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Epoxy resin/poly(ethylene oxide) blends cured with aromatic amine

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Blends of 4,4′-diaminodiphenylmethane-crosslinked diglycidyl ether of bisphenol A/poly(ethylene oxide) (PEO) were investigated. The miscibility of the blends was established on the basis of thermal analysis and dynamic mechanical analysis studies. A single, composition-dependent glass transition temperature (T_g) was seen, and a marked negative deviation from the Fox equation was noticed after the curing reaction. The more PEO content in the blends, the larger is the negative deviation. This is ascribed to the formation of imperfect semi-interpenetrating polymer networks of epoxy/PEO, since the dilution effect of PEO, which is a miscible, inactive diluent, results in an incomplete curing reaction. Therefore, T_g values decrease.

(Keywords: epoxy resin; poly(ethylene oxide); polymer blends)

Introduction

Thermosets based on crosslinked epoxy resins are used extensively as high performance materials, adhesives, matrix materials for fibre-reinforced plastic and electronic encapsulating compounds[1,2]. Considerable attention has been paid to the study of correlations between cured epoxy structure and properties.

The main disadvantage of epoxy resins is low impact resistance, which results from their highly crosslinked structures. Many studies have been conducted to improve toughness. One of the successful modification routines is elastomer toughening[3–6]. For example, carboxyl- terminated butadiene–acrylonitrile rubber, amine- terminated butadiene–acrylonitrile rubber and silicone[7–9] were used as modifiers. The relations between the morphological structure and properties and between the properties and performance are the focus of attention in all these studies. More recently, attempts have been made to toughen epoxy resins with high modulus, high glass transition temperature (T_g) thermoplastics[10–15], especially to modify higher crosslinked epoxides, i.e. tetraglycidyl 4′,4′-diaminodiphenylmethane, novalac epoxy resins. In these cases, the miscibility or solubility of thermoplastics with uncured epoxy resins is necessary.

In many studies, importance was also attached to modification of epoxy thermosets by a compatible polymer. Miscibility, intermolecular specific interactions, reliance of miscibility on molecular weight and control of the morphology of the cured products were examined[16–19]. But only a few investigations have been concerned with epoxy resin/crystalline polymer blends. Clark *et al.*[20] and Noshay and Robeson[21] studied the miscibility of epoxy resin/polycaprolactone (PCL) blends cured with anhydride and amine, respectively. Their results indicated that the miscibilities of epoxy blends with PCL have different reliances on molecular weight due to various intermolecular interactions caused by amine and anhydride-cured products. By means of differential scanning calorimetry (d.s.c.) Guo *et al.*[22,23] investigated the system of epoxy resin/poly(ethylene oxide) (PEO) blends cured with aliphatic amine (tetraethylene pentoamine) and concluded that phase separation takes place as the curing reaction proceeds and with increasing crosslink density. In our laboratory, the ultrasonic behaviours of the DDM-cured epoxy/PEO blends have been examined. The results indicate that the blends possess excellent ultrasonic damping characteristics[24]. In this paper, we present the miscibility of the system by means of d.s.c. and dynamic mechanical analysis (d.m.a.) studies to compare with acid anhydride-cured systems[25].

Experimental

Epoxy resin (diglycidyl ether of bisphenol A (DGEBA)) with epoxide equivalent weight 185–210 was purchased from Shanghai Resin Factory (China). PEO terminated with hydroxy group, with $M_n = 20000$, was obtained from Shanghai Reagent Inc. as described else- where[25]. The curing agent (chemical grade) was 4,4′-diaminodiphenylmethane (DDM), which was produced by Zhangjiagang Reagent Factory (Jiangsu, China).

DGEBA and PEO were mixed at a temperature above the melting point of PEO (80°C) for a sufficiently long time, and then DDM was added to the mixture with continuous stirring until DDM was almost in solution. The blends were cured in polytetrafluoroethylene plates. The curing schedule chosen was 80°C for 2 h plus 150°C for 2 h, to achieve a complete curing reaction[26].

