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Phase behaviour and mechanical properties of epoxy resin containing phenolphthalein poly(ether ether ketone)

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Blends of bisphenol-A-type epoxy resin(ER) and phenolphthalein poly(ether ether ketone) (PEK-C) cured with 4,4′-diaminodiphenylmethane (DDM) were studied using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). The phase behaviour of the DDM-cured ER/PEK-C blends was greatly dependent on the curing condition and was affected by both the thermodynamic and kinetic factors. The homogeneous DDM-cured ER/PEK-C blends were obtained. The studies of DSC and Fourier-transform infrared (*FT*i.r.) spectroscopy indicate that there existed some unreacted oxirane rings of ER in the blends, and the curing reaction was incomplete even though the samples of the blends were further post-cured at 250°C. Mechanical measurements show that incorporation of PEK-C slightly decreased both the fracture toughness (K_{IC} and G_{IC}) and the flexural properties, presumably due to the reduced cross-link density of the epoxy network. SEM observation of the surfaces of fracture mechanical measurement specimens indicates the nature of brittle fracture for the plain ER and the blends. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: epoxy resin; phenolphthalein poly(ether ether ketone); polymer blend)

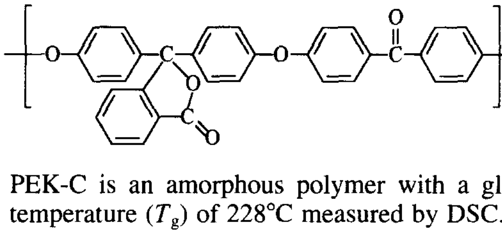
INTRODUCTION

Epoxy resins (ER) are one of the most important classes of thermosetting polymers which are widely used as matrices for fibre-reinforced composite materials and as structural adhesives[1-4]. They are amorphous, highly cross-linked polymers and this structure results in these materials possessing various desirable properties such as high tensile strength and modulus, uncomplicated processing, good thermal and chemical resistance and dimensional stability. However, it also leads to low toughness and poor crack resistance, which should be upgraded before they can be considered for many end-use applications. 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 cross-linked polymer[5-11]. Because the addition of rubbery materials to epoxy resins has been shown to lower their glass transition temperatures (T_g) and thermal and oxidative stability, high performance thermoplastics have been employed to toughen epoxy resins in recent years. 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[12-17]. A review of the developments in the area of thermoplastic-modified epoxy resins is available[18].

However, relatively few systematic studies have been paid to the overall compatibility and phase behaviour in blends of thermoset resins with elastomers or thermoplastics[13,19-28]. Since the resulting morphology and extent of phase separation is known to affect the optical and mechanical properties of the cured blends, the need for an understanding of the phase behaviour in thermosetting blends is of great practical importance.

On the other hand, it is also of academic interesting to examine the phase behaviour of such cross-linked polymer mixtures, i.e. interlocked systems containing one cross-linked and one linear component, which are usually known as semi-interpenetrating polymer networks (semi-IPNs) in the highly cross-linked cases. From the point of view of thermodynamics, an increase in the molecular weight for either of the components of miscible blend would reduce the entropy of mixing. As a result, phase separation induced by cross-linking is expected. Indeed, we have found that phase separation occurs as the cross-linking process proceeds in our earlier investigations[29-33]. However, the complex interrelationship between phase behaviour and composition has not yet been clarified and is currently the subject of a research programme in this laboratory.

Phenolphthalein poly(ether ether ketone) (PEK-C) is a recently developed highperformance engineering thermoplastic[34] with the following repeat unit:



PEK-C

PEK-C is an amorphous polymer with a glass transition temperature (T_g) of 228°C measured by DSC. Owing to its

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relatively lower price, excellent properties and high temperature stability, considerable attention has been given to the blends of PEK-C with other polymers[35–45].

