Miscibility of epoxy resins/poly(ethylene oxide) blends cured with phthalic anhydride

Luo Xiaolie, Zheng Sixun, Zhang Naibin and Ma Dezhu*
Department of Materials Science and Engineering, Structure Research Laboratory,
University of Science and Technology of China, Academia Sinica, Hefei Anhui 230026,
People's Republic of China
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Epoxy resins (EP)/poly(ethylene oxide) (PEO) blends cured with phthalic anhydride were studied by differential scanning calorimetry and dynamic mechanical analysis. Single glass transition temperatures were observed for all blends before and after curing, indicating a high degree of miscibility. At the same time, a marked deviation from the empirical equation (e.g. the Fox equation) was noticed after curing. This is ascribed to the dilution effect of the PEO component and participation of PEO in the cure reaction resulting in incomplete crosslinking, i.e. the formation of imperfect crosslinking network structures. Fourier transform infra-red spectroscopy provided strong evidence that there is a specific interaction between the EP and PEO molecules.

(Keywords: blends; miscibility; epoxy resins)

INTRODUCTION

Epoxy resins (EP) are widely used as the matrices of high performance composite materials because of their stiffness, chemical resistance and high-temperature stability. However, EP are inherently brittle materials due to their high crosslinking density. Therefore, modification is necessary to increase their applications and an active area of study is to improve their toughness. Generally, improving toughness can be achieved by mixing flexible low molecular weight polymers into the EP/curing agent formulation[1]. If the modifiers are fully compatible with the cured epoxide, the modifier can actually act as a plasticizer. Hence, the toughening effect of the modifiers can be controlled by the degree of compatibility and the composition of the cured product. When a reactive liquid elastomer is mixed with the resins and curing agent at relatively low temperature, the elastomeric component begins to separate from the crosslinked resins and forms a second dispersed phase. The dispersed elastomeric domain acts to alleviate crack propagation through various proposed mechanisms. The main objective of rubber modification is the improvement of fracture properties with the smallest possible sacrifice in modulus and strength. CTBN and ATBN (carboxyl- and amine-terminated butadiene acrylonitrile) copolymers are normally used to achieve this end[2–5]. However, because of their highly unsaturated structures, the application is limited. Recently, polysulfide has also been used to modify EP[6]. The silicone elastomer is often used as an effective modifier and blended physically or chemically in EP to improve toughness. There is also a report in the literature of advanced polymers (e.g. polyimide) being applied to toughen EP[7–11].

The modification of EP has been done mainly with non-crystalline polymer and crosslinked EP/crystalline polymer blends have received relatively little attention. Only a few studies have been reported[12–15]. Noshay and Robeson[12] and Clark *et al.*[13] studied the EP/polycaprolactone (PCL) system cured with anhydride and amine. They came to the conclusion that the latter had better miscibility than the former because of the different intermolecular interactions between the two blend components.

Poly(ethylene oxide) (PEO) is a typical crystalline polymer, and although many studies have been carried out on PEO blend systems little work has been published on EP/PEO blends. The literature[14,15] only reports the miscibility of the amine-cured EP/PEO system using thermal analysis.

In this paper, we study EP/PEO blends crosslinked with phthalic anhydride (PA) by means of differential scanning calorimetry (d.s.c.), dynamic mechanical analysis (d.m.a.) and Fourier transform infra-red (*FT*i.r.) spectroscopy. In particular, we focus on miscibility, interactions between molecules and the properties of the cured systems.

EXPERIMENTAL

Materials

Epoxide (diglycidyl ether of bisphenol A, DGEBA) with epoxide equivalent weight of 185–210 was obtained from Shanghai Resin Factory (Shanghai, PRC).

PEO (number-average molecular weight, $M_n = 20\,000$) terminated with hydroxyl group, alternatively known as poly(ethylene glycol) (PEG, type no. 20000), with an additive content of <0.05 wt% was obtained from Shanghai Chemical Reagent Purchase and Supply Station (Shanghai, PRC).

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* To whom correspondence should be addressed

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PA (chemically pure grade) was produced by Xiangyang Chemical Reagent Factory (Shanghai, PRC).

Sample preparation

DGEBA and PEO were mixed at a temperature above the melting point of PEO (87°C) for a certain length of time and then cooled down to ambient temperature for use.

