon-Taylor equation with a k value of 0.31, fitting the experimental data well.

Prud'homme *et al.* have suggested^{32,33} 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 poly(ethylene), poly(vinyl chloride) (PVC) and chlorinated PVC, k increases from 0.26 to 1.0. When such an approach is used for the DGEBA/PES-C blends, we note that the k value (0.31) is smaller, suggesting that the interaction between DGEBA and PES-C is relatively weak. The miscibility of the DGEBA/PES-C blends can be considered to be due mainly to the non-negligible entropy contribution, as the molecular weight of DGEBA is rather low.

The dynamic mechanical spectrum of PES-C is shown in Figure 2. There exists a well defined relaxation peak at 262°C on the $\tan \delta$ versus T plot, corresponding to the glass-rubber transition of PES-C.

All the cured ER samples were transparent. Figure 3 shows their dynamic mechanical spectra. The figure clearly displays a maximum on all the $\tan \delta$ versus T curves, which correspond to the T_g values of the ER cured

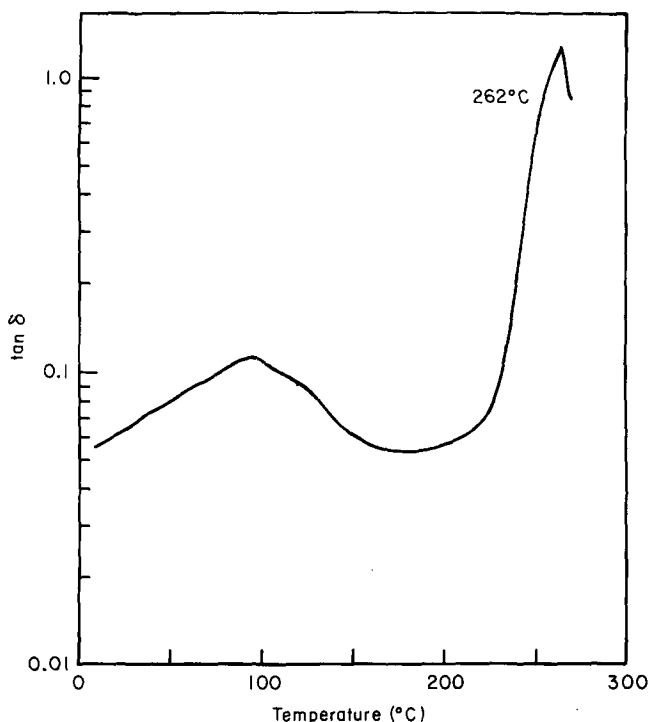


Figure 2 Dynamic mechanical spectrum of PES-C

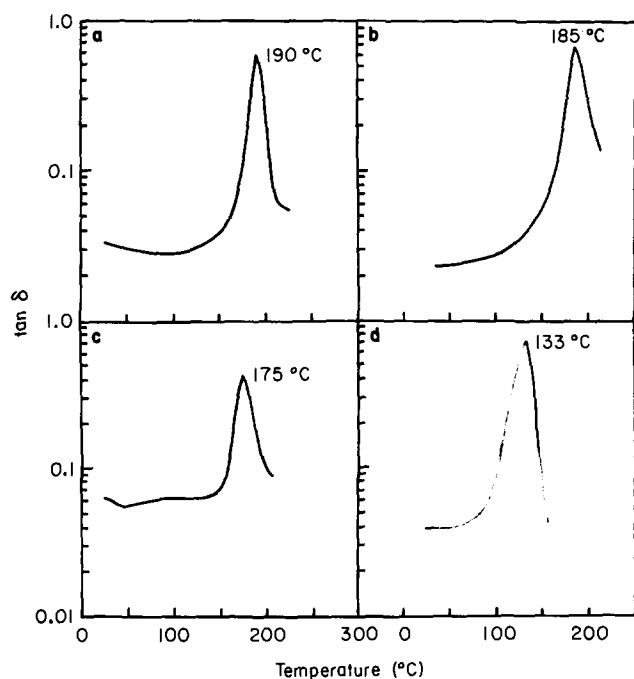


Figure 3 Dynamic mechanical spectra of: (a) 100 DGEBA, 25 DDM; (b) 100 DGEBA, 30 DDS; (c) 100 DGEBA, 50 MA; and (d) 100 DGEBA, 75 PA

with 25 phr DDM (190°C), 30 phr DDS (185°C), 50 phr MA (175°C) and 75 phr PA (133°C), respectively. It is noted that the T_g value obtained for the DDS-cured ER is considerably lower than that documented in the literature (200–220°C)³⁴. This is due to the approximate stoichiometric ratios used in this work.