D.s.c. measurement was performed on a Perkin Elmer DSC-2C thermal analysis apparatus in a dry nitrogen

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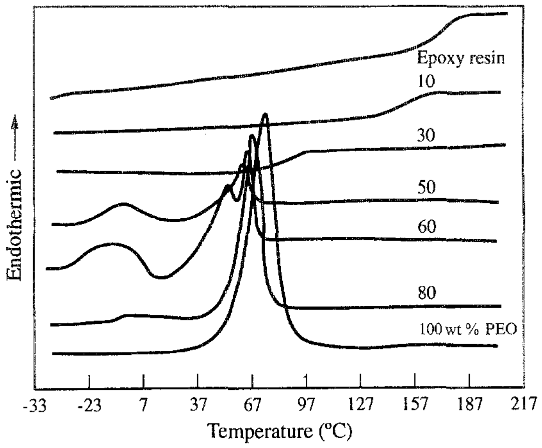


Figure 1 D.s.c. curves of DDM-cured epoxy/PEO blends at a heating rate of 20°C min^{-1}

atmosphere. The instrument was calibrated with indium. To remove the thermal history of the samples, a thermal pretreatment was used. All samples (about 10 mg in weight) were heated up to 160°C and held for 3 min, then quenched to −70°C. All thermograms were recorded at a heating rate of 20°C min^{-1}. The glass transition temperatures (T_gs) were taken as the midpoint of the capacity change. The crystallization temperatures (T_c) and the melting temperatures (T_m) were taken as the temperatures of the maxima and the minima in the endothermic and exothermic peaks, respectively. In a dry nitrogen atmosphere, d.m.a. measurement was conducted on multi-functional internal friction apparatus (torsion pendulum) (Laboratory of Internal Friction and Defect in Solids, Academia Sinica). Forcing vibration mode was used. The testing conditions were as follows: specimen size 60 mm × 4 mm × 1.8 mm; temperature range −150 to 250°C; frequency 0.1 Hz; heating rate 2°C min^{-1}. All specimens were annealed at a temperature above the corresponding T_g for 5 min, and then quenched to −150°C with liquid nitrogen for measurement.

Results and discussion

Differential scanning calorimetry. As found by d.s.c.[22,23], all the uncured epoxy resin/PEO blends were miscible at overall compositions. There was good agreement between the experimental T_g values and those calculated from the Fox equation[27]. When the curing agent (DDM) was added to the binary blends of DGEBA/PEO, the ternary system DGEBA/PEO/DDM was formed. After curing at 80°C for 2 h plus 150°C for 2 h, the ternary blends became a binary system, i.e. the crosslinked epoxy resin blended with PEO.

All the cured DGEBA/PEO blends were transparent above the melting point of PEO, which indicates primarily that the system is miscible in the amorphous state, i.e. semi-interpenetrating polymer networks (semi-IPNs) of epoxy and PEO are formed. When cooled to ambient temperature, the blends with a PEO content greater than 60 wt% became opaque. This resulted from the crystallization of PEO in the blends.

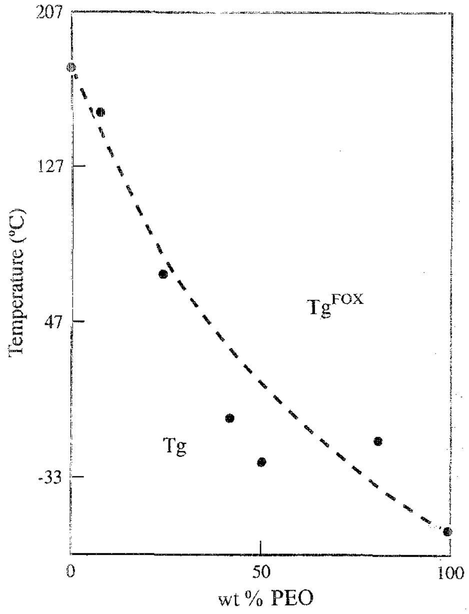


Figure 2 Variation of glass transition temperatures of quenched blend samples as a function of weight per cent of PEO