PA was added into the mixture with continuous stirring until almost all of the PA had dissolved. The blends were cured between polytetrafluoroethylene plates. The standard curing schedule used was 110°C for 1 h and 160°C for 4 h[16]. This practice indicated that PA can easily dissolve when PEO is present in the mixture.

Measurements and apparatus

The differential scanning calorimeter used was a Perkin–Elmer DSC-2. The temperature was calibrated with super pure indium in a dry nitrogen atmosphere. All samples were heated to 160°C and maintained at that temperature for 3 min to remove thermal stress, and then quenched to −90°C. The heating rate used was 20°C min^{-1}. The crystallization temperature (T_c) and the melting temperature (T_m) were taken as the maximum and the minimum of the endothermic and exothermic peaks, respectively; the glass transition temperature (T_g) was taken as the midpoint of the transition.

Cured samples with various PEO contents were mixed with KBr powder and were pressed into flat discs for *FT*i.r. spectroscopy. The spectra were obtained using a Nicolet 170SX-FTIR (resolution 4 cm^{-1}, scanning number 32).

Dynamic mechanical measurement were carried out on Toyo Boldwin DDV IV viscoelastic spectrum apparatus. The test specimen was 60 × 4 × 2 mm (in nitrogen), the temperature range was −150 to 250°C, the frequency used was 35 Hz and the heating rate was 2°C min^{-1}.

RESULTS AND DISCUSSION

D.s.c. and curing reaction

It has been reported that all the uncured DGEBA/PEO blends were miscible in the amorphous phase and the molten state and that all d.s.c. thermograms showed single T_gs with values intermediate between those of the two components[14].

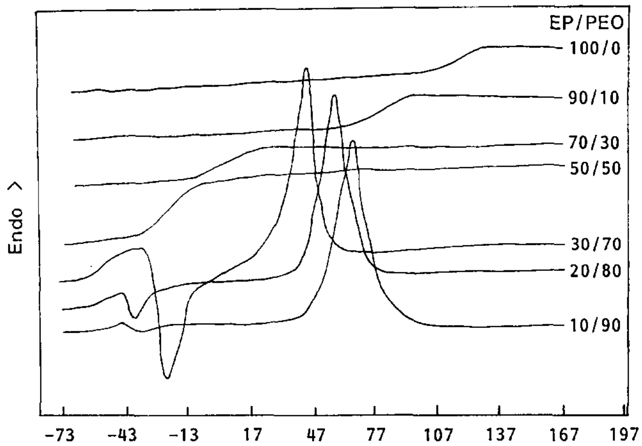

Figure 1 D.s.c. thermograms of DGEBA/PEO blends cured with PA

Table 1 Thermal properties of cured DGEBA/PEO blends (PA 40 p.h.r.)

DGEBA/PEO (w/w)	Cured DGEBA/PEO (w/w)	T_g (°C)	T_m (°C)	T_c (°C)
100/0	100/0	117.0		
90/10	92.6/7.4	79.3		
70/30	76.6/23.4	3.8		
50/50	57.4/42.6	−24.8		
30/70	37.5/62.5	−52.9	45.1	−22.8
20/80	25.9/74.1	−44.0	63.2	−34.7
10/90	12.3/87.7	−38.7	69.3	
1/100	0/100	−61.7	72.3	

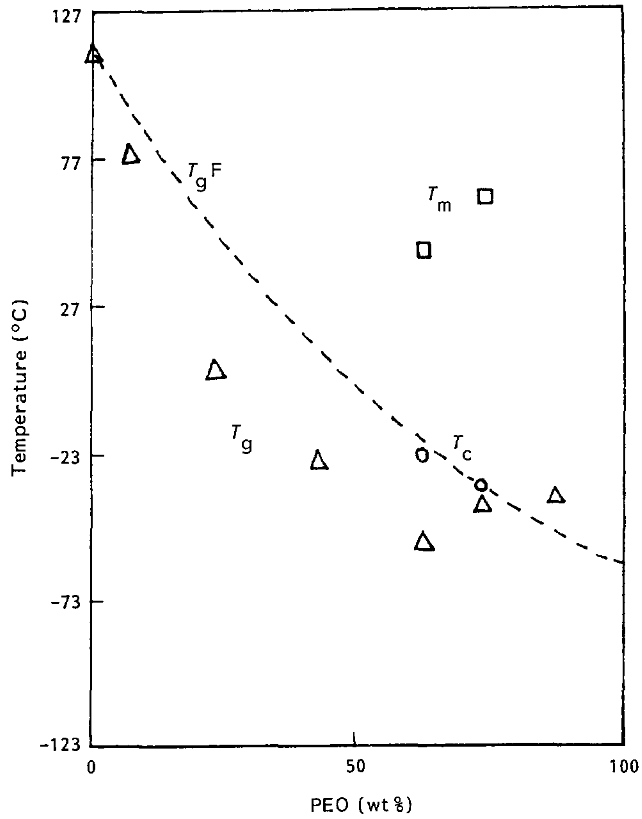

Figure 2 Dependence of T_g, T_c and T_m of quenched DGEBA/PEO blends on the weight per cent of PEO