The cured blend containing 100 DGEBA, 25 DDM and 25 PES-C was transparent. Figure 4 shows its dynamic mechanical spectrum. Only a glass transition peak (169°C) is observed on the $\tan \delta$ versus T curve, suggesting that no phase separation has occurred in the blend. It is also noted that the T_g of the cured blend

(169°C) is rather lower than that of the neat system (190°C). This implies that the cure reaction is not complete. The SEM micrograph of the fractured surface of the DDM-cured ER/PES-C blend (Figure 5a) appears to show no evidence that the blend is heterogeneous. Figure 5b shows an SEM micrograph of the specimen etched by chloroform. It is interesting to notice that the SEM micrograph of the etched specimen displays some loops but the domains within the loops show the same characteristic as the continuous matrix. So the appearance of loops in the micrograph of the etched specimen is not proof of a two-phase system. Since the reaction is not complete and epoxy-amine molecules are still soluble at the end of the reaction, the etching removes the sol fraction of the epoxy network and causes the appearance of the loops. It can be concluded that the cured blend is homogeneous and PES-C is miscible with the DDM-cured ER.

The cured blend containing 100 DGEBA, 30 DDS and 25 PES-C was also transparent. The dynamic mechanical spectrum of the sample is shown in Figure 6, clearly displaying a maximum (173°C) on the $\tan \delta$ versus T curve, which corresponds to the T_g of the DDS-cured blend. Both the transparency and the existence of a single T_g suggest that the blend has a single-phase behaviour. It is noted that the T_g of the blend (173°C) is lower than that of the pure DDS-cured ER (185°C), implying that the reaction is not complete. The SEM micrograph of the fractured surface of the cured blend (Figure 7a) reveals that the blend is homogeneous. However, some heterogeneity seems to be shown by the SEM micrograph of the etched specimen (Figure 7b). This is because the etching removed the sol fraction of the epoxy network as the cure reaction was not complete and some epoxy-amine molecules are still soluble. All these results suggest that the DDS-cured blend is miscible and exhibits a single-phase nature.

The sample of the cured blends containing 100 DGEBA, 50 MA and 25 PES-C was clear. Figure 8 shows its dynamic mechanical spectrum. The figure clearly