These epoxy resin/PEO blends cured with DDM were subjected to d.s.c. measurement. As shown in *Figure 1*, all these d.s.c. thermograms revealed single T_gs intermediate between those of the two pure components and varying with blend composition. The existence of single, composition-dependent T_gs suggests that DGEBA/PEO blends cured with DDM are miscible at overall compositions in the amorphous phase. The T_g–composition behaviours may be illustrated by the prediction of the Fox equation:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

where T_{g_i} is the glass transition temperature of the pure blend component, and T_g is that of cured blends. W_i is the weight fraction (see *Figure 2*). The broken line represents calculation of T_g according to the Fox equation. The figure shows that there is a marked negative deviation between the experimental and Fox T_gs. The more PEO content in the blends, the larger is the negative deviation. The negative deviation could be explained based on the following factor. As a miscible, inactive diluent, PEO was added to the epoxy system and progressively resulted in an incomplete curing reaction due to steric hindrance in the highly viscous system. An imperfect semi-IPN is formed and gives lower T_g values (see detailed discussion later). However, there was a positive deviation at higher PEO content (>80 wt%). The phenomenon is ascribed to the crystallization of PEO during quenching. On the one hand, crystallization of PEO causes stiffening of the amorphous phase by reinforcement of PEO spherulites. On the other hand, crystallization also gives rise to the concentration of the amorphous phase. Both factors result in an additional increase in T_g. Similar phenomena were also seen for other compatible amorphous/crystalline polymer blend systems[22,23,25,28,29].

Figure 1 also shows the T_m and T_c variation of both the quenched PEO and the blend samples as a function of blend composition. T_c of PEO increases with increase of epoxy content in the blends. This indicates that

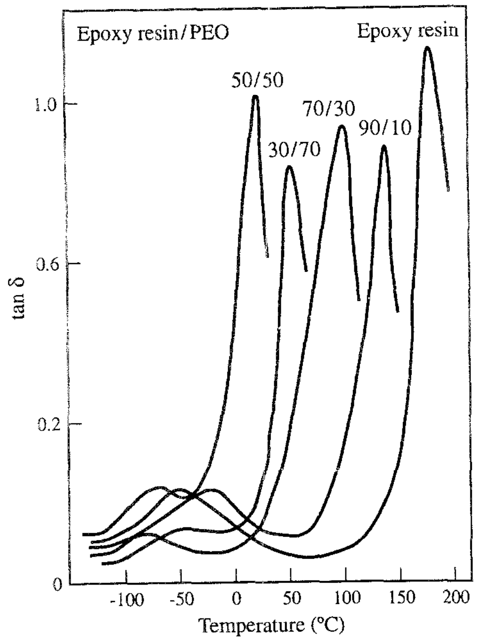


Figure 3 Dynamic mechanical spectra of epoxy/PEO blends with equal molar content of DDM ($r = 1$)

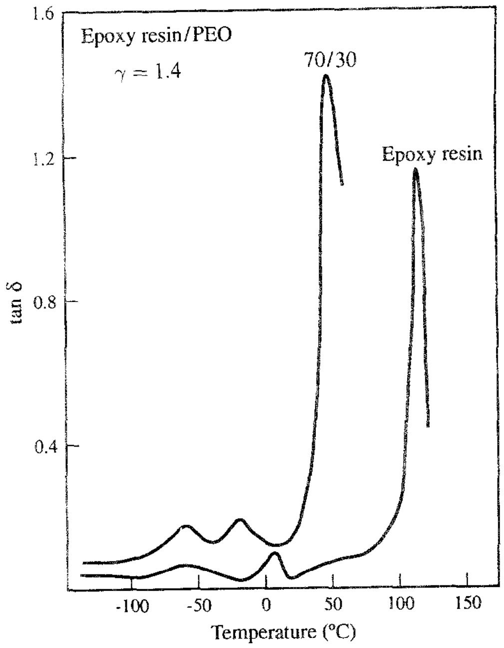


Figure 4 Dynamic mechanical spectra of epoxy/PEO 70/30 blends at r= amine/epoxide = 1.4