After addition of PA and curing at 110°C for 1 h and 160°C for 4 h, the blend systems formed crosslinked network structures. All these cured samples were transparent above the melting point of PEO. On cooling, the systems became hazy due to the crystallization of PEO. The above phenomena infer the miscibilization or occurrence of phase separation at least on a scale with dimensions less than the wavelength of visible light. The heating thermograms of the various DGEBA/PEO blend systems show only single T_gs (*Figure 1*). Data are listed in *Table 1* showing that T_g, T_c and T_m values vary regularly with blend composition. Therefore, it can be concluded that the EP/PEO blend system cured with PA is also miscible in the amorphous phase and molten state. Unlike the uncured DGEBA/PEO blend system[14,15], the cured DGEBA/PEO blend system exhibits an obvious negative deviation from the Fox equation at low PEO content (<70%) and a positive deviation at high PEO content (>70%), as shown in *Figure 2*. This phenomenon may be understood in terms of the degree of curing. Even for pure EP, the curing reaction is completed with difficulty on the basis of stoichiometry because of steric hindrance[14]. When the PEO was added to the system, the opportunity for epoxide groups to encounter and collide with curing agent molecules became less since the miscible PEO constituent acts as a diluent. Besides, the viscosity of the system increases as the curing reaction proceeds. Therefore, addition of the second component (PEO) causes incomplete curing and a great reduction in the formation of a perfect crosslinking network. This correspondingly gives rise to less T_gs for the blend systems. On the other hand, PEO with doubly terminated hydroxyl group will participate in the crosslinking reaction and consume some of the PA molecules, and form a block, crosslinked copolymer[18]. For pure DGEBA, the systems have the maximum T_g at the stoichiometry of PA (40 p.h.r.) due to the largest crosslinking density in this case. Above stoichiometry may lead to an increase in the number of free ends in the network structures and PA will act as plasticizer and cause a decrease in the T_g. As for the DGEBA/PEO blend system [e.g. DGEBA/PEO 70/30 (w/w)], the maximum T_g corresponds to a higher PA content ($\sim$75 p.h.r.). This indicates that the PEO with doubly terminated hydroxyl group takes part in the curing reaction and consumes some of the curative molecules. Therefore, the largest crosslinking density of the systems should correspond to the higher PA content. The extraction test also confirmed that PEO participated in the crosslinking reaction and became a constituent of the network (*Figure 3*). As stated above, both these factors will result in the negative deviation from the Fox equation of the cured DGEBA/PEO blend system. At high PEO content (>70%), the distinct positive deviation from the Fox equation should mainly be attributed to the crystallization of PEO and the increase in EP concentration in the residual amorphous phase. An additional increase in T_g is due to the stiffening of the amorphous phase by the reinforcement from PEO spherulites.

