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Blends of phenolphthalein poly(ether ether ketone) with phenoxy and epoxy resin

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The properties of miscible phenolphthalein poly(ether ether ketone)/phenoxy (PEK-C/phenoxy) blends have been measured by dynamic mechanical analysis and tensile testing. The blends were found to have single glass transition temperatures (T_g) that vary continuously with composition. The tensile moduli exhibit positive deviations from simple additivity. Marked positive deviations were also observed for tensile strength. The tensile strengths of the 90/10 and 75/25 PEK-C/phenoxy blends are higher than those of both the pure components. Embrittlement, or transition from the brittle to the ductile mode of failure, occurs in the composition range of 50–25 wt% PEK-C. These observations suggest that mixing on the segmental level has occurred and that there is enough interaction between the components to decrease its internal mobility significantly. PEK-C was also found to be miscible with the epoxy monomer, diglycidyl ether of bisphenol A (DGEBA), as shown by the existence of a single glass transition temperature (T_g) within the whole composition range. Miscibility between PEK-C and DGEBA could be considered to be due mainly to entropy. However, PEK-C was judged to be immiscible with the diaminodiphenylmethane-cured epoxy resin (DDM-cured ER). It was observed that the PEK-C/ER blends have two T_g, which remain invariant with composition and are almost the same as those of the pure components, respectively. Scanning electron microscopy showed that the PEK-C/ER blends have a two-phase structure. The different miscibility with PEK-C between DGEBA and the DDM-cured ER is considered to be due to the dramatic change in the chemical and physical nature of ER after curing.

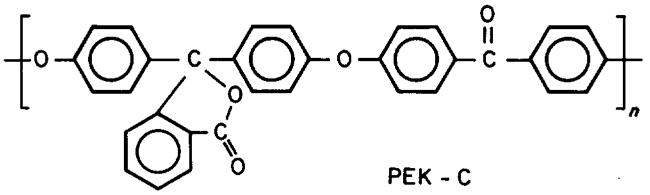
(**Keywords: phenolphthalein poly(ether ether ketone); phenoxy; epoxy resin; polymer blend; polymer miscibility; mechanical behaviour**)

INTRODUCTION

Polymer blends are becoming more and more important in specific sectors of the polymer industry[1,2], as they can frequently meet performance requirements that cannot be satisfied by the currently available commodity polymers. Consequently, their attractiveness increases with the increasing demands for this class of materials.

Miscible polymer blends have provoked particular interest, which can be seen from the increasing papers in both the scientific and technical literature[3–5]. The best commercial advantages one can envision for miscible polymer blends can probably be best described by the word 'versatility', since by simply varying the composition of a miscible blend, innumerable varieties of materials, each with a unique set of properties, can be obtained. Under certain conditions of widely differing price/performance characteristics of the components, the blend obtained can offer a set of properties that may give it the potential of entering application areas not possible for either of the polymers comprising the blend. An excellent example of industrial interest in miscible blend systems is provided by the miscible poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene blends, which were marketed as commercial products by General Electric Co. under the trade name Noryl in the late 1960s[4,6].

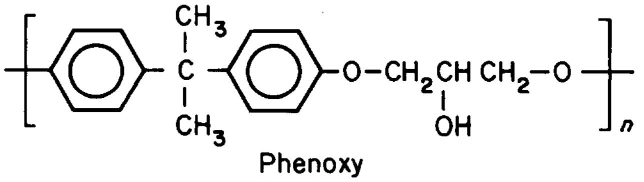
Phenolphthalein poly(ether ether ketone) (PEK-C) is a novel high-performance thermoplastic developed by this laboratory[7]. The repeat unit of PEK-C is as follows:



PEK - C

Its glass transition temperature (T_g) is about 228°C by d.s.c.; it is an amorphous polymer with mechanical properties comparable to the poly(ether ether ketone) (PEEK) developed by ICI[8,9], but better electrical properties. Since PEK-C is a commercially available polymer in China and is relatively lower in price than PEEK, considerable attention has been given to it as a high-performance thermoplastic as well as a matrix for advanced composites[10,11].

Recently, efforts in this laboratory have been given to blends of PEK-C with other thermoplastics in order to extend the range of applications for this polymer. In a previous communication, PEK-C was found to be miscible with polysulphone (PSn) and with poly(hydroxy ether of bisphenol A) (phenoxy)[12]:



Phenoxy

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Mechanical properties of PEK-C/PSn blends have also been investigated[13]. It has been shown that the blends exhibited T_g values between 185 and 228°C, the T_g of PSn and PEK-C, respectively. This may give compositions that will exhibit short-term load-bearing capabilities between 175 and 215°C (heat distortion temperature, ASTM D-635, for amorphous polymers are generally 10–15°C lower than the glass transition temperatures). PEK-C, because of its higher monomer cost and more difficult polymerization procedure, is significantly higher in cost than PSn. Thus, it is expected that combinations of the two polymers should allow a balance in the price/performance profile, with PEK-C yielding advantages in higher T_g and better strength and PSn offering a very important price advantage.

In this paper, we present first the results of our investigation on the mechanical properties of PEK-C/phenoxy blends. Since phenoxy may be considered to be a model epoxy resin[14,15], PEK-C should be miscible with uncured bisphenol-A-type epoxy resin, i.e. diglycidyl ether of bisphenol A (DGEBA). This led us to examine further blends of PEK-C with a DGEBA monomer and the related cured epoxy resin (ER). As crosslinking may greatly reduce the degree of miscibility in epoxy resin/poly(ethylene oxide) blends[16], particular attention is given to the different miscibility with PEK-C between the monomer and the cured ER. On the other hand, epoxy resins, like other highly crosslinked thermosets, are difficult to toughen. The present investigations on miscibility, dynamic mechanical properties and morphology of PEK-C/ER blends are also of practical significance for toughening thermosets by using a high-performance thermoplastic.

