

MECHANICAL RELAXATION AND INTERMOLECULAR INTERACTION IN EPOXY RESINS/POLY(ETHYLENE OXIDE) BLENDS CURED WITH PHTHALIC ANHYDRIDE*

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ABSTRACT

The miscibility of the blend, composed of a bisphenol A epoxy resins (Diglycidyl ether of bisphenol A) (DGEBA) and poly(ethylene oxide) (PEO) and crosslinked by phthalic anhydride (PA) was studied using dynamic mechanical method. Single glass transition temperatures intermediate between the two pure components were observed for all blend levels. The secondary relaxation mechanism should relate to not only diester linkage, but also hydroxyether structural unit in the system. Fourier transform infrared spectroscopy (FTIR) is applied to study the curing reaction and intermolecular specific interaction of the system. The results indicate the PEO participates the crosslinking reaction, accelerates the curing reaction and make the reaction more perfect. The shifts of the hydroxyl band and carbonyl band demonstrate the presence of the intermolecular interaction in the cured blend. Moreover, the molecular interaction between the side hydroxyl in the hydroxyether units and the ether bond in PEO macromolecules is stronger.

INTRODUCTION

As a type of excellent materials, the crosslinked epoxy resins have been

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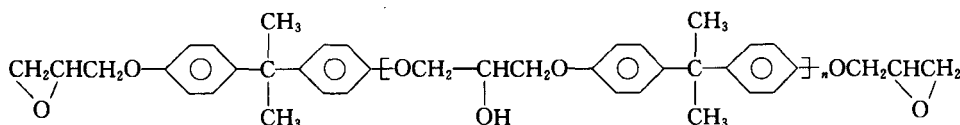
extensively studied. The properties of the cured epoxy resins depend on their structure, composition, and condition of the curing reaction. Up to now considerable attention has been paid on the curing reaction of epoxy resins, and it mainly concerns the curing mechanism of amine-crosslinked^[1-6] and anhydride-crosslinked systems, especially for the system that a tertiary amine can be used as catalyst for the epoxy resins/anhydride reaction^[7-13]. But the previous studies less concerned with epoxy resins blend system, in particular the second blend constituent is terminated with reactive groups (e. g. hydroxyl group). In fact, the addition of the second component to the epoxy/anhydride mixture will give rise to the change of physical properties of the system, and cause a different reaction processes. The change of curing degree and the complex crosslinked network will result in modification of the crosslinked epoxy resins.

In the present work, the curing reaction of the blends composed of epoxy resins (DGEBA)/hydroxyl-terminated poly(ethylene oxide) (PEO) with phthalic anhydride (PA) is discussed. The dynamic mechanical properties of the cured products are investigated to understand the relationship between the relaxation behavior and the structure of crosslinking network. FTIR was applied to investigate the curing reaction and reveal the specific intermolecular interaction in the cured blend system.

EXPERIMENTAL

1. Materials and preparation of samples

Epoxy resins (Diglycidyl ether of bisphenol A) (DGEBA, E-51) with epoxide equivalent weight 185—210 were purchased from Shanghai Resin Factory. Its formula is schemed as follows:



where $n = 1$ (20%), $n = 0$ (80%).

Poly (ethylene oxide) (PEO), $\bar{M}_n = 2000$, terminated with hydroxyl group, was produced by Nippon Oil & Fats Ltd. Co. (Japan) and supplied by Shanghai Chemical Agent Co. (China). Additive content is less than

0.05 wt%.

Phthalic anhydride (PA), chemical pure grade, was produced by Xiangyang Chemical Agent Factory of Shanghai.

FTIR spectra of the mixture films of DGEBA/PEO/PA were measured at ambient temperature once every one hour during curing process. The cured samples of various concentration of PEO were mixed with KBr powder and pressed into thin pieces for FTIR measurements. The curing condition is 110°C, 1 hour plus 160°C, 4 hours. Under such curing condition only those blend samples, in which PEO does not crystallize, were measured by DMA.