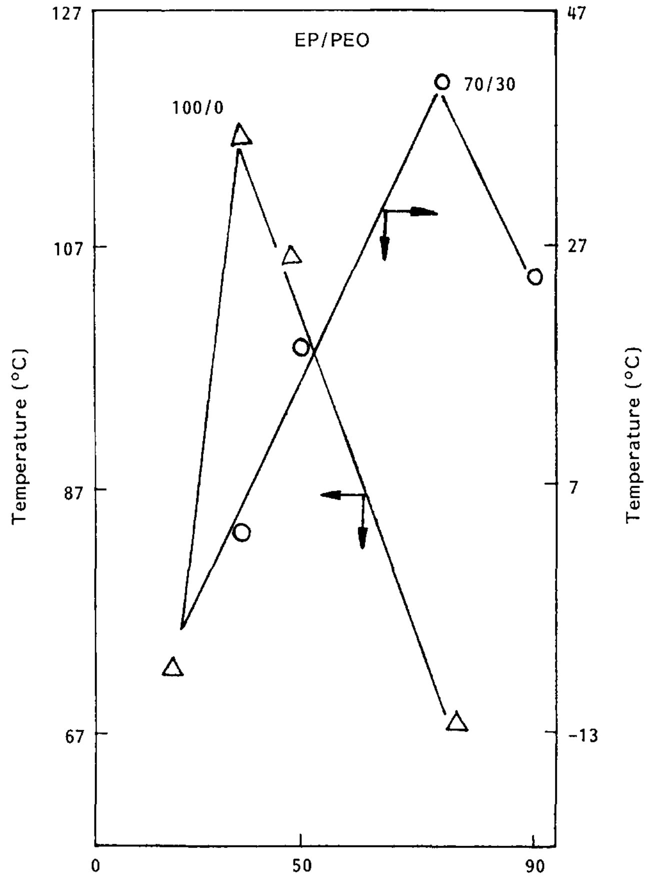

Figure 3 Dependence of T_g of cured DGEBA and cured DGEBA/PEO 70/30 blend on the amount of PA

Figure 2 also shows that the T_c and T_m of quenched samples changed as a function of blend composition. For pure PEO and DGEBA/PEO blends with high PEO content (e.g. DGEBA/PEO 10/90), no crystallization exothermic peaks can be observed because PEO crystallizes quite rapidly and completely during the quenching. For the uncured blend systems, when the PEO content is < 10%, the phenomena of crystallization and melting almost disappear. When the curing agent (PA) was added into the blend, after the standard curing schedule, the blend systems formed a crosslinked network structure. However, T_ms of PEO in the blends similarly decrease with an increase in DGEBA, but the T_cs increase. The above phenomenon is a characteristic of miscible polymer blends. The depression of the melting points of the crystallization component in the miscible blends has been explained by Imken *et al.*[17] and Nishi and Wang[19] thermodynamically and indicates that there is a negative interaction parameter (x_{12}) between the two polymer constituents. Addition of DGEBA results in the increase in T_g (before or after curing) and thus reduces the molecular chain mobility, and also reduces the perfection of crystallization. The amount of curing agent affects crystallization of PEO by changing the crosslinking density of the systems. The T_ms decrease with increasing amount of curing agent, and the T_cs increase because the increase in PA (the increase in crosslinking density) causes PEO crystallization to be difficult and reduces the perfection of PEO crystals.

Dynamic mechanical analysis

The dynamic mechanical behaviour of epoxy resin has been studied in various works. The research has been primarily concerned with the following aspects: (1) high temperature relaxation (0–250°C), which reflects the relationship between condensed state structure and viscoelastic behaviour of EP at high temperatures; and (2) low temperature (−100 to −40°C) relaxation behaviour, which aims to link both dynamic mechanical properties and short range structures (e.g. the mechanism of low temperature relaxation). The dynamic mechanical spectra of all the various blend compositions of EP cured with PA are shown in *Figure 4*. All the crosslinked structures of the DGEBA/PEO blends clearly exhibit a single, sharp T_g intermediate between the constituent values for the amorphous samples. Similar data with various PA contents (by p.h.r.) are shown in *Figure 5*. Therefore, results of the dynamic mechanical property further confirm the experimental results obtained by d.s.c., namely that the DGEBA/PEO system is miscible. In addition, a pronounced secondary loss transition in the range of −100 to −40°C, which is called a β relaxation, is also seen. The structural unit inherent for amine-cured EP presumed to be responsible for this low temperature transition is ($-CH_2-CH(OH)-CH_2-O-$),

