PHASE SEPARATION IN ANHYDRIDE-CURED EPOXY RESIN CONTAINING PHENOLPHTHALEIN POLY(ETHER ETHER KETONE)

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Abstract—Dynamic mechanical analysis and scanning electron microscopy were used to study phase separation of three blends of anhydride-cure bisphenol-A-type epoxy resin with phenolphthalein poly(ether ether ketone). Phase separation was observed for all the blends. The overall compatibility and the resulting morphology of the cured blends are dependent on the choice of cure agent. The phenomena have been discussed from the points of view of both thermodynamics and kinetics. The effects of the choice of hardener on phase separation are considered to be primarily due to differences between the chemical natures of the hardeners.

INTRODUCTION

Epoxy resins form a major class of thermosetting polymers, widely employed as matrices for composite materials and as structural adhesives [1–4]. They are amorphous, highly-crosslinked polymers and this structure gives the materials high modulus, high 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 the toughness is to incorporate a second phase of dispersed rubbery

thermoset resins with elastomers or thermoplastics [13, 19–23]. Since the resulting morphology and extent of phase separation is known to affect the optical and mechanical properties of the cured blends, understanding of the phase separation processes in thermosetting blends is necessary and of great importance.

In this paper, we present the results of work on the morphology and phase behaviour of anhydride-cured epoxy resin containing phenolphthalein poly(ether ether ketone) (PEK-C), a novel amorphous high performance thermoplastic developed by this laboratory [24]. The repeat unit of PEK-C is:
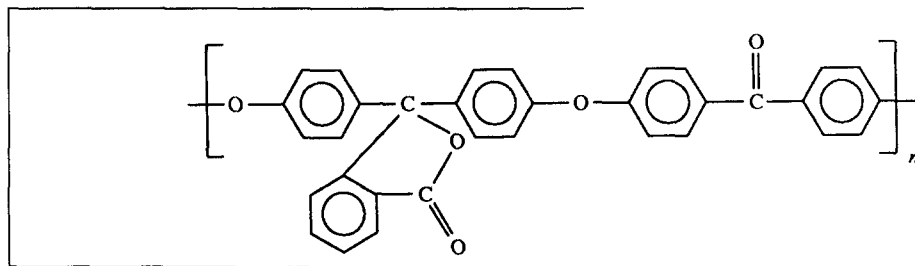
particles in the crosslinked polymer [5–11]. The addition of rubbery materials to epoxy resins enhances their fracture toughness while lowering their glass transition temperatures (T_g); thermal and oxidative stability will result. Recently, high performance thermoplastics have been also used to toughen epoxy resins [12–18]. 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.

Few systematic studies have been done on the overall compatibility and phase separation in blends of

Since PEK-C is miscible with poly(hydroxyether of bisophenol A) (phenoxy) [23, 25] and phenoxy may be considered to be a model expoxy resin [26, 27], PEK-C should be miscible with uncured bisphenol-A-type epoxy resin, i.e. diglycidyl ether of bisphenol-A (DGEBA). Indeed, this effect has been demonstrated [23]. This fact enables us to examine the cured blends of PEK-C with a DGEBA epoxy resin with attention being paid particularly to the effect of crosslinking and the choice of cure agent on the overall compatibility and the resulting morphology of the cured blends. Three anhydrides were used as cure agents, viz. maleic anhydride (MA), phthalic anhydride (PA) and hexahydrophthalic anhydride (HHPA).

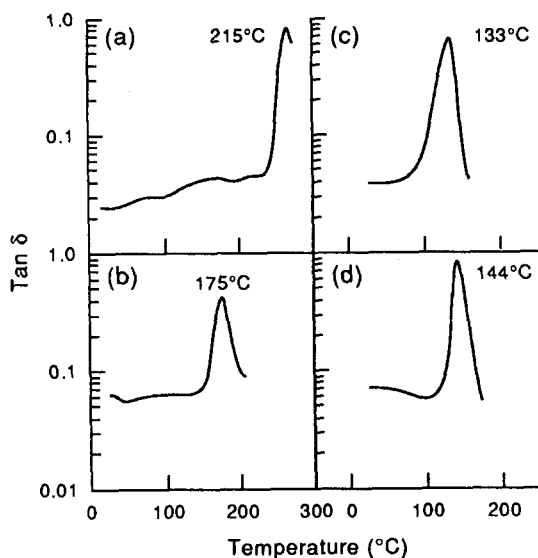*To whom all correspondence should be addressed.