In our previous works[44,45] we have studied the morphology and phase behaviour of ER/PEK-C blends cured with various curing agents. PEK-C was found to be miscible with both uncured bisphenol-A-type epoxy resin, i.e. diglycidyl ether of bisphenol A (DGEBA), and poly(hydroxyether of bisphenol A). The latter can be considered as being a model epoxy resin, i.e. it is the linear high-molecular weight polymer of DGEBA. However, it has been shown that all the cured ER/PEK-C blends studied were heterogeneous and had a two-phase structure. In this paper, we further examine the ER/PEK-C blends cured with 4,4′-diaminodiphenylmethane (DDM), but in contrast the homogeneous DDM-cured ER/PEK-C blends were obtained at a different curing condition. Particular attention is paid to the phase behaviour and mechanical properties of the resulted blends.

EXPERIMENTAL

Materials and preparation of samples

The PEK-C was supplied by Xuzhou Chemical Factory, Xuzhou, Jiangsu, China. It had a reduced viscosity of 1.10 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 hardener used was 4,4′-diaminodiphenylmethane (DDM) (purity: $> 98\%$) and was used in stoichiometric ratios of epoxide/amine.

To prepare the DDM-cured ER/PEK-C blends, PEK-C was first dissolved in DGEBA with continuous stirring at 180°C. The mixture obtained was degassed under vacuum at 150°C for 1 h 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 mould of Teflon which was highly polished. The samples were cured successively at 80°C for 2 h, 150°C for 2 h, and finally 180°C for 2 h. In order to examine whether the curing temperature is high enough, the as-prepared samples of the 88/12 DDM-cured ER/PEK-C blend were chosen to be post-cured at 250°C for further studies using DSC and *FT*i.r.

Differential scanning calorimetry (DSC)

Calorimetric measurement was performed on a Perkin Elmer DSC-7 thermal analysis apparatus in a dry nitrogen atmosphere. The instrument was calibrated with an Indium standard. All the DSC thermograms were recorded at a heating rate of 20°C min^{-1}. The midpoint of the slope change of the heat capacity plot of the second scan was taken as the glass transition temperature (T_g).

Fourier transform infrared (FT *i.r.*) *spectroscopy*

A Nicolet 750 *FT*i.r. spectrometer was used to study the curing reaction of epoxy resin. The sample together with KBr was pressed into a pellet and used for measurements. All spectra were recorded at room temperature and a minimum of 64 scans at a resolution of 4 cm^{-1} were signal averaged.

Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements were carried out on a Rheovibron Model DDV-III-EA dynamic viscoelastometer (Toyo Baldwin Co., Japan). The frequency used was 35 Hz and the heating rate was 3.0°C min^{-1}. The specimen dimension was 6.0 × 0.4 × 0.2 cm^3.

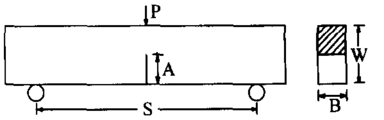


Figure 1 The schematic diagram of three-point bending specimen for measuring fracture toughness

Flexural properties

The flexural properties were measured by a three-point bending test, according to ASTM D790, on a Hongshan static fracture testing machine (Hongshan Testing Machine Factory, Tianshui, Ganshu, China). The specimens were placed on two supports with a span of 48 mm and the load was applied by means of a loading nose midway between the supports. The cross-head speed was 2.8 mm min^{-1} and a minimum of five specimens were tested to obtain the average value in all cases.

Fracture toughness

Fracture toughness was measured by the notched three-point bending test with a cross-head speed of 1.3 mm s^{-1} according to ASTM E399. The schematic diagram of three-point bending specimens is shown in *Figure 1*. Central vee-notched 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. 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.

Morphological observations

To investigate the phase morphology of the DDM-cured ER/PEK-C blends, the specimens were fractured under cryogenic conditions using liquid nitrogen. The fracture surfaces of the toughness measurement were also observed to examine the fracture characters of the cured blends. A Hitachi X-60 scanning electron microscope (SEM) was used for observation, before which the surfaces were coated with thin layers (200 Å) of gold.