Table 1 Dynamic mechanical data for cured DGEBA/PEO blends ($r = 1$)

	Transition (°C)	
PEO (wt%)	T_g	T_β
0	155	−59
10	103	−50
30	74	−78
50	4	−80
70	30	−80
100	−57[a]	–

[a] Dynamic mechanical datum of PEO by Robeson *et al.*[38]

crystallization of PEO in the blends becomes progressively more difficult. For the samples with higher PEO content, no crystallization exothermic peaks were observed owing to the rapid, complete crystallization of PEO during quenching. Correspondingly, the depression of T_m of PEO also was seen. The existence of crosslinked epoxy, which possesses a higher T_g, hinders the crystallization of PEO and also decreases the structural perfection of crystals. Melting point depression of crystalline polymers in miscible blends has been explained by Nishi and Wang[30] and Imken *et al.*[31] thermodynamically, which is indicative of a negative Flory–Huggins interaction parameter χ_{12}.

Dynamic mechanical analysis. Figure 3 shows the viscoelastic behaviours of DGEBA/PEO blends cured with DDM. A single, sharp $\tan\delta$ peak was identified for each cured blend, which corresponded to the glass transition. The T_gs were composition dependent, and intermediate between those of the two pure components. The data are listed in *Table 1*. These results are in good agreement with those from d.s.c. studies and further confirm the full miscibility of the blend system. In addition to the major transition, a pronounced secondary transition (usually designated the β relaxation) in the range of -100°C to 0°C, was also exhibited. In terms of the amine-crosslinked epoxy system, the transition was attributed to the local-mode motion of the hydroxy ether group[32–34]:

$$-(-CH_2-CH(OH)-CH_2-O-)-$$

From *Table 1* it is observed that there was a shift of T_β values to lower temperature with addition of PEO to the system. But for blends with a PEO content of 10 wt%, T_β was much higher than that of pure epoxy resin. It could be related to association of hydroxylether units with PEO. The hydrogen bonding makes motion of hydroxylether units difficult. With increasing PEO content, the motion of the units will become easier, i.e. T_β shifts to lower temperatures due to the plasticization effect of PEO. It should be pointed out that new relaxation peaks (centred at *c.* 10°C) appeared in the dynamic mechanical spectra for cured pure epoxy with excessive curing agent (r = amine/epoxide = 1.4). With addition of PEO to the system, the peak shifted to lower temperature (−25°C) (see *Figure 4*). The relaxation could be relative to the excessive DDM molecules.

Variation of T_g related to DGEBA/DDM ratio for the blends. D.s.c. scans have been carried out on various amine/epoxide molar ratios ranging from 0.7 to 1.4 for pure epoxy and epoxy/PEO blends. In the standard curing conditions for the non-catalysed diamine/epoxide system, the epoxide amine addition reaction is practically complete, as shown by the disappearance of the corresponding exotherm in d.s.c. thermograms, and at the same time indicates that no significant side reaction occurs.

After the curing reaction, the four active hydrogens of diamine molecules are present in the form of the