EXPERIMENTAL

Materials

The PEK-C resin was supplied by Xuzhou Chemical Factory, Xuzhou, Jiangsu, China. It has a specific gravity of 1.31 and a number-average molecular weight of 12 000. The phenoxy resin was obtained from Guanzhou Chemical Factory, Guanzhou, Guangdong, China. It has a specific weight of 1.18 and a weight-average molecular weight of 43 000. The diglycidyl ether of bisphenol A (DGEBA), E-51, with epoxy equivalent 185–210, was supplied by Wuxi Resin Factory, Wuxi, Jiangsu, China. 4,4′-Diaminodiphenylmethane (DDM) (purity >98%) was used as hardener in stoichiometric epoxide/amine ratios. The solvent used in this study was AR grade chloroform.

Preparation of blends

Blends of PEK-C with phenoxy and 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 dried in a vacuum oven at room temperature for 2 weeks and further at 100°C for 2 weeks.

All the PEK-C/phenoxy blends so obtained were pressed into sheets of thickness of about 0.04 cm at a temperature between 180 and 300°C, depending on the composition. Blend compositions studied were 0/100, 10/90, 25/75, 50/50, 75/25, 90/10 and 100/0 in weight proportions of PEK-C/phenoxy.

PEK-C/ER blends were prepared by mixing PEK-C, DGEBA and DDM in the smallest possible volume of chloroform according to stoichiometric ratio, considering DGEBA as difunctional and DDM as tetrafunctional. 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.

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°C min^{-1}. Sample dimensions were $4.0 \times 0.4 \times 0.04$ cm^3.

Tensile tests

The experiments were carried out on an Instron model 1122 testing machine at room temperature. Samples were cut into standard dumbbell test pieces with a neck of 3×0.40 cm^2. More than five successful determinations were used to obtain the average value. Crosshead speed was 5 cm min^{-1} corresponding to relative strain rate of 1.67 min^{-1}.

Differential scanning calorimetry

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

Morphological observations

The specimens were fractured under cryogenic conditions using liquid N_2. The fractured surface was then immersed in chloroform at room temperature for 4 h. The PEK-C phase was preferentially etched by the solvent while the cured ER phase remained unaffected. 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 thin layers of platinum of 200 Å.

RESULTS AND DISCUSSION

PEK-C/phenoxy blends

Dynamic mechanical properties.

(*a*) *Pure PEK-C.* Dynamic mechanical properties of PEK-C are shown in *Figure 1*. Five relaxation peaks are observed at 235, 170, 110, 20 and −100°C on the tan δ vs. T plot, and denoted by α, β, γ, δ and ε relaxations, respectively. It can be seen that the α relaxation corresponds to the glass–rubber transition and is due to micro-Brownian motion of the polymer chains. Li *et al.*[17] have shown that the ε relaxation peak is due to the overlapping of three relaxations, which are those of the phenylcarbonyl groups, the phenyl ether groups and the aryl side-groups of the phenolphthalein residue. For the β, γ and δ relaxations, their origins are not known at present. Since the β and γ peaks occur just below the glass transition temperature, it is considered that they may be due to restricted three-dimensional motion of molecular chains. A detailed study is in progress.

(*b*) *Pure phenoxy.* Dynamic mechanical properties of phenoxy are shown in *Figure 2*. Three well defined relaxation peaks observed at 100, 20 and −70°C, and

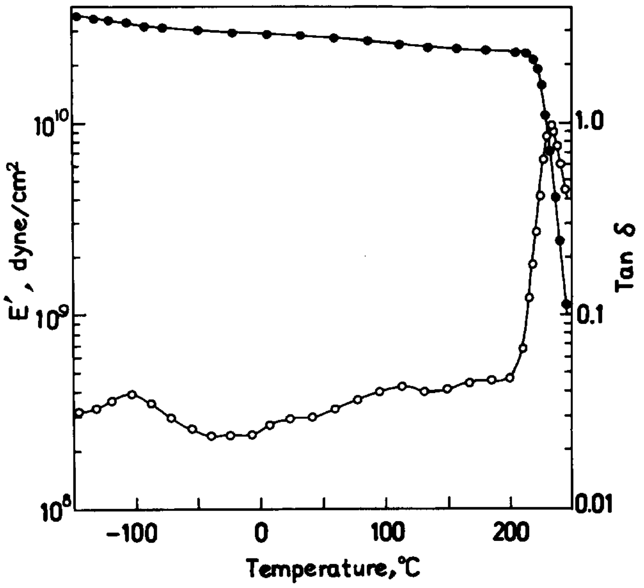


Figure 1 Dynamic viscoelastic properties of PEK-C: (●) storage modulus E'; (○) tan δ (10 dyne/cm^2 = 1 Pa)

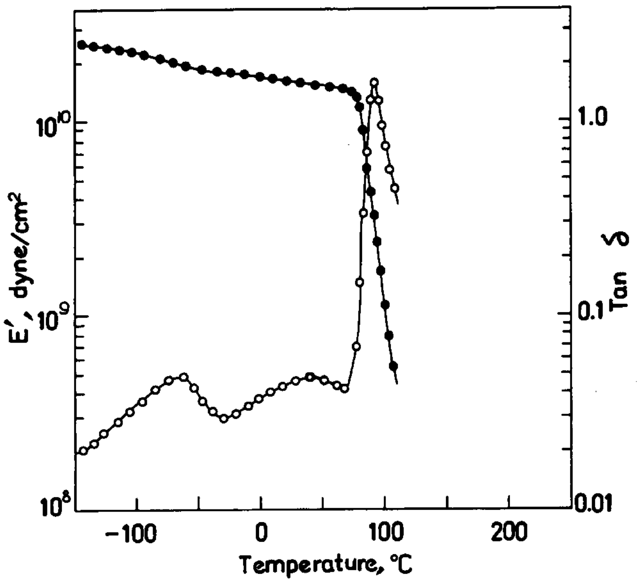


Figure 2 Dynamic viscoelastic properties of phenoxy: (●) storage modulus E'; (○) tan δ (10 dyne/cm^2 = 1 Pa)

denoted by α, β' and β relaxations, are in good agreement with those reported in the literature[18–20].