RESULTS AND DISCUSSION

Phase behaviour

All the DDM-cured ER/PEK-C blends were transparent. The phase behaviour and morphology of the blends were studied by means of DSC, DMA and scanning electron microscopy (SEM). The DSC study showed that all the DDM-cured ER/PEK-C blends display only one glass transition. The T_g values obtained are presented in *Table 1*. It can be seen from *Table 1* that the T_g of the DDM-cured ER is 165°C. With addition of PEK-C, T_g first increases to 168°C for the 96/4 DDM-cured ER/PEK-C blend and exhibits a maximum of 170°C for the 94/6 DDM-cured ERFPEK-C blend. However, with a further increase of PEK-C, T_g begins to decrease, and the T_g value of the 88/12 DDM-cured ER/PEK-C blend (162°C) even falls below that of the plain DDM-cured ER. This phenomenon has been observed in our previous studies in the other ER/thermoplastic blends[44–47]. The first increase of T_g of the blends is due to the high T_g of PEK-C (228°C by DSC). The sequential decrease of T_g can be attributed to the reduced

Table 1 Glass transition temperature and mechanical properties of the DDM-cured ER/PEK-C blends

PEK-C (wt%)	T_g (°C)	Flexural (GPa)	Flexural strength (MPa)	Maximum strain (%)	K_{IC} (MN $m^{-3/2}$)	G_{IC} (kJ m^{-2})
0	165	2.29 ± 0.10	119 ± 8	6.0 ± 0.7	1.24 ± 0.03	0.56 ± 0.02
4	168	2.12 ± 0.08	103 ± 9	5.9 ± 0.5	1.14 ± 0.05	0.52 ± 0.03
6	170	2.12 ± 0.05	99 ± 8	5.6 ± 0.9	1.12 ± 0.06	0.50 ± 0.04
8	168	2.13 ± 0.03	100 ± 3	5.4 ± 0.2	1.15 ± 0.04	0.52 ± 0.03
12	162	2.22 ± 0.14	96 ± 5	5.0 ± 0.3	1.14 ± 0.04	0.49 ± 0.02

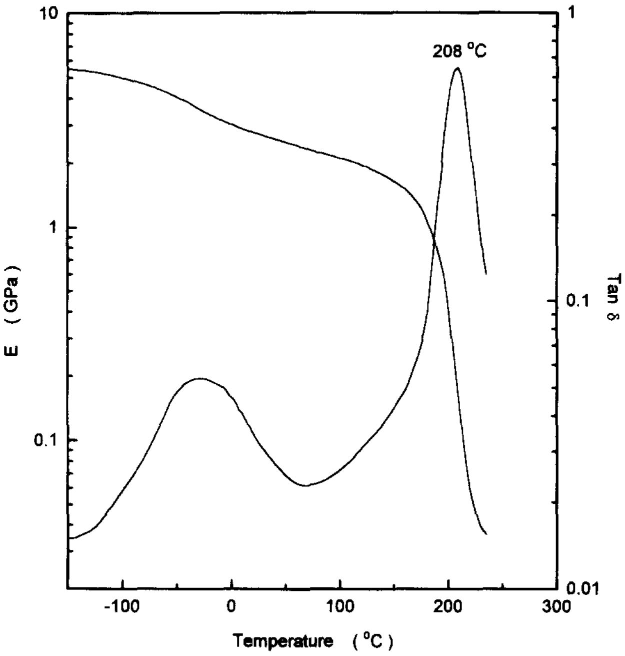


Figure 2 Dynamic mechanical spectrum of the 88/12 DDM-cured ER/PEK-C blend

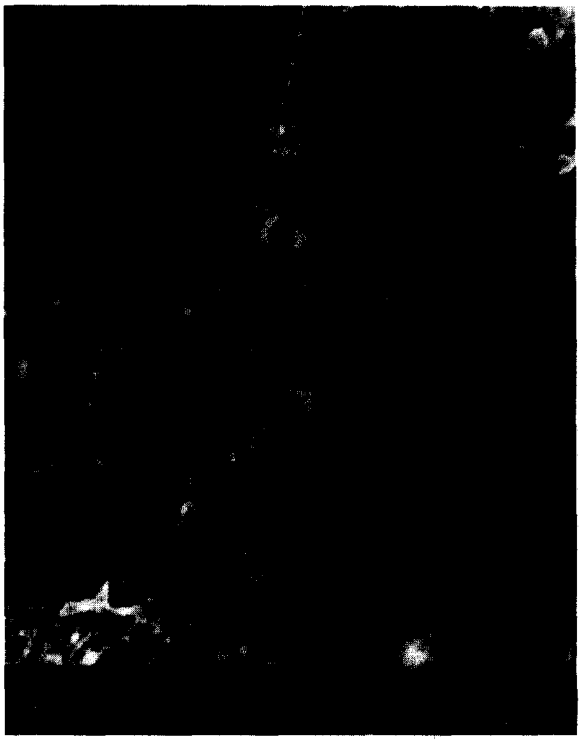


Figure 3 SEM micrograph of the fracture surface of the 88/12 DDM-cured ER/PEK-C blend frozen by liquid nitrogen