Fig. 1. Dynamic mechanical spectra of (a) PEK-C, (b) 100 DGEBA, 50 MA, (c) 100 DGEBA, 75 PA and (d) 100 DGEBA, 80 HHPA.

EXPERIMENTAL PROCEDURES

Materials

The PEK-C resin was supplied by Xuzhou Chemical Factory, Xuzhou, Jiangsu, Peoples' Republic of China. It has a reduced viscosity of 0.66 dl/g when measured in 0.5 wt% solution in chloroform at 25°. DGEBA, E-51, with epoxy equivalent 185–210, was supplied by Wuxi Resin Works, Wuxi, Jiangsu, Peoples' Republic of China. The hardeners were MA (purity: >98%), PA (purity: >98%) and HHPA (purity: >98%). They were all used in approximately stoichiometric ratios epoxide/amine. The solvents were A.R. grade chloroform and cyclohexanone.

Preparation of samples

The ER/PEK-C blends were prepared by mixing preweighed PEK-C, DGEBA and hardener in the smallest possible volume of chloroform (for MA as hardener) or
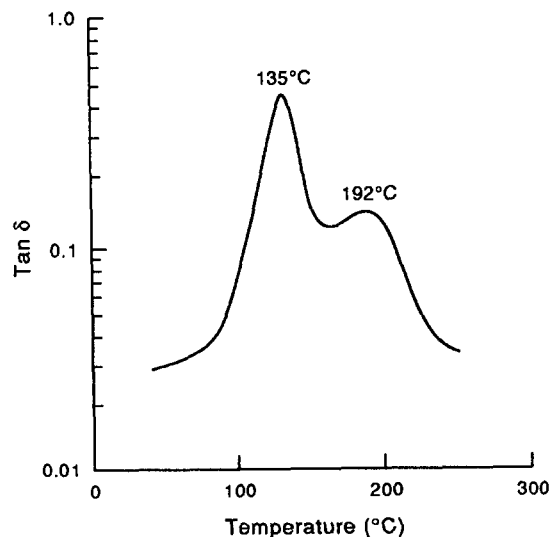

Fig. 2. Dynamic mechanical spectrum of 100 DGEBA, 50 MA, 25 PEK-C.

cyclohexanone (for PA or HHPA as hardener). The solution was cast onto an Al plate to form a film. The residual solvent was removed under vacuum at room temperature. The films thus obtained were then cured successively at 150° for 8 hr, 200° for 4 hr and 250° for 4 hr.

Dynamic mechanical measurements

Dynamic mechanical measurements were carried out on a Rheoviborn Model DDV II dynamic viscoelastometer (Toyo Baldwin Co., Japan). The frequency was 3.5 Hz and heating rate 3.0°/min. Sample dimensions were 4.0 × 0.4 × 0.04 cm.

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 15 hr. 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 a thin layer of Pt of about 200 Å.