It is well known that the α relaxation corresponds to the glass–rubber transition. Ochi *et al.*[18–20] showed that the β relaxation is a complex one, i.e. the overlap of the relaxation of hydroxy ether segment with that of other parts in the polymer chain, and that the β' relaxation is due to the motion of the phenylene group in the polymer chain.

(*c*) *The blends. Figures 3* and *4* illustrate the temperature dependence of E' and tan δ for the blends, respectively. The moduli curves (*Figure 3*) are relatively featureless. However, it can be seen that the modulus of the blend lies between those of the two component polymers and increases with increasing PEK-C content. The temperature at which the modulus E' decreases abruptly is also observed to increase with increase in PEK-C content, indicating that the blend has a single, composition-dependent glass transition temperature. On the other hand, the tan δ vs. T plots exhibit interesting features (*Figure 4*). The curves, as a set, can be conveniently divided into two regions by an isosbestic point around −90°C. The existence of this isosbestic point implies that the relaxation strengths obey the simple rule of mixtures at this point. This phenomenon was also observed for miscible blend systems of poly(phenylene oxide)/polystyrene (PPO/PS)[21,22] and PEK-C/PSn[13].

Below −90°C, all relaxations of the blends are stronger than that of pure phenoxy. This is due to the stronger ε relaxation in PEK-C than that around approximately the same temperature in phenoxy. The relaxation strengths in the blend are between those of the two pure components and increase with increasing PEK-C content.

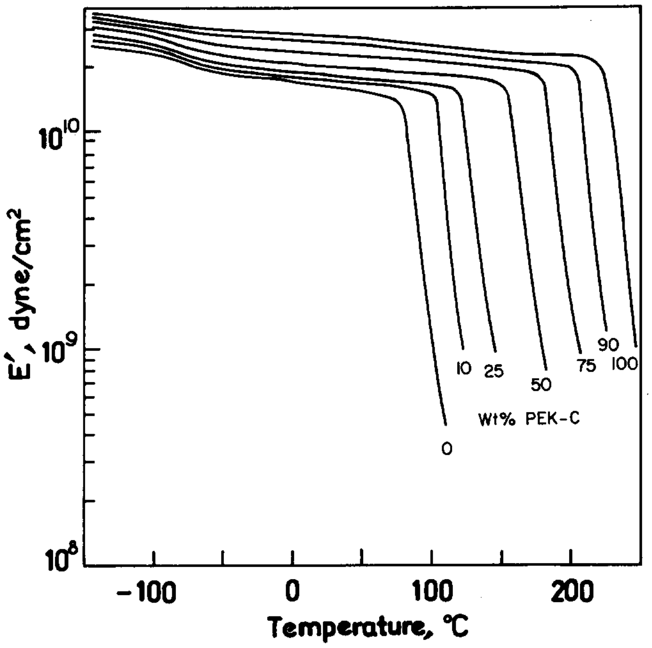


Figure 3 Temperature dependence of storage modulus E' of PEK-C/phenoxy blends (10 dyne/cm^2 = 1 Pa)

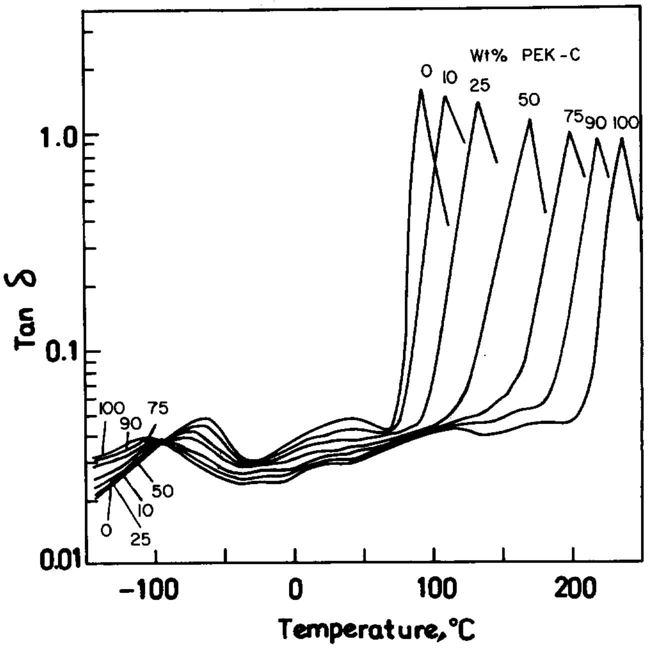


Figure 4 Temperature dependence of tan δ of PEK-C/phenoxy blends

Above −90°C, all relaxations are stronger than that of pure PEK-C. In phenoxy, this is due to the α, β' and β relaxations. The relaxation strengths in the blend lie between those of the pure polymers and increase with increase of phenoxy content.

The temperature at which the α peak occurs is designated as the glass transition temperature (T_g) of the blend. The T_g is composition-dependent, indicating that PEK-C and phenoxy are compatible.

Tensile properties. No yield was observed on the stress–strain curves of the pure PEK-C resin and its blends with high PEK-C content, which is the feature of brittle fracture. However, phenoxy exhibited ductile fracture, while the blends with high phenoxy content exhibited major ductile fracture and minor brittle fracture. The changes of tensile modulus and stress at break or yield are plotted in *Figures 5* and *6*, respectively, as a function of blend composition. The tensile moduli calculated from the initial slope of the stress–strain curves show positive deviations from simple additivity (*Figure 5*), as expected for miscible blends[23–25]. These positive deviations suggest that there is enough interaction between the components to decrease its internal mobility significantly.