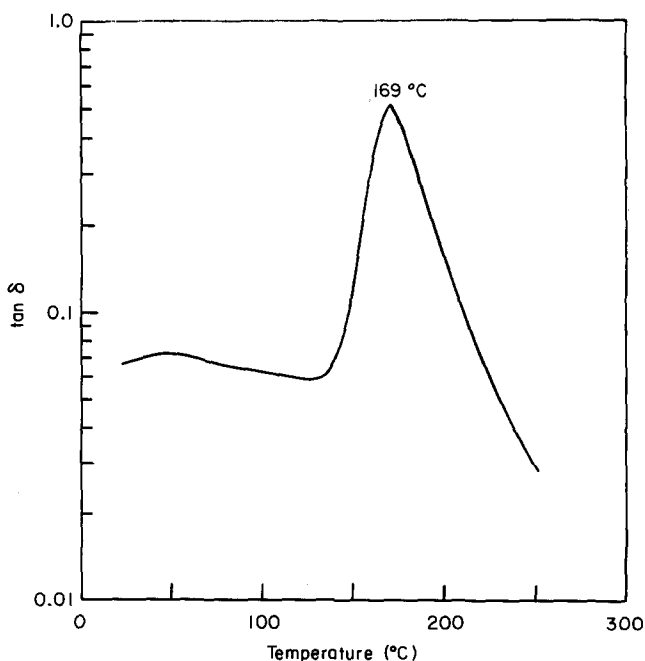


Figure 4 Dynamic mechanical spectrum of 100 DGEBA, 25 DDM, 25 PES-C

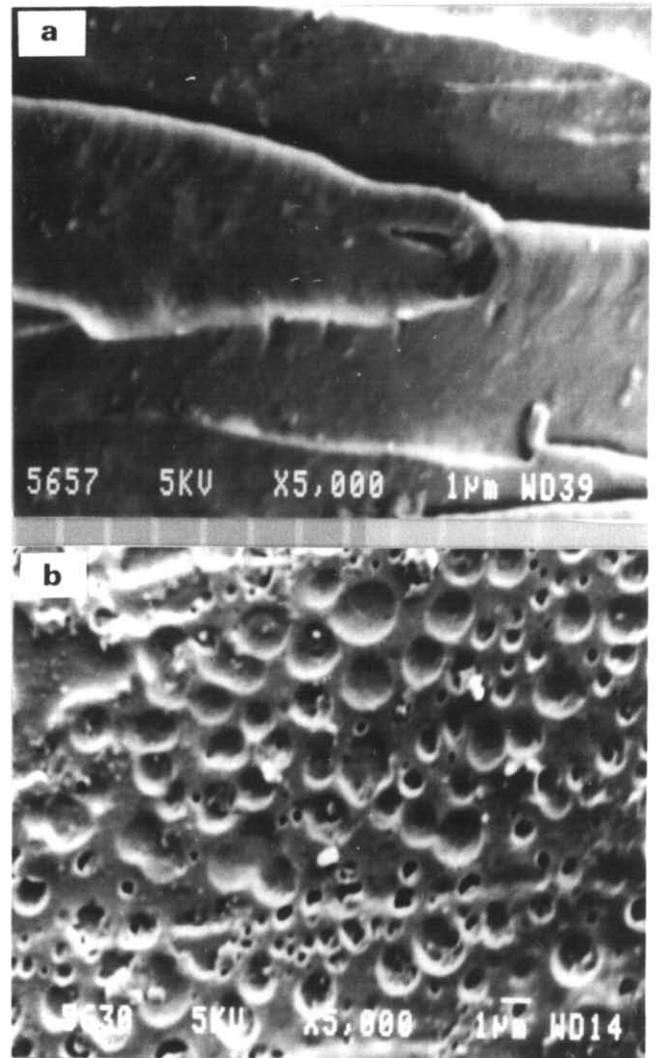
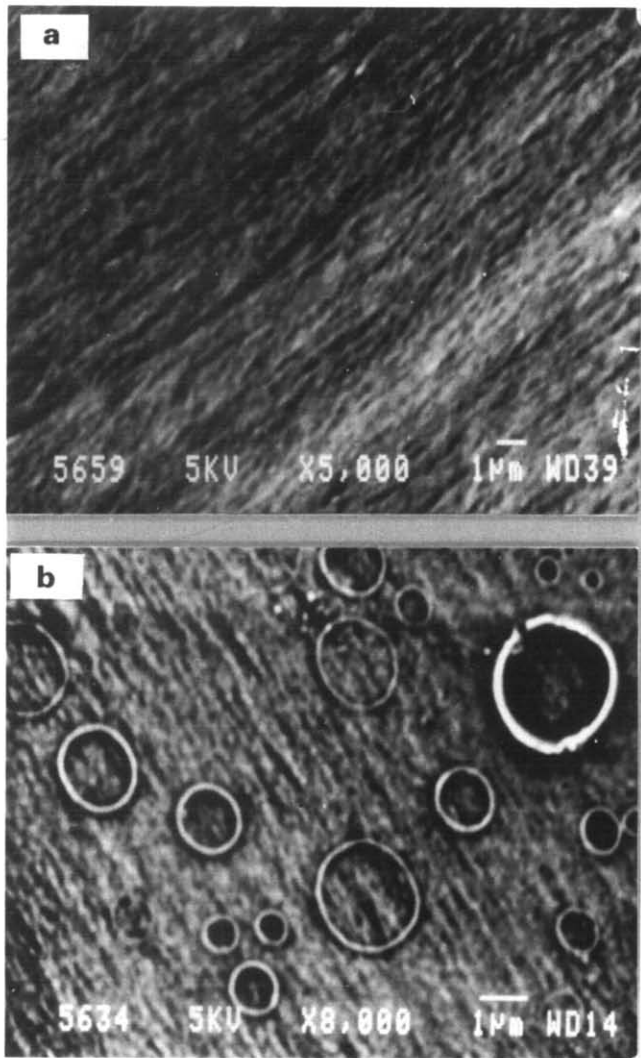