RESULTS

In previous work, we showed by DSC that PEK-C is miscible with DGEBA [23]. Dynamic mechanical spectra of PEK-C and three anhydride-cured ER are shown in Fig. 1. They all display a well-defined relaxation peak at 215, 175, 133 and 144° on the tan δ vs T plot, corresponding to the glass-rubber transitions of PEK-C, 100DGEBA/50MA,
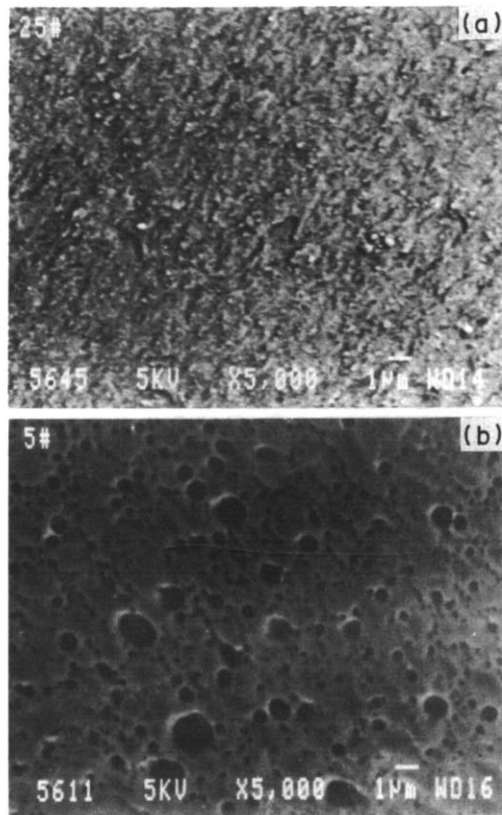

Fig. 3. Fracture surface of 100 DGEBA, 50 MA, 25 PEK-C. (a) Unetched, (b) etched in chloroform for 15 hr.
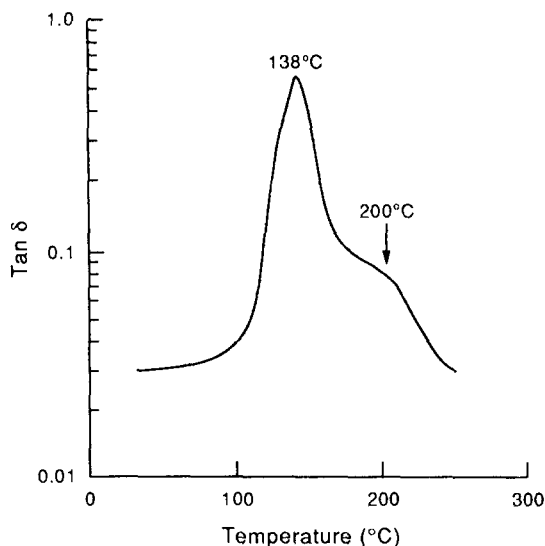
Fig. 4. Dynamic mechanical spectrum of 100 DGEBA, 75 PA, 25 PEK-C.

100DGEBA/75PA and 100DGEBA/80HHPA cured epoxy resins, respectively.

The sample of MA-cured ER containing phr 25 PEK-C was opaque. Figure 2 shows its dynamic mechanical spectrum which clearly displays two maxima on the tan δ vs T curve, respectively corre-
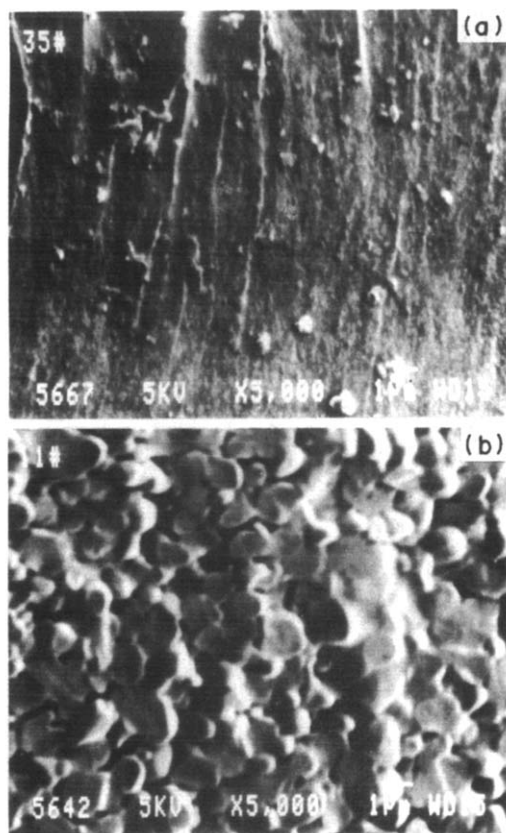