2. Measurement and apparatus

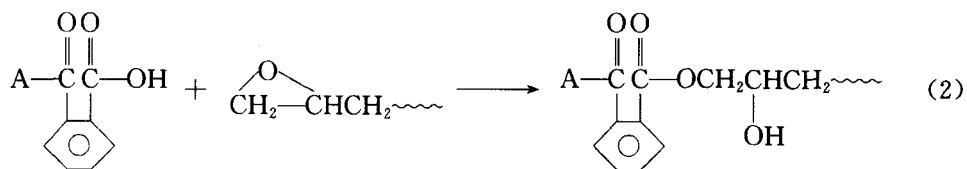
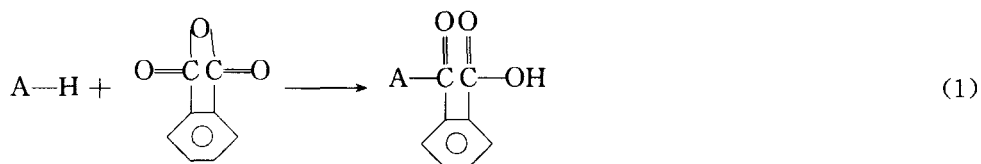
FTIR spectra were obtained at the resolution of 4 cm⁻¹ and with the scanning number of 32 on a Nicolet, 170SX-FTIR apparatus.

Dynamic mechanical spectra were measured on a Toyo Baldwin DDV IV Viscoelastomeric analyzer with the sample dimension: 60 × 4 × 20 mm. Temperature range: -150 ~ 250°C, frequency: 35Hz, heating rate: 2°C/min.

RESULTS AND DISCUSSION

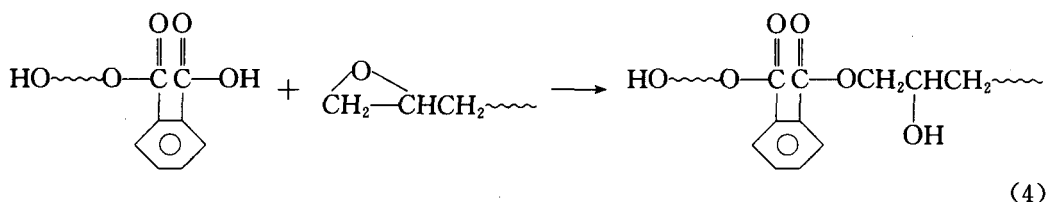
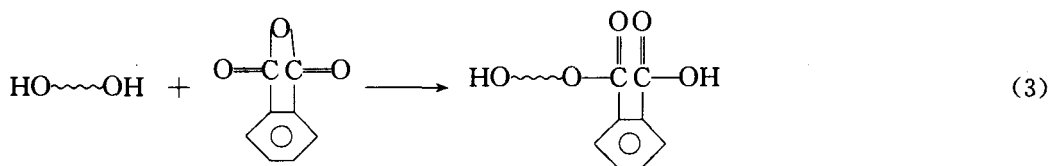
1. The curing reaction

The reaction of mechanism between epoxy resins and anhydride, is well understood^[15], it involves nucleophilic reaction of hydroxyl groups in the hydroxyether, resulting in anhydride ring cleavage and forming an ester linkage and carboxyl group. The latter reacts with epoxide ring, again forming an ester linkage and, simultaneously, a new side hydroxyl in the hydroxyether. Such reaction process is shown in the following scheme^[16]:



Here A-H represents epoxy resin and "H" is the active hydrogen of the side

hydroxyl group in the hydroxyether. In the present study, poly(ethylene oxide) (PEO) terminated with hydroxyl groups is used as the second blend constituent in the mixture with epoxide crosslinked by phthalic anhydride. The primary hydroxyl groups, i. e., the end hydroxyl groups of PEO macromolecules is more active than the side hydroxyl groups of the hydroxyether in epoxy resin. Therefore, the opening ring reaction between the end groups of PEO and anhydride can more easily occur than that between the side hydroxyl groups in epoxide and anhydride molecules. The reaction process in such case is shown as follows:



Here $\text{HO} \sim \text{OH}$ represents the PEO macromolecules. The another hydroxyl group in the PEO macromolecules also can take part in such reaction. In the end, the PEO molecular chain will form the "block"s in the network.

FTIR results^[17] indicated that the addition of PEO to the systems accelerated the disappearance of the characteristic bands of phthalic anhydride ($V_{s,C=O} \sim 1850\text{cm}^{-1}$, $V_{as,C=O} \sim 1773\text{cm}^{-1}$), simultaneously, turning up a strong stretching vibration band assigned to the ester carbonyl vibration $V_{s,C=O}$ in the vicinity of 1730cm^{-1} in the curing reaction as shown in Figs 1 and 2. The curing reaction is carried out at 110°C for 1 hour and 160°C for 4 hours in the mixture with the curative amount (ca. 40 phr.). The crosslinking reaction is accelerated, in addition to the reactive activity of the primary end hydroxyl in PEO, the another reason is the flexibility of PEO molecular chain, which can permit that the reactivable groups can approach each other sufficiently.