In *Figure 6*, the open circles represent failure by yielding, neck formation, or cold drawing, while the full circles represent failure by crazing or brittle fracture. Marked positive deviations are observed for tensile strength. In fact, the tensile strengths of the 90/10 and 75/25 PEK-C/phenoxy blends are higher than those of both the pure components. Embrittlement, or transition from the brittle to the ductile mode of failure, occurs in the composition range of 50–25 wt% PEK-C. As indicated in the figure, some tensile specimens break by either brittle or ductile failure at the same blend composition. The fraction of total specimens tested that fail in the predominant mode is indicated in the parentheses in the figure. In all cases, the yield stress for the specimens that underwent ductile failure is higher than the break stress for the specimens with the same composition that failed in a brittle mode. These observations may be explained in terms of the failure criteria proposed by Nicolais and DiBenedetto[25,26], according to which brittle failure will occur if an individual specimen defect grows to a critical defect size before the stress–strain curve reaches a maximum.

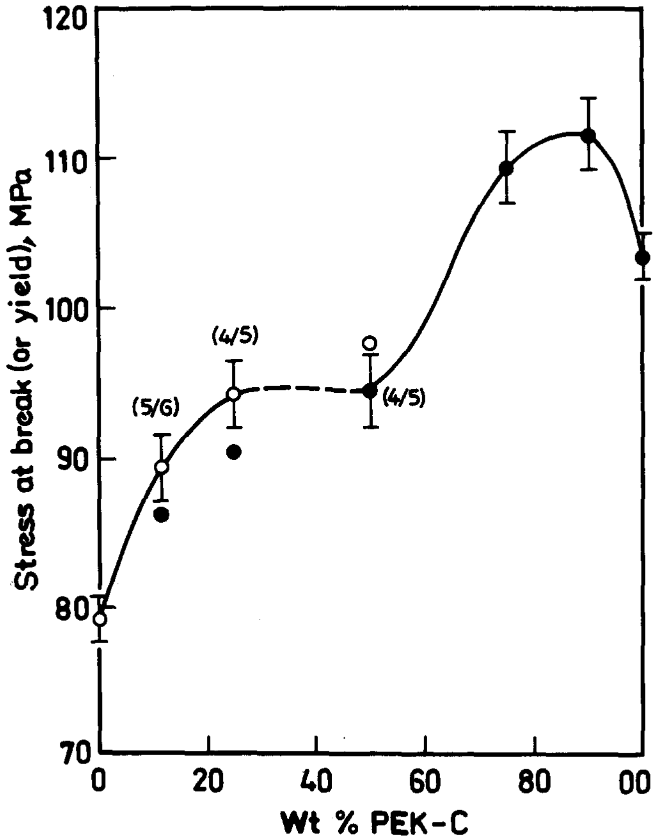


Figure 6 Composition dependence of strength of PEK-C/phenoxy blends: (●) brittle fracture; (○) ductile yield. Values in parentheses indicate fraction of the sample population tested that fails by predominant mode in the embrittlement region

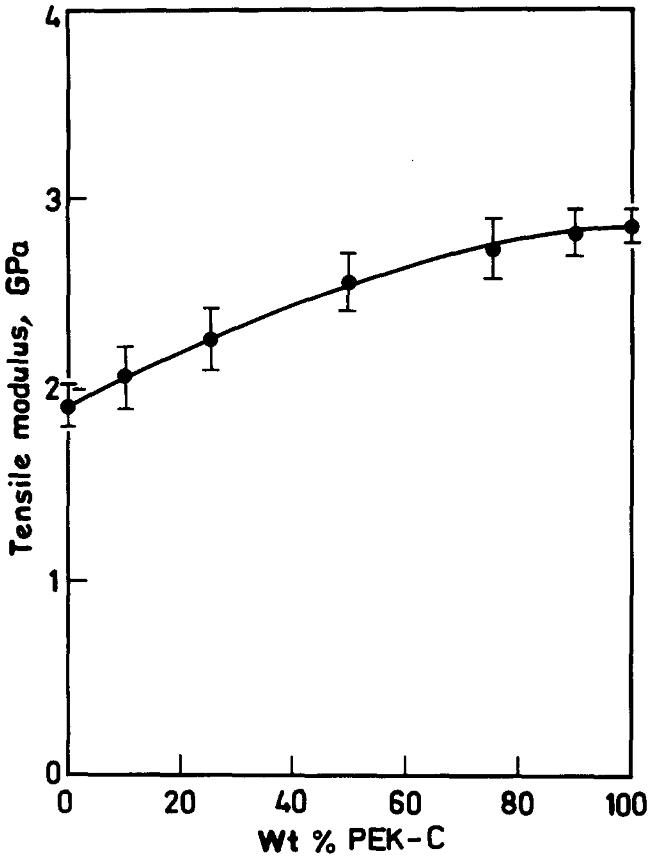


Figure 5 Dependence of tensile modulus at room temperature (20°C) on composition for PEK-C/phenoxy blends

PEK-C/DGEBA blends

All the PEK-C/DGEBA blends were transparent. D.s.c. study showed that each blend has a single composition-dependent T_g, indicating its single-phase nature. Thus, PEK-C is miscible with DGEBA over the entire composition range. *Figure 7* 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 Fox equation[27], is written as:

$$1/T_g(\text{blend}) = W(\text{PEK-C})/T_g(\text{PEK-C}) + W(\text{DGEBA})/T_g(\text{DGEBA}) \qquad (1)$$