Fig. 5. Fracture surface of 100 DGEBA, 75 PA, 25 PEK-C. (a) Unetched, (b) etched in chloroform for 15 hr.

sponding to the T_g's of the PEK-C-rich phase (192°) and the MA-cured ER phase (135°). It is evident that phase separation had occurred in the MA-cured ER/PEK-C blend and PEK-C is not 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 PEK-C (215°) and the MA-cure ER (75°), respectively. The lowering of T_g of PEK-C in the cured blend implies that there is some uncured and/or insufficient cured ER dissolved in the PEK-C phase. This effect in turn results in the crosslinking density being much reduced in the blend, so lowering the T_g of the ER phase, as the ER-phase became relatively not in stoichiometric ratio epoxide/amine.

The SEM micrograph of the fractured surface of a MA-cured ER/PEK-C blend [Fig. 3(a)] clearly shows that the blend is heterogeneous. For confirmation, the fractured surface of the specimen was further etched to remove PEK-C, so that the morphology of these specimens may be more clearly shown. The SEM micrograph of the etched specimen is given in Fig. 3(b). A two-phase structure with well-defined domain of PEK-C dispersed in a continuous phase of MA-cured ER is clearly seen. The size of domains is in the range 0.1–2 μm.

The sample of PA-cured ER containing phr 25 PEK-C was transparent. The dynamic mechanical spectrum of the sample (Fig. 4) clearly displays a sharp peak on the tan δ vs T curve, corresponding to T_g of the PA-cured ER phase (138°). It can also be seen that there is a shoulder at the high temperature side of the tan δ vs T curve, corresponding to T_g of the PEK-C-rich phase. The T_g roughly estimated from the shoulder is ca 200°. It is noted that the T_g of the PA-cured ER phase in the blend (138°) is somewhat higher than that of the pure PA-cured ER (133°), implying that there is some PEK-C in the cured ER phase of the blend. These results suggest that the PA-cured ER/PEK-C blend in partially miscible.

The SEM micrograph of the fractured surface of a PA-cured ER/PEK-C blend [Fig. 5(a)] reveals that
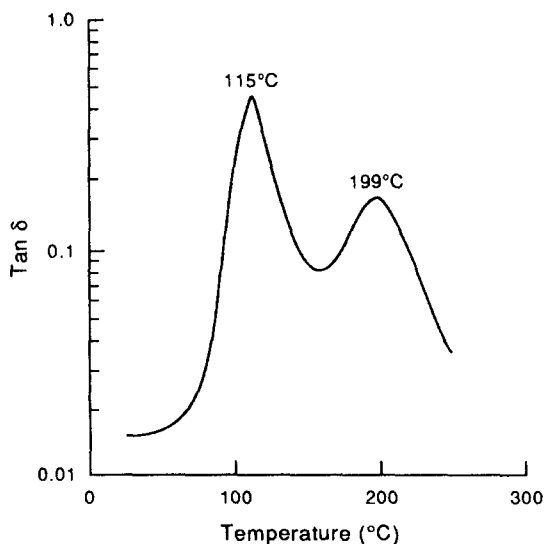