cross-linking density of the epoxy network because the curing of epoxy resin in the blends was incomplete as will be seen below. Both the transparency and the existence of a single T_g suggest all the blends exhibited a homogeneous phase behaviour.

The dynamic mechanical spectrum of the 88/12 DDM-cured ER/PEK-C blend is presented in *Figure 2*, clearly displaying a maximum at 208°C on the tanδ *versus T* curve, which corresponds to the T_g of the cured blend. This result further shows that no phase separation occurred in the blend during the curing process. The SEM micrograph of the fractured surface of the blend fractured under cryogenic conditions using liquid nitrogen (*Figure 3*) appears to show no evidence that the blend is heterogeneous.

From the above results, it is reasonable to conclude that all the DDM-cured ER/PEK-C blends obtained were homogeneous and had a single phase. This is very different from our previous study[44] in which the DDM-cured ER/PEK-C blends prepared at a higher initial curing temperature of 150°C were found to be heterogeneous. The discrepancy of these two studies can be considered to be due to the different curing conditions. The phase behaviour and morphology of a thermosetting polymer blend is determined by both thermodynamic and kinetic factors. For the blend in which one or both two components can cross-link, semi-interpenetrating network (semi-IPN) or interpenetrating network (IPN) may form. In this semi-IPN or IPN, the components which are initial immiscible may exhibit some characteristics of miscibility, i.e. the semi-IPN or IPN can be considered as a compatibilized immiscible polymer blend. On the other hand, the resulting increase in molecular weight causes a decrease in the configurational entropy of mixing as the cure proceeds. Therefore curing may cause phase separation in an initial miscible blend. The phase separation process is governed not only by the thermodynamic factor, but also the kinetic factor. Raising the curing temperature increases the rate of the curing reaction and reduces the time for gelation. If gelation occurs prior to phase separation, no domains appear. On the other hand, raising the curing temperature enhances the mobility of molecule, so that phase separation occurs relatively simply. Curing reaction and phase separation are competitive. The heterogeneous DDM-cured ER/PEK-C blends were obtained in our previous study[44] where the initial curing temperature was 150°C, whereas only the homogeneous DDM-cured ER/PEK-C blends were obtained in this study at an initial curing temperature of 80°C. These results show that elevatating the curing temperature is more beneficial for phase separation, which implies that the latter factor is dominant in the DGEBA/DDM/PEK-C system.

FT*i.r. studies*

*FT*i.r. spectroscopy was employed to examine whether the curing reaction was complete in the blends. Shown in

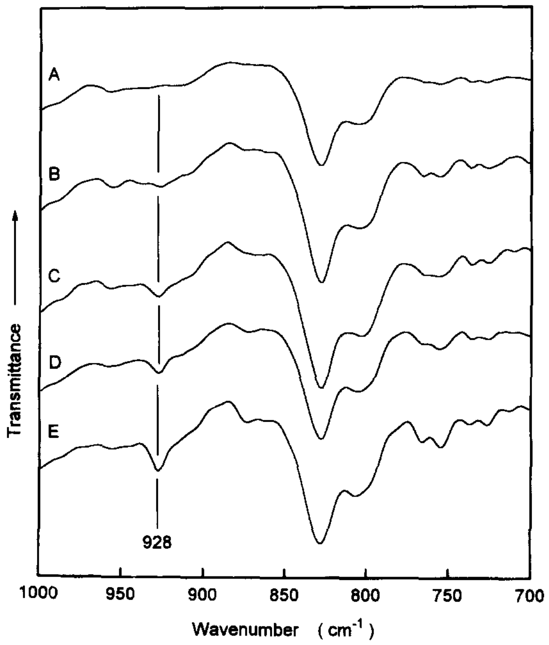


Figure 4 FTIR spectra in the 700–1000 cm^{-1} region of the DDM-cured ER/PEK-C blends. ER/PEK-C: (a) 100/0; (b) 96/4; (c) 94/6; (d) 92/8; (e) 88/12