Figure 5 Fracture surface of 100 DGEBA, 25 DDM, 25 PES-C: (a) unetched; (b) etched in chloroform for 15 h

Figure 7 Fracture surface of 100 DGEBA, 30 DDS, 25 PES-C: (a) unetched; (b) etched in chloroform for 15 h

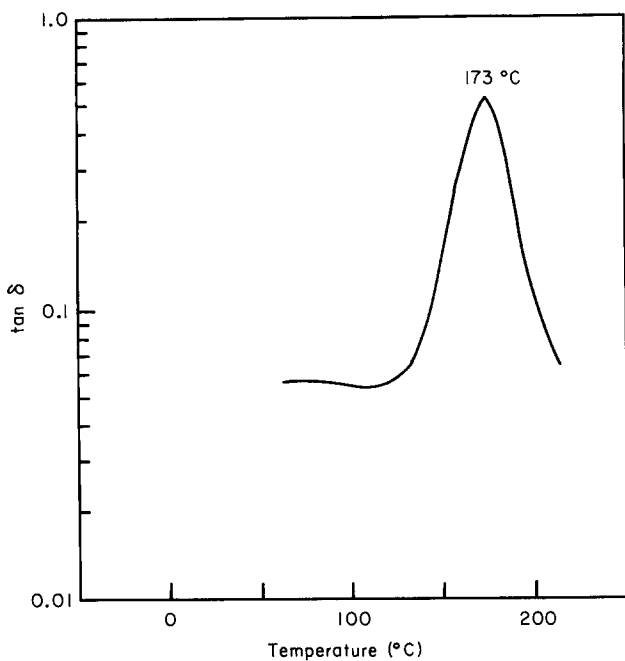


Figure 6 Dynamic mechanical spectrum of 100 DGEBA, 30 DDS, 25 PES-C

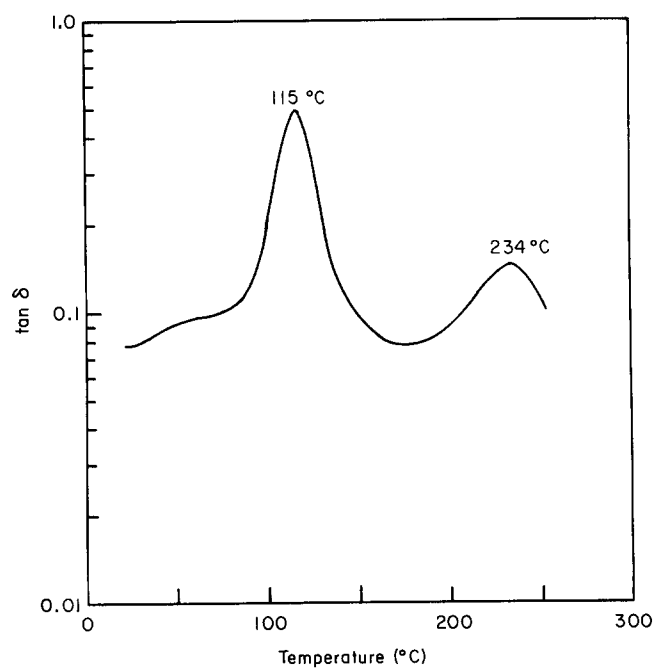


Figure 8 Dynamic mechanical spectrum of 100 DGEBA, 50 MA, 25 PES-C

displays two maxima on the $\tan \delta$ versus T curve, which respectively correspond to the T_g values of the PES-C-rich phase (234°C) and the MA-cured ER phase (115°C). It is evident that phase separation had occurred in the MA-cured ER/PES-C blend and PES-C is not completely miscible with MA-cured ER. It can also be seen from the figure that the two T_g values are lower than those of pure PES-C (262°C) and the MA-cured ER (175°C), respectively. The decrease in T_g values of PES-C in the cured blend