From the reaction processes described above, it is obvious that both end hydroxyl in PEO and side hydroxyl in hydroxyether react with phthalic anhydride and produce an ester linkage and a carboxyl group. The latter

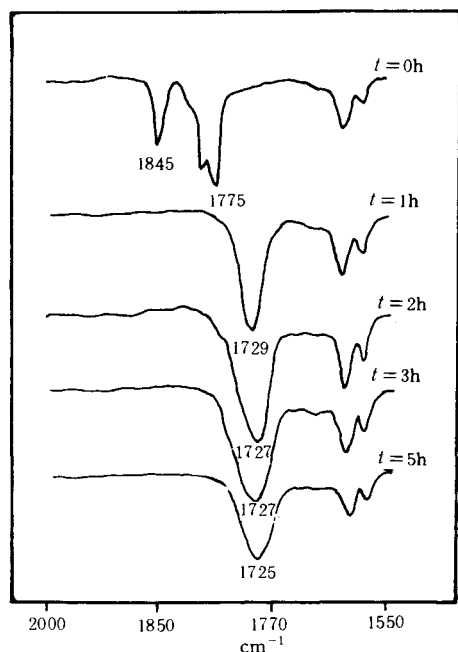


Fig. 1 The carbonyl group stretching band recorded at different cure time for EP/PEO 50/50 blends cured with PA

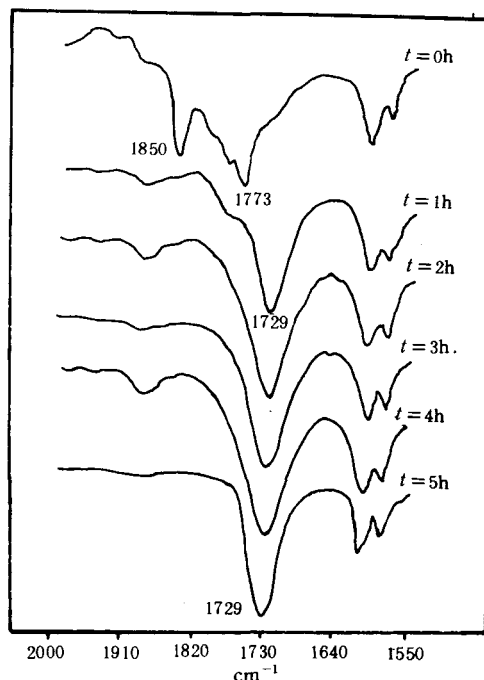


Fig. 2 The carbonyl group stretching band recorded at different cure time for pure EP cured with PA

reacts with the epoxide group and again forms an ester linkage and a new side hydroxyl. Such results mean that the amount of the hydroxyl groups in the system should not decrease with the reaction, except the carboxyl group could not react with the epoxide group. In any case, after the curing reaction the diester groups and the hydroxyether groups coexist.

2. Miscibility of EP/PEO blend cured with PA

On the basis of the thermal analysis results^[14], it can be concluded that EP/PEO blends cured with phthalic anhydride are miscible at melting and amorphous state. Here we presented the results of the study on dynamic mechanical properties of the system. Loss tangent curves as a function of temperature for PA-cured epoxy resins with various blend compositions are shown in Fig. 3. All cured DGEBA/PEO blends clearly exhibit a single, sharp glass transition temperature intermediate between the pure constituent values for the amorphous blend samples. This is indicative of the miscibility, which is in good agreement with DSC results. In addition to the major transition (i. e. glass transition), all the dynamic mechanical spectra

show a low temperature ($-80^{\circ}\sim-40^{\circ}\text{C}$) secondary relaxation peak, which is usually called as β relaxation. For amine-cured system, the β relaxation is commonly referred to as the local mode motion of hydroxyether structural unit ($-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-$)^[18]. In the system cured with an acid anhydride, Shimbo and Ochi^[19] suggested that the relaxation was ascribed to the motion of diester linkage structure formed during the curing reactions. It is surprised that they do not think the hydroxyether structure units in the anhydride-cured system. But in fact it is not so as described above. Therefore, the β relaxation of the blend system cured with acid anhydride should be considered in association with both diester linkage and hydroxyether structural units.

From Fig. 3, it is observed that the β relaxation strength of EP/PEO 50/50, 70/30 blends becomes lower, this is attributed to anti-plasticizing effect^[20]. Similar phenomena have also been observed in blend epoxy resins/PCL^[21], PVC/PCL^[22], and epoxy resin/nonstoichiometric diaminodiphenylmethane(DDM) mixture^[24]. At the same time, with increasing PEO added to the system, the β relaxation peak position shifted to lower temperature. Fig. 4 shows the plotting of glass transition temperature measured by DSC versus PA/epoxy mass ratio.