where T_g(blend) is the glass transition temperature of the

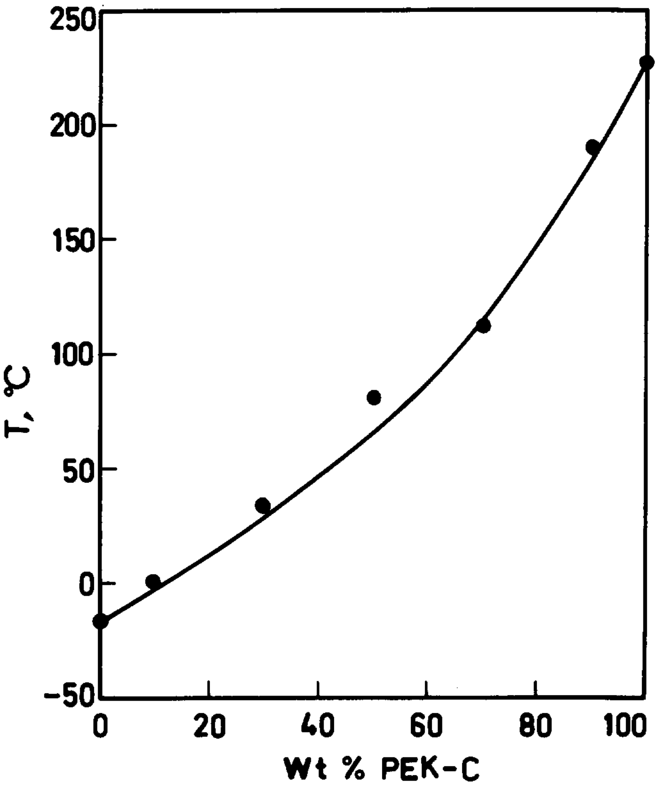
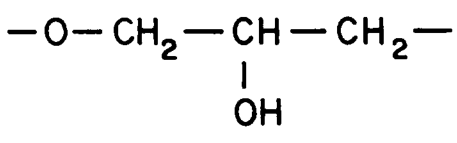


Figure 7 Glass transition behaviour for PEK-C/DGEBA blends: (●) experimental data; (——) calculated curve by Fox equation

blend, T_g(PEK-C) and T_g(DGEBA) are those of plain PEK-C and DGEBA, respectively, and W(PEK-C) and W(DGEBA) are the corresponding weight fractions. As shown in *Figure 7*, the experimental T_g data fit the calculated curve of equation (1) quite well. It should be pointed out that the entropy contribution is not negligible for miscibility of the PEK-C/DGEBA blends as the molecular weight of DGEBA is rather low.

PEK-C/ER blends

Dynamic mechanical properties. Dynamic mechanical properties of DDM-cured ER (*Figure 8*) show three typical relaxations of the epoxy network. They are at 190, 50 and −35°C and denoted by α, ω and β relaxations, respectively. The α relaxation is associated with the glass transition. The ω relaxation, of very low amplitude, is attributed to motions of less crosslinked zones in the network by Pogany[28] and Arridge[29]; however, Ochi *et al.*[19] suggested that it was associated with motions of *p*-phenylene. The β relaxation is generally considered as the combination of two relaxations: one at low temperature associated with motions of diphenylpropane units and the other with motions of hydroxy ether groups at higher temperature[30,31]:



$$-O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-$$

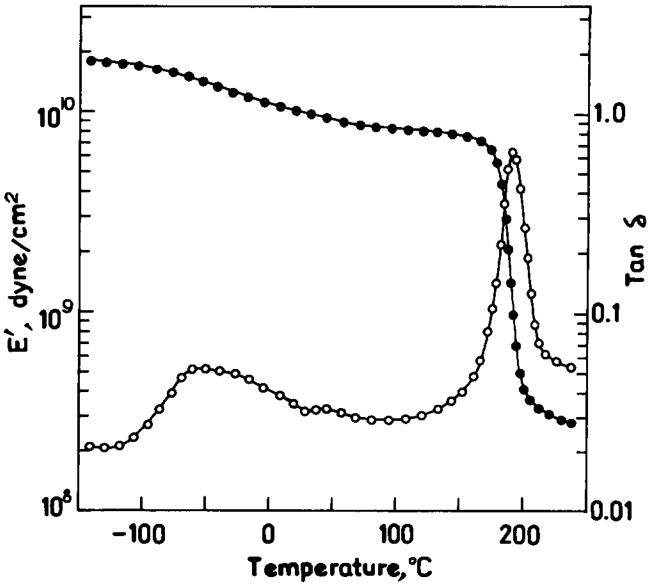


Figure 8 Dynamic viscoelastic properties of the DDM-cured ER: (●) storage modulus E'; (○) tan δ (10 dyne/cm^2 = 1 Pa)

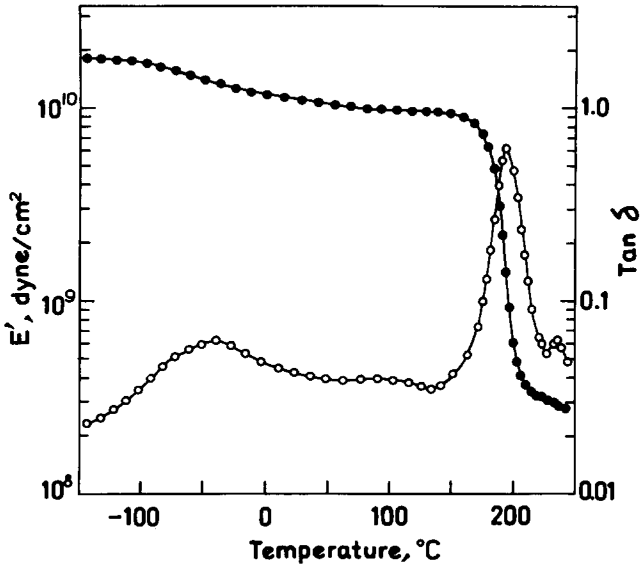


Figure 9 Dynamic viscoelastic properties of the DDM-cured 10/90 PEK-C/ER blend: (●) storage modulus E'; (○) tan δ (10 dyne/cm^2 = 1 Pa)