and of the cured ER phase implies that there is some uncured and/or insufficiently cured ER dissolved in the PES-C phase. This further resulted in decreasing crosslink density of the epoxy network, and hence lowering of the T_g of the ER phase as it moved relatively away from the epoxide/amine stoichiometric ratio.

The SEM micrograph of the fractured surface of the MA-cured ER/PES-C blend (Figure 9a) seems not to show the characteristic of an inhomogeneous blend. Nevertheless, the SEM micrograph of the etched sample (Figure 9b) clearly shows a heterogeneous characteristic, which is very different from those for either the DDM-cured blend (Figure 5b) or the DDS-cured blend (Figure 7b). It reveals a two-phase structure of the blend. The cavities correspond to the domains of the PES-C-rich

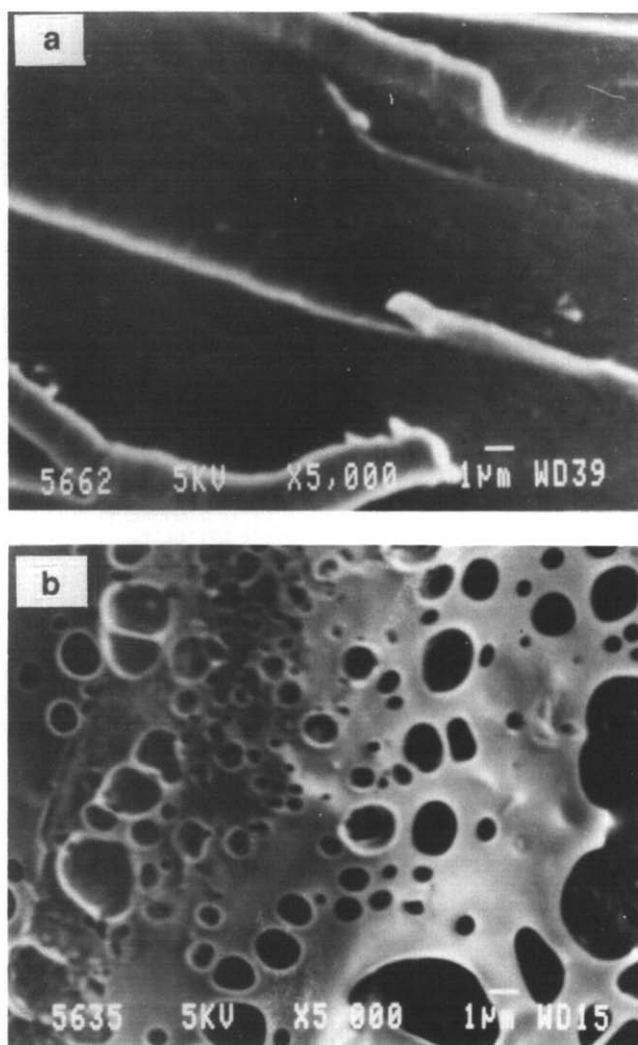


Figure 9 Fracture surface of 100 DGEBA, 50 MA, 25 PES-C: (a) unetched; (b) etched in chloroform for 15 h