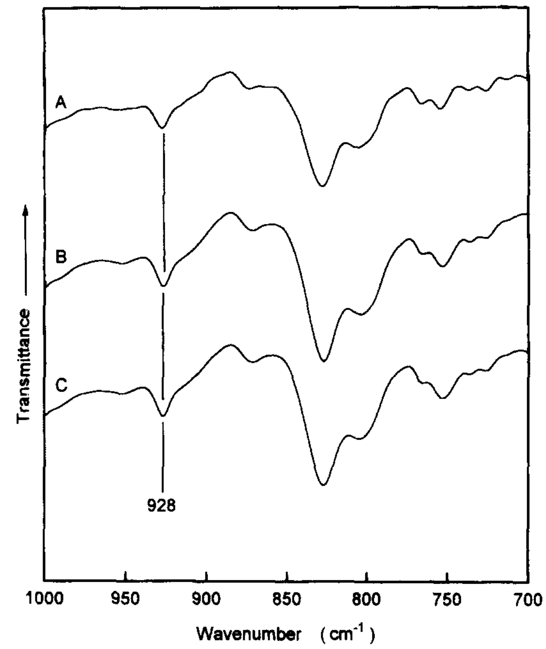


Figure 5 FTIR spectra in the 700–1000 cm^{-1} region of the 88/12 DDM-cured ER/PEK-C blend: (a) not post-cured; (b) post-cured at 250°C for 30 min; and (c) postcured at 250°C for 2 h

Figure 4 are the *FT*i.r. spectra of the DDM-cured ER/PEK-C blends in the range of 700–1000 cm^{-1}. For the plain DDM-cured ER, no obvious absorption can be observed in the region of 900–950 cm^{-1} (curve A). This means that there is basically no unreacted oxirane ring in the plain ER, i.e. ER cured completely. However, for all the DDM-cured ER/PEK-C blends, a significant absorptive peak is observed at about 928 cm^{-1}, responsible for the characteristic absorption of the unreacted oxirane ring. The appearance of absorptive peak at about 928 cm^{-1} suggests that there remained some amount of the unreacted oxirane ring of ER in the DDM-cured blends. It is clear that the curing reaction was incomplete due to the high viscosity of the PEK-C. As we have mentioned, PEK-C was dissolved in DGEBA to form a homogeneous solution. The addition of the high viscous PEK-C into the DGEBA led to a marked increase in the viscosity of the system. Therefore, the segment motion became more and more difficult with increasing PEK-C content. As a result, the curing reaction became difficult to complete. It is possible to estimate the extent of the curing reaction from the relative strength of the absorptive peak at 928 cm^{-1}, which appears to increase with increasing PEK-C content. This result demonstrates that the unreacted oxirane ring of ER in the blend increased with PEK-C content. The curing reaction became progressively incomplete due to the increasing system viscosity.

There are two factors influencing the T_g of the DDM-cured ER/PEK-C blends. One is the lowering in cross-link density of epoxy network because the curing reaction was incomplete in the blends, and this has been proved to lead to the decrease of T_g of several DDM-cured ER blends[44–47]. The other factor is the high T_g of PEK-C which should result in the increase of T_g of the homogeneous DDM-cured ER/PEK-C blends. The competition of these two factors leads to T_g of the blends displaying a maximum at the 94/6 DDM-cured ER/PEK-C blend. That is why the T_g value of the 88/12 DDM-cured ER/PEK-C blend is lower than that of the plain cured ER for the factor of the lowering in cross-link density is predominant in this blend.