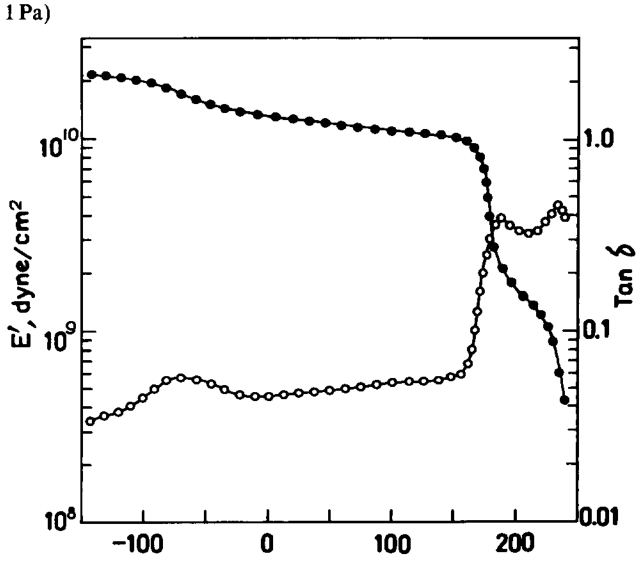


Figure 10 Dynamic viscoelastic properties of the DDM-cured 50/50 PEK-C/ER blend: (●) storage modulus E'; (○) tan δ (10 dyne/cm^2 = 1 Pa)

Dynamic mechanical properties of the DDM-cured PEK-C/ER blends of three different compositions are shown in *Figures 9–11*. All the figures clearly display two maxima on the tan δ vs. T curves, which correspond to the T_g values of PEK-C and the DDM-cured ER,

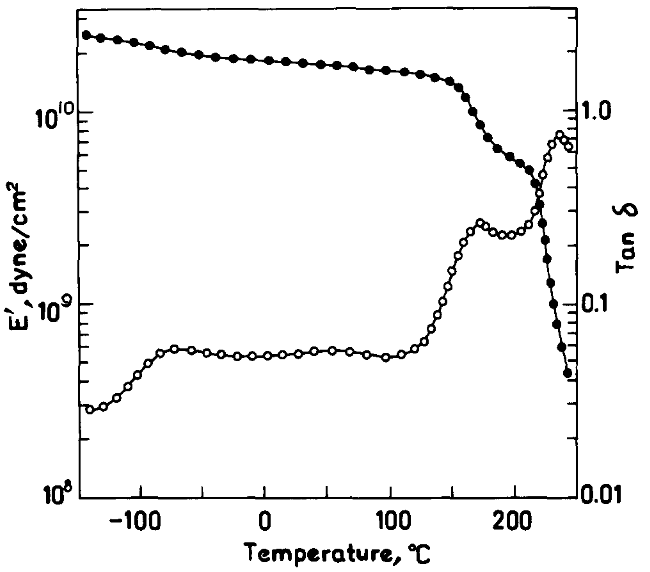


Figure 11 Dynamic viscoelastic properties of the DDM-cured 75/25 PEK-C/ER blend: (●) storage modulus E'; (○) tan δ (10 dyne/cm^2 = 1 Pa)

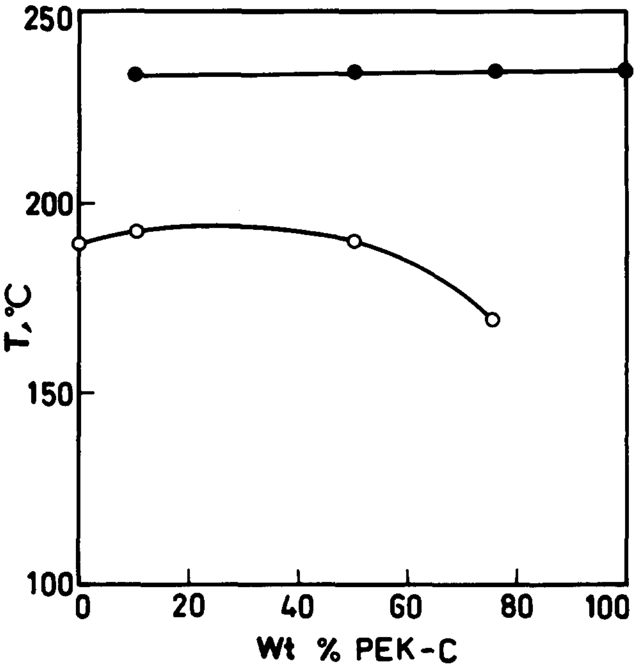


Figure 12 Transition behaviour for the DDM-cured PEK-C/ER blends: (●) T_g of the PEK-C phase; (○) T_g of the ER phase