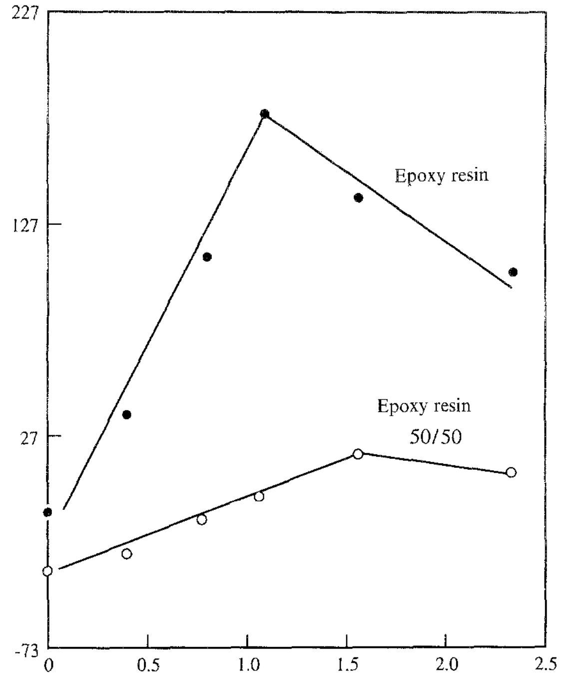
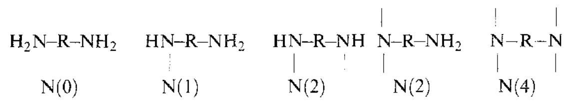


Figure 5 Variation of T_g with DDM/epoxide ratios for pure DGEBA and epoxy resin/PEO 50/50 blend

following structure:



$$\underset{N(0)}{H_2N{-}R{-}NH_2} \quad \underset{N(1)}{HN{-}R{-}NH_2} \quad \underset{N(2)}{HN{-}R{-}NH} \quad \underset{N(2)}{N{-}R{-}NH_2} \quad \underset{N(4)}{N{-}R{-}N}$$

where X is the number of active hydrogens that participate in the reaction, i.e. node point number after reaction, $N(X)$ is the number of the structures with X node points. The structure with $X = 4$ (i.e. $r = 1$) is firmly crosslinked, and determines the T_gs of cured epoxides[35]. *Figure 5* shows the T_g behaviour of both pure DGEBA and DGEBA/PEO blends with various epoxide/amine molar ratios. For the pure epoxy systems, the equal stoichiometry of epoxide/amine systems gave the maximum T_g, as predicted[36]. However, as seen in the figure, the highest T_g was observed in the amine excess region (r= epoxide/DDM = 1.4) for cured DGEBA/PEO 50/50 wt blends. This can be explained as follows. The probability of contact between the epoxide ring and amine group will decrease due to the dilution effect of PEO used as a miscible inactive diluent, and the curing reaction does not go to completion because of steric hindrance in the standard curing condition, i.e. N(4) difficulty comes to the maximum. Only if there is excess curing agent for the blends is the system able to obtain the largest N(4) and highest crosslinking density. It should be pointed out that PEO does not participate in the crosslinking reaction in the curing condition, as demonstrated by a simple extraction test, i.r. and d.s.c. methods. So far, the reason for the deviation between the experimental and Fox-calculated T_g values can be understood.

Conclusion

Epoxy resin/PEO blends cured with DDM are miscible at overall composition. This was demonstrated by d.s.c. and d.m.a. studies. D.s.c. thermograms of all the cured blends gave single, composition-dependent glass transition temperatures (T_g). At the same time, a marked negative deviation from the Fox equation was noticed for the blends. The results indicate that addition of PEO to the DGEBA/DDM system gives rise to an incomplete curing reaction due to the dilution effect of PEO as an inactive diluent. Therefore the systems have lower T_g values, intermediate between the T_gs of the two pure components, which vary regularly. Similarly, d.m.a. spectra also show single, sharp major relaxation peaks. For miscible blends, the crosslinked epoxides possess an infinitely great molecular weight. But the cured blend is still homogeneous in the amorphous state. The specific intermolecular interaction between the two components can play a significant role in the formation of miscible epoxy/PEO semi-IPNs. It has been shown by i.r. spectra[37] that there are hydrogen bonding interactions involving amine-crosslinked epoxy resins. In this case, the cured blend could also possess hydrogen bonding interactions between the amine-crosslinked DGEBA and PEO, e.g. between hydroxyl groups, which are generated from the reaction of the amine hydrogen and epoxide group, and ether bond of PEO ($-O-H\cdots O<$).

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