However, another problem arises in whether the curing temperature is high enough. To solve this problem, the 88/12 DDM-cured ER/PEK-C blend was chosen for the further studies. The as-prepared samples of the DDM-cured ER/PEK-C blend were post-cured at 250°C for 30 min and 2 h, respectively. Then the samples were measured using DSC and *FT*i.r. again. The DSC study showed that the blend samples post-cured for 30 min and 2 h still display only one glass transition and the T_g basically remains invariant compared with that of the control ER/PEK-C blend. The *FT*i.r. results are shown in *Figure 5*, and it can be seen that post-curing at 250°C does not lead to a disappearance of the absorptive peak at 928 cm^{-1}. The relative strength of this absorptive peak is almost not influenced by the post-curing, i.e. the post-curing did not make the unreacted oxirane ring react again. This is because that the blend had vitrified, and the uncured oxirane ring and curing agent were then very difficult to move towards each other, even when the curing temperature was elevated to 250°C.

Mechanical properties

The data of flexural properties of the DDM-cured ER/PEK-C blends are summarized in *Table 1*. From the data listed in *Table 1*, it can be seen that the flexural modulus of the blend tends to only slightly decrease with the increase of PEK-C content. However, the flexural strength and maximum strain of this system appear to decrease monotonously with an increase of PEK-C content in the blends.

The fracture toughness was measured by the notched three-point bending test. The critical stress-intensity factor, K_{IC}, was calculated using the following equation:

$$K_{\mathrm{IC}} = P_c S / B W^{3/2} f(A/W) \qquad (1)$$

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 crack length (see *Figure 1*). The critical strain energy release rate, G_{IC}, was calculated from K_{IC} as

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

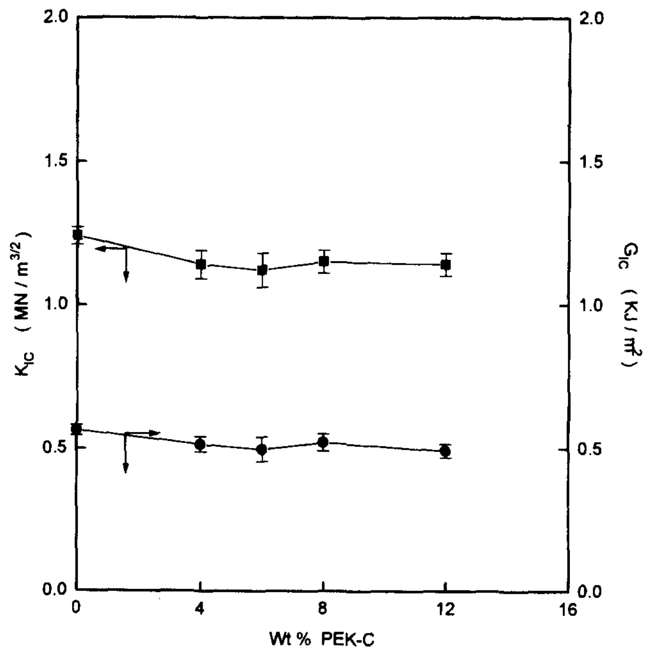


Figure 6 Composition dependence of fracture toughness K_{IC} (■) and G_{IC} (•) for the DDM-cured ER/PEK-C blends

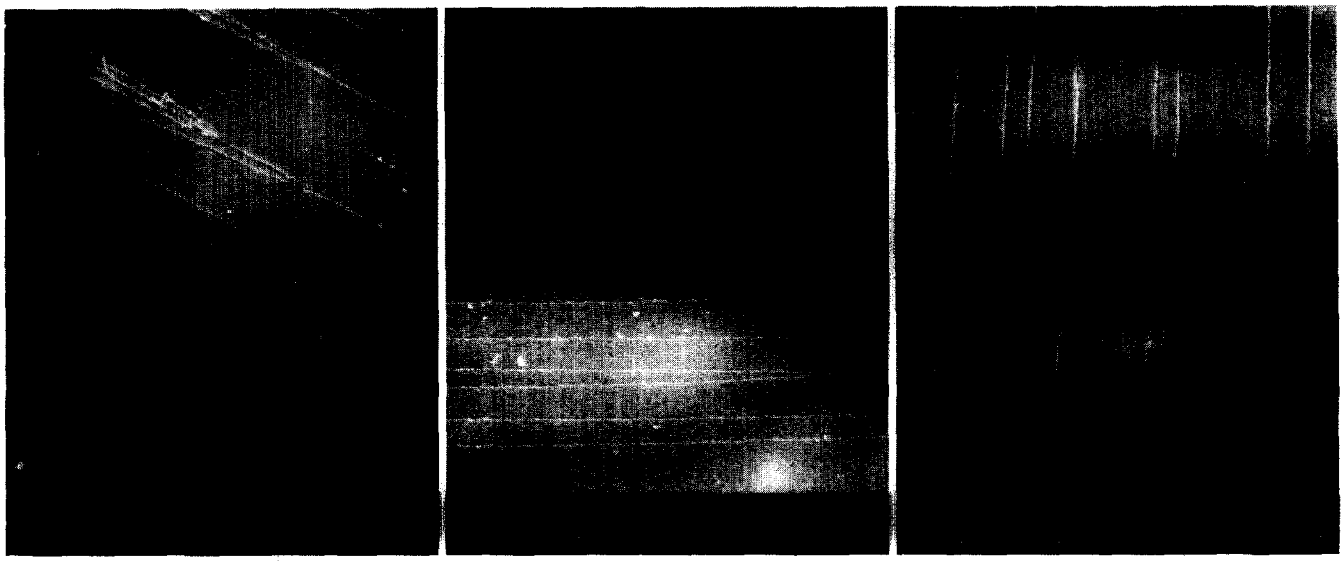
where ν is Poisson's ratio and E is the elastic modulus obtained from flexural testing.