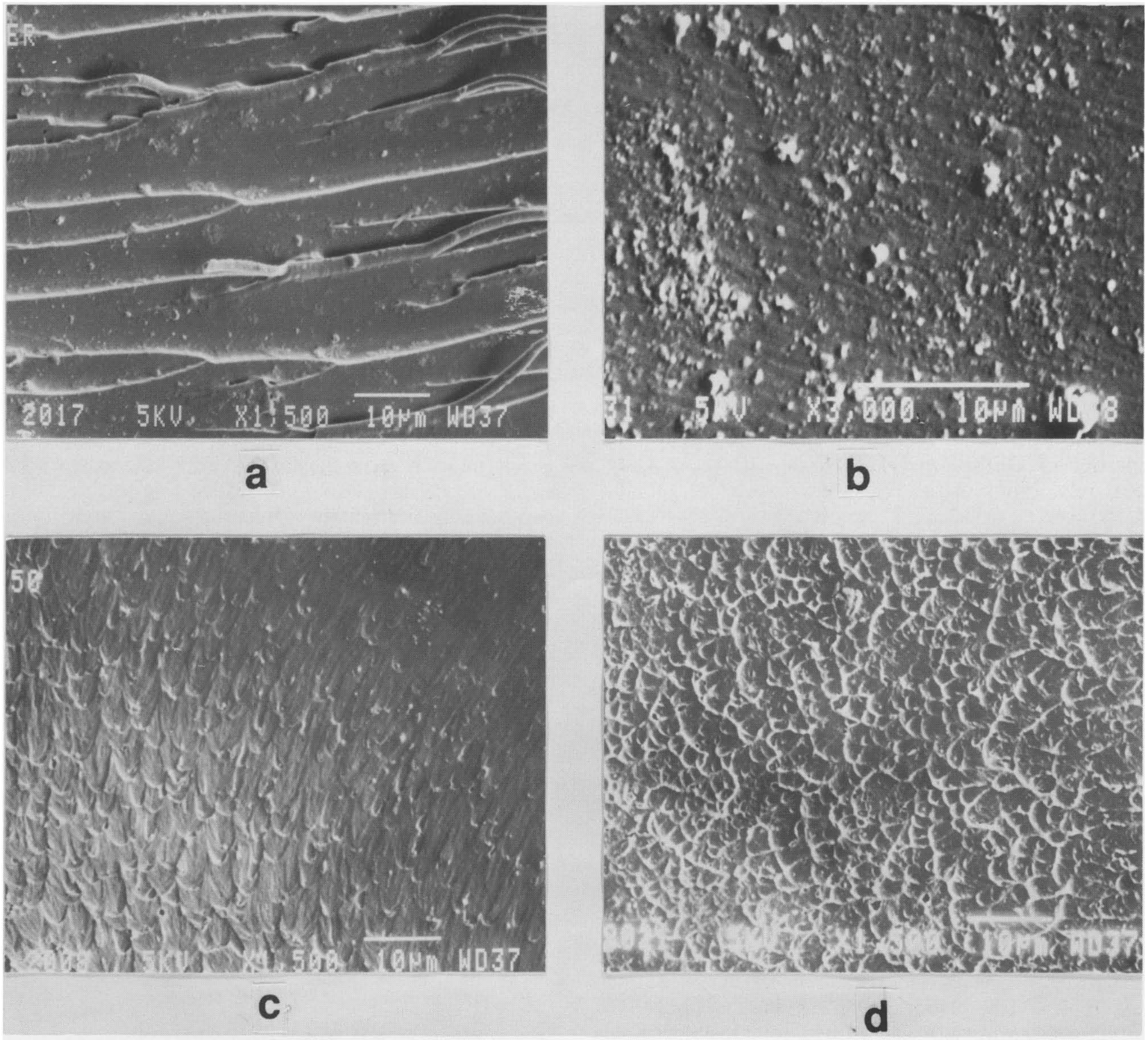


Figure 13 Scanning electron micrographs of fractured surfaces of (a) 0/100, (b) 10/90, (c) 50/50 and (d) 75/25 PEK-C/ER blends

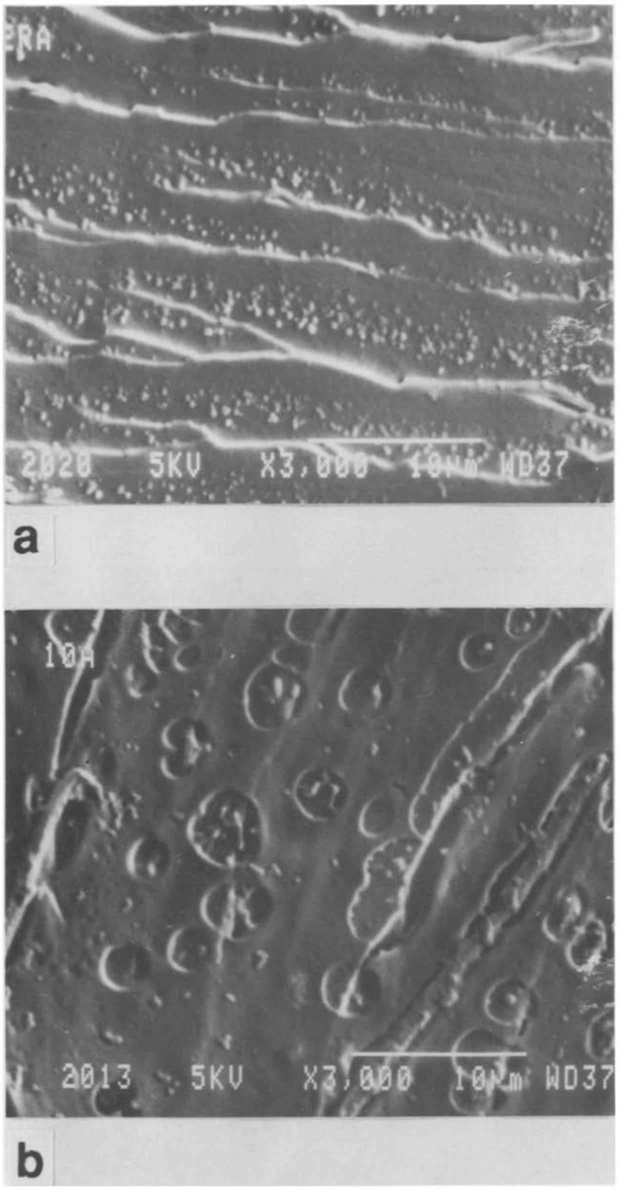


Figure 14 Scanning electron micrographs of fractured surfaces of (a) pure ER and (b) 10/90 PEK-C/ER blends etched with chloroform

respectively. *Figure 12* summarizes T_g data of these blends as a function of composition, from which it is seen that two T_g values of the blends are approximately equal to those of the pure components, respectively, except that the T_g of the ER phase in the 75/25 PEK-C/ER blend is lower than that of the pure ER. The lowering of the T_g of the ER phase may be due to the fact that crosslinking density is much reduced in the blend as ER is relatively low in concentration. All these indicate that PEK-C and DDM-cured ER are immiscible.