It is interesting to note that for pure epoxy system, the maximum of T_g is nearly at the halfstoichiometric of curative amount (ca. 40 phr). Theoretically, the cure formulation at the stoichiometry of the curing agent leads to the largest degree of crosslinking, and then the highest glass transition temperature. In fact, the reaction between epoxy resin and PA difficulty is realized stoichiometrically^[27]. It depends on the activity of the reactive groups and diffusion effect of the reaction molecules during the curing process. As the curing process proceeds, the system viscosity becomes larger and larger, it will cause the loss of mobility of reacting molecules in the developed network and lead to incomplete curing reaction. Therefore there are some unreacted PA molecules remaining in the system. The similar results have been reported^[23,24,25]. Of course the excess epoxide groups may directly react with the hydroxyl groups in system especially at the high temperature^[26]. While the flexible PEO macromolecules are added to the system (for example EP/PEO 70/30), the maximum of T_g corresponds to higher PA amount i. e. 75 phr, much closer to stoichiometry. This may be contributed to the plasticization effect of PEO in crosslinked epoxy resins, and the diffusion hindrance of the reactive groups are reduced.

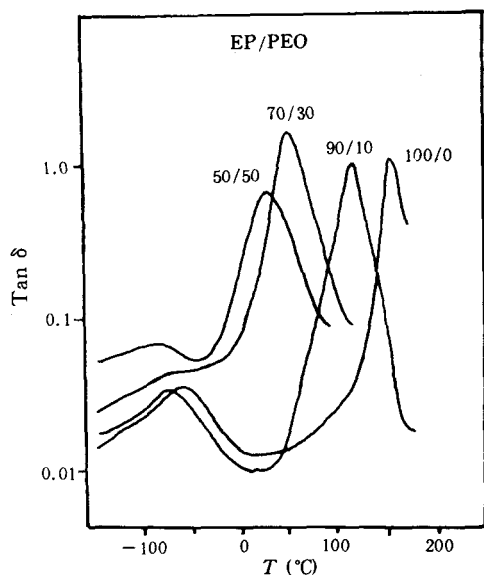


Fig. 3 Dynamic mechanical spectra of PA-cured EP/PEO blends

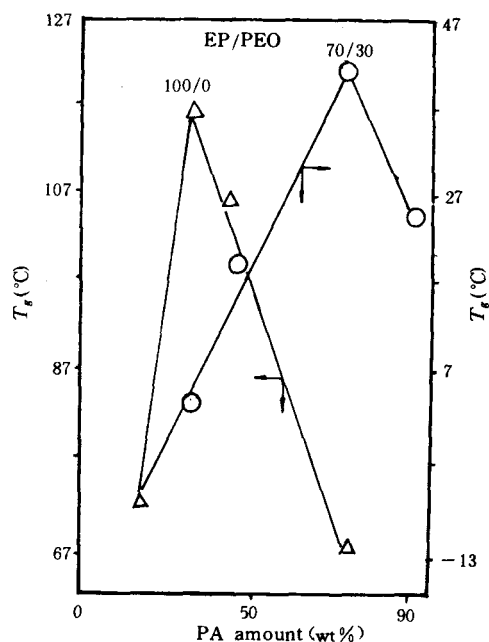


Fig. 4 The plot of glass transition temperatures versus PA/epoxy resin mass ratio

3. The intermolecular interaction

For Fig. 1, there is the distinct band shift of the ester $V_{C=O}$ in the vicinity of 1730cm^{-1} for the cured blends of epoxy resin/PEO. But such phenomenon has not been observed in pure epoxy resin system as shown in Fig. 2, the position of all carbonyl vibration does not change almost. Such difference may be concerned with the different intermolecular interaction.