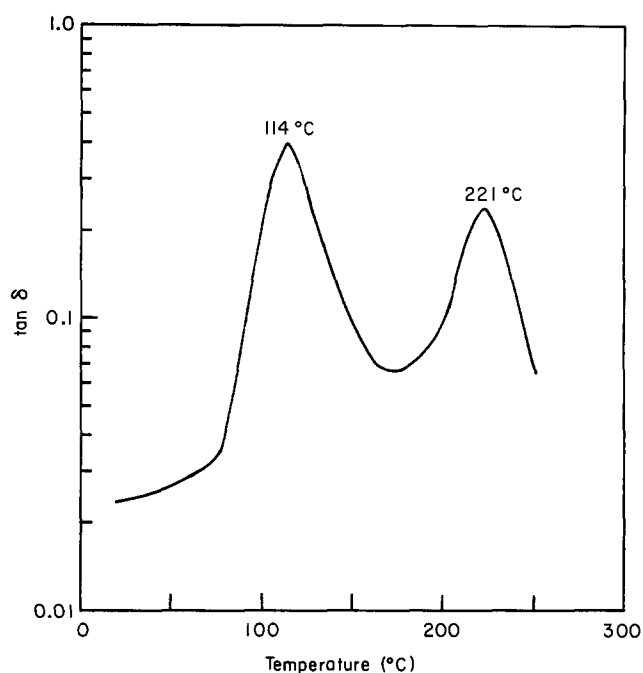


Figure 10 Dynamic mechanical spectrum of 100 DGEBA, 75 PA, 25 PES-C

phase, which had been etched by the solvent. The domain size of the PES-C-rich phase should be the same as that of the cavities, i.e. in the range 0.2–5 μm diameter. The appearance of the characteristic of a homogeneous blend for the unetched specimen (Figure 9a) shows that the two phases interact well in the blend although the PES-C is not completely miscible with the MA-cured ER.

The cured blend containing 100 DGEBA, 75 PA and 25 PES-C was opaque. D.m.a. study clearly revealed two T_g values, respectively attributed to the PES-C-rich phase (221°C) and the PA-cured ER phase (114°C) (Figure 10). It is obvious that phase separation had occurred in the cured blend. It can be seen from the figure that the two T_g values are lower than those of pure PES-C (262°C) and the PA-cured ER (144°C), respectively. The decrease in T_g values of PES-C in the cured blend and the PA-cured ER phase is a result of dissolution of uncured and/or insufficiently cured ER in the PES-C phase.

The SEM micrographs of both the unetched and the etched specimens clearly reveal a two-phase structure: domains of PES-C-rich phase are dispersed in a continuous phase of PA-cured ER (Figure 11). The size of the domains is in the range 0.2–5 μm diameter. The interfaces between PES-C and the PA-cured ER are poorly bonded and PES-C is immiscible with the PA-cured ER.

DISCUSSION

Our results presented here have shown that PES-C is miscible over the entire composition range with the uncured ER, i.e. DGEBA, owing mainly to the entropy contribution, and the PES-C/DGEBA blends do not exhibit phase separation up to about 280°C. However, PES-C exhibits different miscibility with the four cured ER. The overall compatibility and the resulting morphology of the cured blends are dependent on the choice of cure agent. The cured blends exhibit two categories of phase behaviour: (a) for the blends cured with amines