Morphology. The SEM micrographs of the fractured surfaces of pure ER and the PEK-C/ER blends (*Figure 13*) clearly show that the blends are heterogeneous. For confirmation, the fractured surfaces of the specimens were further etched to remove PEK-C, so that the morphology of these specimens may be more clearly shown. The SEM micrographs of the etched specimens of pure ER and 10/90 PEK-C/ER blend are given in *Figure 14*. A two-phase structure with well defined domains of PEK-C dispersed in a continuous phase of cured ER is clearly seen for the 10/90 PEK-C/ER blend (*Figure 14b*), while the cured ER was almost intact (*Figure 14a*). Evidently, PEK-C is immiscible with the cured ER although it is miscible with both uncured ER, i.e. DGEBA, and phenoxy[14,15], which may be considered as a model epoxy resin. This, we think, very probably results from the competition between demixing due to crosslinking and molecular interdiffusion. Thus, the formation of DDM-cured ER network started phase separation. The 'network effect' makes the cured ER more stable in the isolated state than in the form of a homogeneous blend. This must imply that the exotherm of the cure reaction was more than the endotherm of the demixing of the blend, leading to an overall decrease in the free energy of the system. And the chemical and physical nature of ER changed dramatically as the cure occurred.

CONCLUSIONS

The results presented here show that PEK-C and phenoxy are compatible over the entire composition range. In the blends, the secondary relaxations are stronger than that of pure PEK-C above −90°C. This is considered to be due to the stronger α, β' and β relaxations in phenoxy. At temperatures below −90°C, all relaxations are stronger than that of pure phenoxy. This is due to the stronger ε relaxation in PEK-C than that around the approximately same temperature in phenoxy. The positive deviations for tensile moduli suggest that there is enough interaction between the components to decrease its internal mobility significantly. Remarkably positive deviations for tensile strength are also observed as expected for miscible blends. The tensile strengths of the 90/10 and 75/25 PEK-C/phenoxy blends are higher than those of both the pure components. Embrittlement, or transition from the brittle to the ductile mode of failure, occurs in the composition range of 50–25 wt% PEK-C. This can be explained in terms of the failure criteria proposed by Nicolais and DiBenedetto. The PEK-C/DGEBA blends are also found to be miscible over the entire composition range, which is mainly attributed to the entropy contribution. However, PEK-C is not miscible with the DDM-cured ER, as the PEK-C/ER blends have two T_g corresponding to those of the components and remain almost unchanged with composition. SEM study confirmed that the PEK-C/ER blends have a two-phase structure. The cause of the phase separation is discussed.

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REFERENCES

1 Utracki, L. A. *Polym. Eng. Sci.* 1984, **24**, 1283
2 Rappaport, M. *Plast. Eng.* 1985, **41**(2), 30
3 Paul, D. R. and Newman, S. (Eds.), 'Polymer Blends', Vols. 1 and 2, Academic Press, New York, 1978
4 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979
5 Walsh, D. J., Higgins, J. S. and Maconnachie, A. (Eds.), 'Polymer Blends and Mixtures', Martinus Nijhoff, Dordrecht, 1985
6 Cizek, E. P., U.S. Patent 3383435, 1968 (assigned to General Electric Co.)

7 Zhang, H., Chen, T. and Yuan, Y., Chinese Patent 85108751, 1985

8 Searle, O. B. and Pfeiffer, R. H. *Polym. Eng. Sci.* 1985, **25**, 474

9 Ahwood, T. E., Dawson, P. C., Freeman, J. L., Hoy, L. R., Rose, J. B. and Stanliland, P. A. *Polymer* 1981, **22**, 1103

10 Guo, Q., *et al. Eur. Polym. J.* 1990, **26**, 355

11 Guo, Q., *et al.* in preparation

12 Guo, Q., Huang, J. and Chen, T. *Polym. Bull.* 1988, **20**, 517

13 Guo, Q., Huang, J., Chen, T., Zhang, H., Yang, Y., Hou, C. and Feng, Z. *Polym. Eng. Sci.* 1990, **30**, 44

14 Robeson, L. M., Hale, W. F. and Merriam, C. N. *Macromolecules* 1981, **14**, 1644

15 Coleman, M. M. and Moskala, E. J. *Polymer* 1983, **24**, 251

16 Guo, Q., Peng, X. and Wang, Z. *Polym. Bull.* 1989, **21**, 593

17 Li, B., Zhang, H., Yang, Y., Ni, S. and Chen, T. *Polym. Mater. Sci. Eng.* (Chinese) 1987, **3**, 35

18 Shimbo, M., Ochi, M., Saga, M. and Takashima, N. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 2185

19 Ochi, M., Ieasko, H. and Shimbo, M. *Polymer* 1985, **26**, 457

20 Ochi, M., Kageyama, H. and Shimbo, M. *Polymer* 1988, **29**, 320

21 Yee, A. F. *Polym. Eng. Sci.* 1977, **17**, 213

22 Kambour, R. P., in ref. 5, p. 331

23 Fried, J. R., MacKnight, W. J. and Karasz, F. E. *J. Appl. Phys.* 1979, **50**, 6052

24 Joseph, E. A., Lorenz, M. D., Barlow, J. W. and Paul, D. R. *Polymer* 1982, **23**, 112

25 Kambour, R. P. and Smith, S. A. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 2069

26 Nicholais, L. and DiBenedetto, A. T. *J. Appl. Polym. Sci.* 1971, **15**, 1585

27 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1**, 123

28 Pogany, G. A. *Br. Polym. J.* 1969, **1**, 177

29 Arridge, R. G. C. and Speak, J. H. *Polymer* 1972, **13**, 450

30 Williams, J. G. *J. Appl. Polym. Sci.* 1979, **23**, 3433

31 Ochi, M., Okazaki, M. and Shimbo, M. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 689