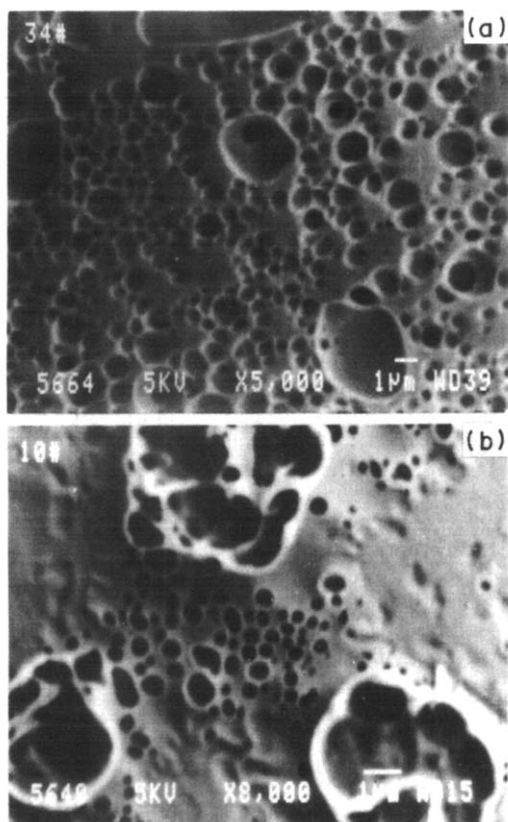Fig. 6. Dynamic mechanical spectrum of 100 DGEBA, 80 HHPA, 25 PEK-C.

Fig. 7. Fracture surface of 100 DGEBA, 80 HHPA, 25 PEK-C. (a) Unetched, (b) etched in chloroform for 15 hr.

the blend is somewhat heterogeneous. The heterogeneity is further shown by the SEM micrograph of the etched specimen [Fig. 5(b)]. It is noted that the blend also shows some characteristic of dual connectivity of phases, i.e. bicontinuous phases. It is interesting from the figure that the cured ER rich phase is dispersed in the PEK-C-rich continuous phase. The domain of the cured ER have sizes in the range 1–3 μm dia. The formation of ER dispersed phase, which is the major composition, implies that the cured ER first segregated from the mixture when phase separation started.

The sample of HHPA-cured ER containing phr 25 PEK-C was opaque. DMA study clearly revealed two T_g's, attributed to the PEK-C-rich phase (199°) and the HHPA-cured ER phase (115°) (Fig. 6). It is obvious that phase separation occurred in the cured blend and PEK-C is immiscible with HHPA-cured ER. The figure also clearly shows that both T_g values are lower than those of pure PEK-C (215°) and the HHPA-cured ER (144°). The lowering of T_gs of PEK-C in the cured blend and the cured ER phase is due to dissolution of some uncured and/or insufficient cured ER in the PEK-C phase.

The SEM micrographs of both the unetched and the etched specimens clearly reveal a two-phase structure; domains of PEK-C-rich phase are dispersed in a continuous phase of HHPA-cured ER (Fig. 7). The sizes of the domain are in the range 0.5–5 μm dia.

DISCUSSION

Our results show that PEK-C is not completely miscible with the three anhydride-cured ER although it is miscible over the entire composition range with both uncured ER, i.e. DGEBA, and phenoxy [23, 25] which may be considered as a model epoxy resin. The overall compatibility and the resulting morphology of the cured blends depend on the choice of cure agent.

The formation of cured ER network caused phase separation in the blends which can be considered as due to the dramatic change in the chemical and physical nature of ER during crosslinking [28, 29]. Phase separation is controlled by both thermodynamic and kinetic factors. As the cure proceeds, the resulting increase in molecular weight causes 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 mixing [30]. At the same time, opening of the epoxy rings, with the formation of polar hydroxyl groups, alters the enthalpy of mixing. Bucknall and Partridge [13] have shown that this factor alone is sufficient to cause phase separation in the poly(ether sulphone)/ER blends, by calculations of solubility parameters using Small's method [31]. On the other hand, differences in kinetics must also be considered. The choice of hardener determines 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 and therefore depend directly on the kinetics of cure.

The PA-cure ER is the most compatible with PEK-C of the three studied. This fact can be primarily considered to be due to PA and PEK-C being aromatic. The HHPA-cured ER/PEK-C blend is least compatible and phase-separated to the largest extent. The aliphatic nature of HHPA make HHPA-cured ER very different in chemical structure from aromatic PEK-C.