The values of K_{IC} and G_{IC} of the DDM-cured ER/PEK-C blends are also presented in *Table 1*, and the plots of K_{IC} (solid squares) and G_{IC} (solid circles) *versus* blend composition are shown in *Figure 6*. It can be seen from *Table 1* and *Figure 6* that both the K_{IC} and G_{IC} of the blends change little with blend composition, although they are slightly lower than that of the DDM-cured ER. PEK-C cannot act as a toughness modifier in the homogeneous DDM cured ER/PEK-C blends. The lacking of toughening in homogeneous blends has also been reported by Chen *et al.* in the ER/polyetherimide system[48] and Jayle *et al.* in the ER/polycarbonate system[49]. The decrease in fracture toughness as well as in flexural properties is presumably due to the fact that the blends were incompletely cured and hence the cross-link density of the epoxy network was reduced.

The SEM micrographs of the surfaces of fracture mechanics test ends can provide some information about the fracture mechanism. Shown in *Figure 7* are the SEM micrographs with low magnification of the K_{IC} fracture surfaces of the DDM-cured ER/PEK-C blends. For the plain DDM-cured ER [*Figure* 7(a)] as well as the DDM-cured blends [*Figure* 7(b) and (c)], the cracks spread freely and regularly, and oriented in the direction of loading, which are typical characteristics of brittle fracture. However, comparing the crack density and the crack depth of the specimens, it can be found that crack of all the DDM-cured ER/PEK-C blends is even shallower and straighter than that of the DDM-cured ER, which is in accordance with the results of the fracture toughness measurements.

CONCLUSIONS

The results presented here show that the DDM-cured ER/PEK-C blends obtained were homogeneous. Both the thermodynamic and kinetic factors affected phase behaviour of the blends. The phase behaviour was found to be greatly dependent on the curing conditions, and a low initial curing temperature is beneficial for obtaining the homogeneous DDM-cured ER/PEK-C blends. The curing reaction was incomplete in the blends because of the high viscosity of PEK-C, resulting in the decrease in the cross-link density of epoxy network and hence the decrease of T_g at compositions containing 8 and 12 wt% PEK-C. *FT*i.r. studies revealed that there existed some amount of the unreacted oxirane ring of epoxy resin in the blends. Post-curing at 250°C did not make the unreacted oxirane ring react again. This is because that the blend had vitrified, and the uncured oxirane ring and the curing agent were then very difficult to move towards each other, even though the curing temperature was elevated to 250°C. Addition of PEK-C slightly reduced both the fracture toughness and flexural properties of epoxy resin. Morphological investigation of the surfaces of fracture mechanic measurement specimens indicates the nature of brittle fracture for the plain ER and the blends.



(a) (b) (c)

Figure 7 SEM micrographs of K_{IC} fracture surfaces of (a) 100/0, (b) 96/4 and (c) 92/8 DDM-cured ER/PEK-C blends

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