In the blends with PEO the amount of diester and the hydroxyether groups is more, therefore the molecular interaction will be stronger. The band of hydroxyl group at 3500cm^{-1} for blends EP/PEO 50/50 crosslinked with PA (40 phr) also underwent obvious shift to low wavenumber as shown in Fig. 5. Before curing, the hydroxyl band occurred at 3499cm^{-1} . The hydrogen bond is weaker and it may exist both between different hydroxyl groups and between hydroxyl groups and ether bonds. With the curing reaction proceeding, the stretching vibration band of hydroxyl groups shifted from 3499cm^{-1} to 3449cm^{-1} . This means that the stronger hydrogen

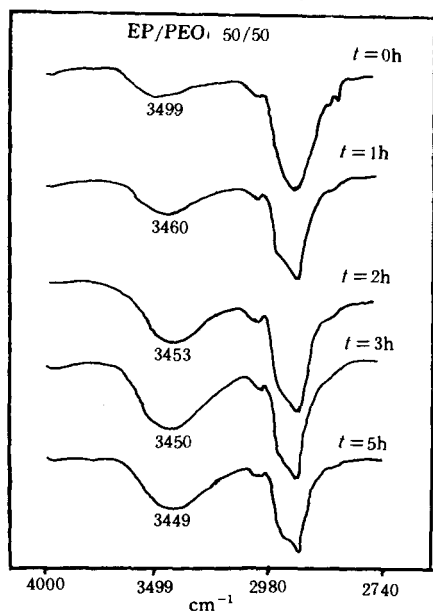


Fig. 5 Hydroxyl vibration region of FTIR spectra recorded at different curing time for PA-cured EP/PEO blends

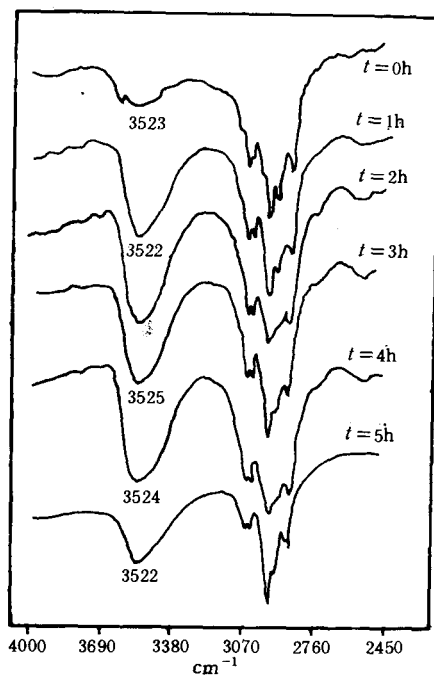


Fig. 6 Hydroxyl vibration region of FTIR spectra recorded at different curing time for cured pure EP

bonds have been formed. In the curing reaction the amount of the hydroxyether structure units becomes more and more. When only EP is crosslinked with PA, in the curing reaction there is not the shift of the hydroxyl group band as shown in Fig. 6. This means that in the curing reaction the hydrogen bond does not undergo evident change. Therefore after curing reaction the hydrogen bonds mainly exist between the side hydroxyl groups in the hydroxyether structure units and the ether bonds in PEO macromolecules. Just such hydrogen bond interaction determined the shift of the hydroxyl band. This conclusion has been proved further by the following experimental results as shown in Fig. 7.

In EP/PEO blends with curing agent PA (40 phr) the band of the hydroxyl group has shifted to much lower wavenumber with increasing the amount of the PEO in blends. Such FTIR experimental results have demonstrated that the hydrogen bond formed between the side hydroxyl groups in hydroxyether structure units and the ether groups in PEO is

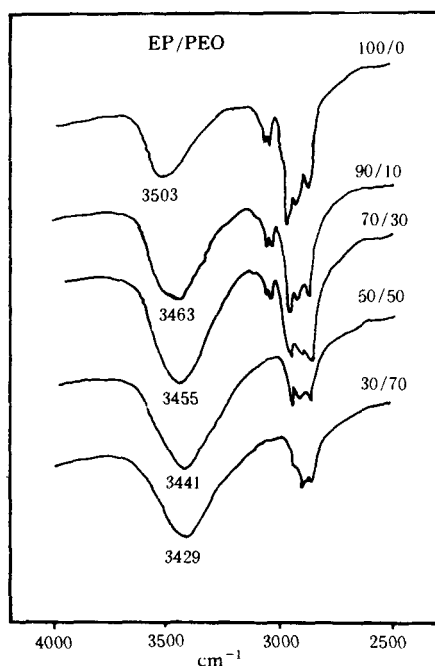


Fig. 7 Hydroxyl vibration region for PA-cured different composition EP/PEO blends

stronger than that between the side hydroxyl groups and the ether bonds in epoxy resin. Coleman et al.^[13] investigated the intermolecular interaction in phenoxy resin/PEO system and also showed that the hydrogen bond between phenoxy resin and PEO stronger than self-associated hydrogen bonding in pure phenoxy resin.

Keywords:

Crosslinked blend of epoxy resin; Miscibility; Mechanical relaxation; Curing reaction; Intermolecular interaction

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