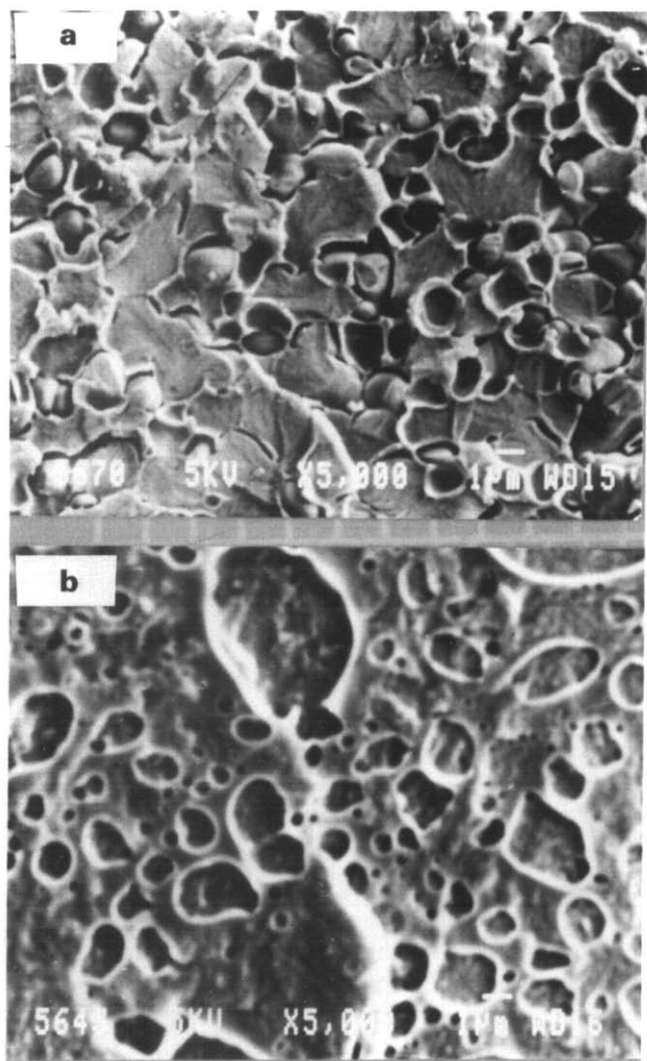


Figure 11 Fracture surface of 100 DGEBA, 75 PA, 25 PES-C: (a) unetched; (b) etched in chloroform for 15 h

(DDM and DDS), no phase separation occurs as indicated by either d.m.a. or SEM; and (b) for the blends cured with anhydrides (MA and PA), both d.m.a. and SEM clearly show evidence of phase separation, but SEM study shows that the two phases interact well in the MA-cured blend while the interface between the phases in the PA-cured blend is poorly bonded.

The formation of cured ER network-caused phase separation in the blends can be considered to be due to the dramatic change in the chemical and physical nature of ER during crosslinking^{35,36}. Phase separation is controlled by both thermodynamic and kinetic factors¹³. As the cure proceeds, the resulting increase in molecular weight will cause a decrease in the configurational entropy of mixing, so that the enthalpy term, which is usually positive, becomes increasingly more important in determining the free energy of mixing³⁷. At the same time, opening of the epoxy rings, with the formation of polar hydroxyl groups, alters the enthalpy of mixing. Difference in reaction kinetics is another factor that must also be taken into account. The choice of hardener will determine the rate of reaction at any given temperature, and hence the period during which phase separation can take place. Rates of diffusion decrease during the curing reaction, and therefore depend directly on the kinetics of cure.

It is noted that PES-C exhibits more overall compatibility with the amine-cured epoxy resins than with the anhydride-cured epoxy resins. Similarly it has been shown by other authors that poly(ϵ -caprolactone) (PCL) exhibits more overall miscibility with amine-cured epoxy resins than with anhydride-cured epoxy resins^{38,39}. Clark *et al.*³⁹ have found that PCL with average molecular weight about 20000 was partially miscible with amine-cured epoxy resins although it was largely immiscible with anhydride-cured epoxy resins reported by Noshay and Robeson³⁸. The difference in the overall compatibility and then in the final morphology between the amine-cured and anhydride-cured systems can be considered to be due to the sum of both thermodynamic and kinetic factors. As noticed by Clark *et al.*³⁹, there exists the opportunity for hydrogen bonding in amine-cured epoxy resin/PCL blends, which, from the viewpoint of thermodynamics, reduces the free energy of mixing and thus enhances the miscibility. In the present case, it is also an important factor in causing the different overall miscibility with PES-C between the amine-cured and anhydride-cured systems. The presence of hydroxyl groups in the amine-cured system offers an excellent potential for hydrogen-bonding interaction with ester groups and/or ether oxygens of PES-C in blends. Furthermore, the mechanism of epoxy-amine reaction is different from that of epoxy-anhydride reaction. The epoxy-amine reaction is a step-growth copolymerization but the epoxy-anhydride reaction is a chain-growth copolymerization. Thermodynamically this difference also plays an important role. Finally, the reaction kinetics are not the same, which considerably influences the overall compatibility and the resulting morphology.

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