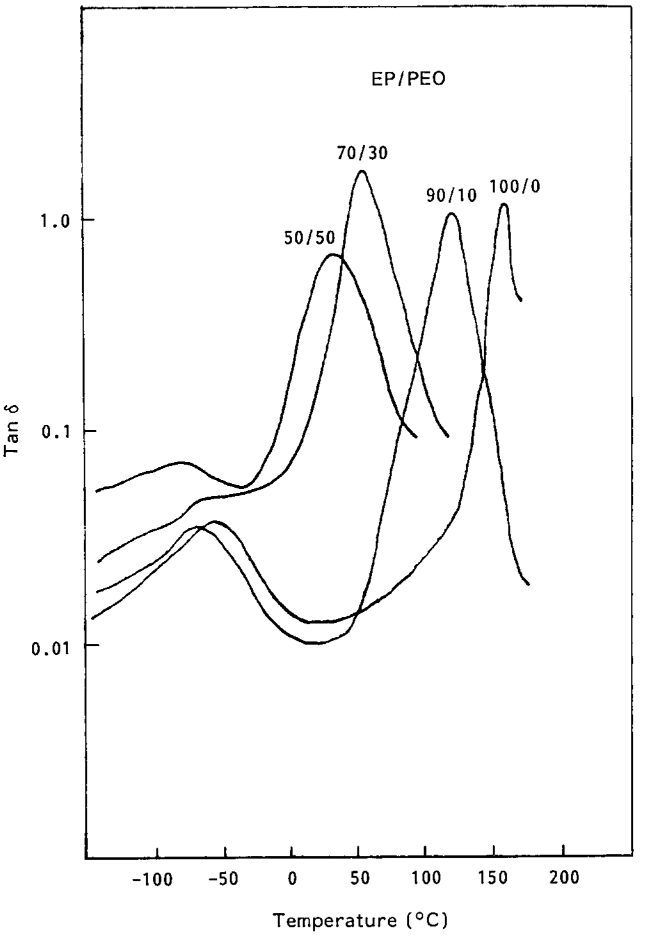

Figure 4 Dynamic mechanical spectra of DGEBA/PEO blends cured with PA (40 p.h.r.)

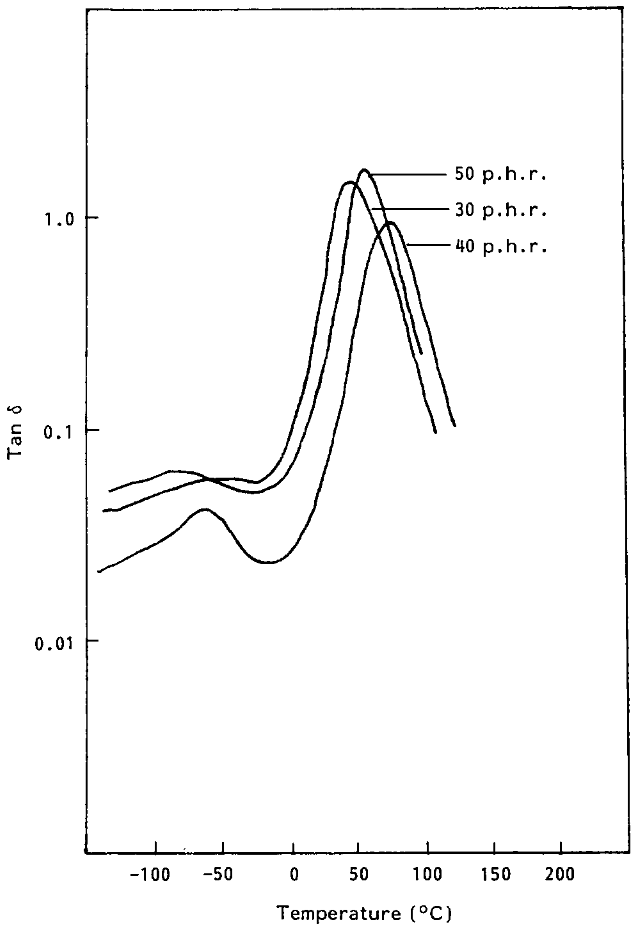

Figure 5 Dynamic mechanical spectra of DGEBA/PEO 70/30 blends containing the various amounts of PA indicated

and the transition corresponds to the rotational mode of this unit[20,21]. For anhydride-cured EP systems, Shimbo *et al.*[22] proposed that the secondary transition is ascribed to the motion of diester segments included in the network structures. For the anhydride-cured blend DGEBA/PEO systems, both these relaxation units are present, which can be illustrated by the *FT*i.r. results (see below). Therefore, the pronounced secondary loss transition should be ascribed to the motion shared by both the hydroxyl ether unit and the diester segments in the network structures. From *Figure 6* it is seen that the β relaxation also shifts to low temperature as a function of PEO concentration like the T_gs.