REFERENCES

1. W. G. Potter. *Epoxide Resins.* Springer-Verlag, New York (1970).
2. C. A. May and Y. Tanaka (Eds). *Epoxy Resin Chemistry and Technology.* Marcel Dekker, New York (1973).
3. R. S. Bauer (Ed.). *Epoxy Resin Chemistry, ACS Symposium Series No. 114.* American Chemical Society, Washington, D.C. (1979).
4. R. S. Bauer (Ed.). *Epoxy Resin Chemistry II, ACS Symposium Series No. 221.* American Chemical Society, Washington, D.C. (1983).
5. E. H. Rowe, A. R. Siebert and R. S. Drake. *Mod. Plast.* **47**, 110 (1970).
6. J. M. Sultan and F. MaGarry. *Polym. Engng Sci.* **13**, 29 (1973).
7. R. S. Drake, D. R. Egan and W. T. Murphy. *Epoxy Resin II, ACS Symposium Series No. 221,* Chap. 1. American Chemical Society, Washington, D.C. (1983).
8. E. Yorkitis *et al.* In *Rubber-Modified Thermoset Resins* (edited by K. Riew and J. K. Gillham). *Advances in Chemistry Series, No. 208.* American Chemical Society, Washington, D.C. (1984).

9. J. S. Riffle, I. Yilgor, A. K. Banthia, C. Tran, G. L. Wilkes and J. E. McGrath. *Epoxy Resin II, ACS Symposium Series, No. 221*, p. 21. American Chemical Society, Washington, D.C. (1983).

10. J. A. Cecere, J. L. Hedrick and J. E. McGrath. *Polym. Prepr.* **26**, 298 (1985).

11. A. J. Kinloch. In *Polymer Blends and Mixtures* (edited by D. J. Walsh, J. S. Higgins and A. Maconnochie), p. 393. Martinus Nijhoff Publishers, Dordrecht (1985).

12. J. Diamant and R. J. Moulton. *SAMPE Quarterly*, Oct. 13 (1984).

13. C. B. Bucknall and J. K. Partridge. *Polymer* **24**, 639 (1983).

14. R. S. Raghava. *J. Polym. Sci.; Polym. Phys. Edn* **25**, 1017 (1987).

15. J. L. Hedrick, J. C. Hedrick, I. Yilgor, G. L. Wilkes and J. E. McGrath. *SAMPE National Meeting, Proceedings*, **30**, 947 (1985).

16. J. A. Cecere and J. E. McGrath. *Polymer Prepr.* **27**, 299 (1986).

17. C. B. Bucknall and A. H. Gilbert. *Polymer* **30**, 213 (1989).

18. Z. Fu and Y. Sun. *Chinese J. Polym. Sci.* **7**, 367 (1989).

19. L. T. Manzione, J. K. Gillham and C. A. McPherson. *J. appl. Polym. Sci.* **26**, 889 (1981).

20. J. B. Enns and J. K. Gillham. *J. appl. Polym. Sci.* **28**, 2567 (1983).

21. C. B. Bucknall, P. Davies and I. K. Partridge. *Polymer* **26**, 109 (1985).

22. C. B. Bucknall and J. K. Partridge. *Polym. Engng. Sci.* **26**, 54 (1986).

23. Q. Guo, J. Huang, B. Li, T. Chen, H. Zhang and Z. Feng. *Polymer* **32**, 58 (1991).

24. H. Zhang, T. Chen and Y. Yuan. *Chinese Pat.* 85, 108, 751 (1985).

25. Q. Guo, J. Huang and T. Chen. *Polym. Bull.* **20**, 517 (1988).

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

27. M. M. Coleman and E. J. Moskala. *Polymer* **24**, 251 (1983).

28. Q. Guo, X. Peng and Z. Wang. *Polymer Bulletin* **21**, 593 (1989).

29. Q. Guo, X. Peng and Z. Wang. *Polymer* **32**, 53 (1991).

30. P. J. Flory. *Principles of Polymer Chemistry*. Cornell University Press, Ithaca, New York (1953).

31. P. A. Small. *J. Appl. Chem.* **3**, 71 (1953).