FT*i.r. spectroscopy*

From the d.s.c. study and the dynamic mechanical properties of DGEBA/PEO cured with PA, it has been concluded that the system is miscible. Here we present *FT*i.r. spectra of the system to interpret the intermolecular specific interactions. The EP used in the study has a small number of pendent hydroxyl groups. After the curative (PA) was added to the DGEBA/PEO blends, the blends were cured using the standard schedule, and a number of hydroxyl groups were produced. *Figure 6* shows the *FT*i.r. spectra from 2500 to 4000 cm^{-1} of the cured blends. The vibrations are assigned to hydroxyl group stretching bands. For pure EP cured with PA, the band at 3503 cm^{-1} should be assigned as the stretching vibration of self-associated hydrogen bonding hydroxyl groups. The hydrogen-bonded hydroxyl band is observed

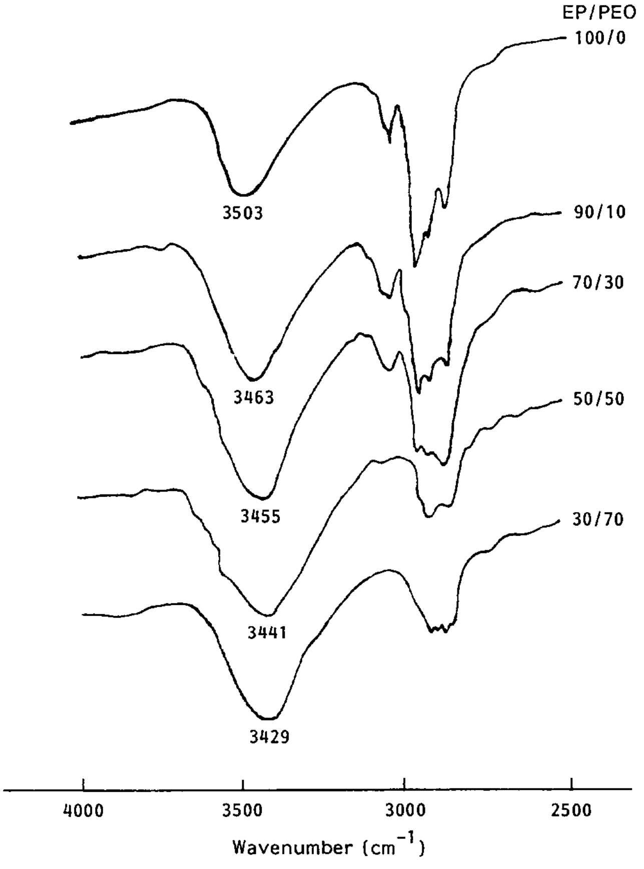

Figure 6 *FT*i.r. spectra in the hydroxy group region for DGEBA/PEO blends cured with PA (40 p.h.r.) after the standard curing schedule

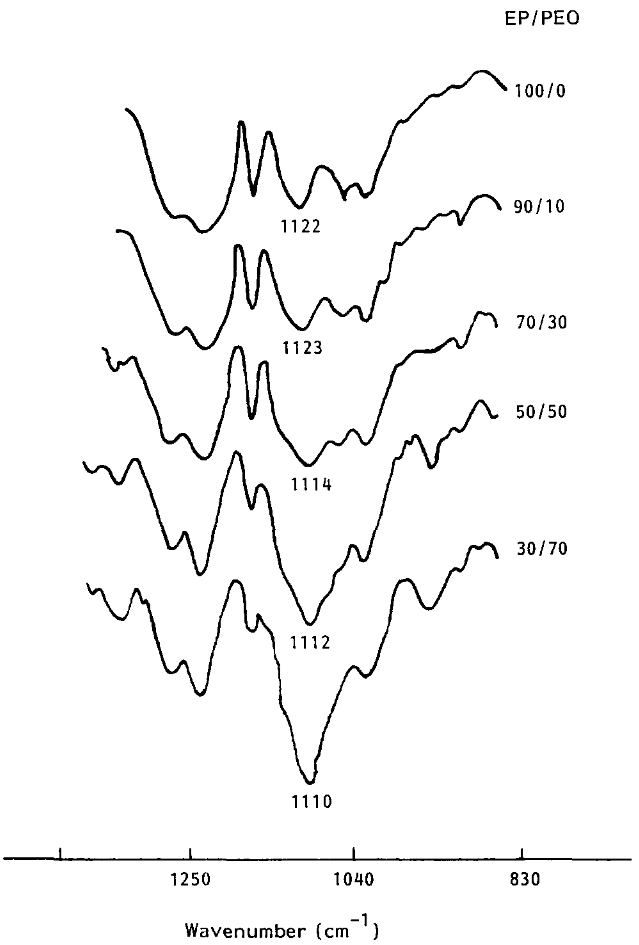

Figure 7 *FT*i.r. spectra of ether bond strips for DGEBA/PEO cured with PA (40 p.h.r.) after the standard curing schedule

to shift to lower frequency after PEO was blended into the system. The implication of the shift is that the hydrogen bonding interaction between epoxide hydroxyl and PEO is stronger than the corresponding self-associated hydrogen bonding in epoxide as in the investigation of phenoxy/PEO reported by Coleman and Moskala[23]. *Figure 7* shows the *FT*i.r. spectra of ether bond strips for DGEBA/PEO cured with PA (40 p.h.r.). Again, a shift to lower frequency was observed. The above data demonstrate that an intermolecular interaction involving both the hydroxyl group of cured DGEBA and the ether bond of PEO (i.e. $-O-H\cdots O\langle$) is present. The *FT*i.r. spectra provide strong evidence that the polymer blend pairs in anhydride-cured DGEBA/PEO are miscible.

CONCLUSIONS

The study of EP/PEO blends using d.s.c. and d.m.a. confirmed that the systems are miscible before or after curing with PA. A single T_g with a value intermediate between both the pure constituent values for the amorphous samples was observed. The extraction test indicated that PEO took part in the crosslinking reaction and caused incomplete curing of the EP and greatly reduced the degree of perfection of the crosslinking network. The presence of DGEBA in the blends hindered the crystallization of PEO, depressed the melting point of PEO and elevated the T_c. This indicated that there is a negative interaction parameter (x_{12}) between the two polymer components. *FT*i.r. spectroscopy suggested the presence of intermolecular interactions, i.e. intermolecular interaction occurring in DGEBA/PEO blends cured with PA was found to be stronger than that occurring in pure cured DGEBA.

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REFERENCES

1 Lee, H. and Neville, K. 'Handbook of Epoxy Resins', McGraw-Hill, New York, 1967
2 Riew, C. K., Rowe, E. H. and Siebert, A. R. *Am. Chem. Soc. Adv. Chem. Ser.* 1976, **154**, 326
3 Romondrik, W. A. and Sohn Geibel, J. F. *Am. Chem. Soc. Symp. Ser.* 1982, **221**, 85
4 Kunz, S. C. and Beaumont, P. W. R. *J. Mater. Sci.* 1983, **16**, 3141
5 Kinloch, A. J., Shaw, S. T., Tod, D. A. and Huston, D. L. *Polymer* 1983, **24**, 1341
6 Kemp, T. J., Wilfor, A., Howarth, O. W. and Lee, T. C. P. *Polymer* 1992, **33**, 1860
7 Bucknall, C. B. and Gilbert, A. H. *Polymer* 1983, **30**, 213
8 Guo, Q. *Polymer* 1993, **34**, 70
9 Guo, Q., Huang, J., Li, B., Chen, T., Zhang, H. and Feng, Z. *Polymer* 1991, **32**, 58
10 Bucknall, C. B. and Gilbert, A. H. *Polymer* 1989, **30**, 213
11 Hourston, D. J. and Lane, J. M. *Polymer* 1992, **33**, 1397
12 Noshay, A. and Robeson, L. M. *J. Polym. Sci., Polym. Chem. Edn* 1974, **12**, 689
13 Clark, J. N., Daly, J. H. and Garton, A. *J. Appl. Polym. Sci.* 1984, **29**, 3381
14 Guo, Q., Peng, X. and Wang, Z. *Polym. Bull.* 1989, **21**, 593
15 Guo, Q., Peng, X. and Wang, Z. *Polymer* 1991, **32**, 53
16 Yang, Y. 'Synthesis Cohesive', Science Press, Beijing, 1986
17 Imken, R. L., Paul, D. R. and Barlow, J. W. *Polym. Eng. Sci.* 1976, **16**, 593
18 Luo, X., Zheng, S. and Ma, D. *J. Polym. Sci., Polym. Phys. Edn* in press
19 Nishi, T. and Wang, T. T. *Macromolecules* 1975, **8**, 909
20 Kaelble, D. H. *Soc. Plast. Eng. J.* 1959, **15**, 1071
21 Cuddy, E. F. and Moacanin, J. *J. Polym. Sci. A* 1970, **8**, 1627
22 Shimbo, M., Ochi, M. and Iesako, H. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 1461
23 Coleman, M. M. and Moskala, E. J. *Polymer* 1983, **24**, 251