Heat distortion temperatures, glass transition temperatures and extent of chemical cure of some amine-hardened epoxide resins

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The relationship between chemical cure and heat distortion temperature has been examined for some epoxides cured with aliphatic amines. The systems studied exhibit differences in the kinetic nature of the curing reaction and the amount of epoxide left after cure. On postcuring at higher temperatures, heat distortion temperatures are significantly increased, and reach steady values in some, but not all, cases. In some cases large increases in heat distortion temperature can occur without reaction of epoxide groups: this may be due to physical changes in the supermolecular structure of the epoxide. Heat distortion and glass transition temperatures have similar values. In consequence, heat distortion temperatures of components of an epoxide-isoprene copolymer have been examined in relation to theories of the glass transition.

INTRODUCTION

The temperature at which a material begins to distort when it is heated under load is of great practical importance: irrespective of whether the material is being used in the glassy or leathery state, it is to be avoided during service of the material within a structure. In the specific case of epoxides, heat distortion temperature (T_d) usually represents an upper limit of service temperature as structural adhesives and composite matrix resins. It is widely recognised that heat distortion temperatures and glass transition temperatures (T_g) are related and may have quite close values. T_d measured in commercial thermomechanical analysers is often regarded as T_g. This supposition has been examined first, as it determines whether T_d can be discussed in terms of glass transition theories.

We have previously examined performance of an epoxide-isoprene copolymer as an adhesive for single lap joints in aluminium alloy[1]. Close agreement between increasing joint strengths and heat distortion temperatures on postcuring was noted. Now we report a more detailed study of the heat distortion temperatures of this same copolymer, looking at the role and nature of the chemical reaction between epoxide and hardener and the effect of the isoprene component. The ratio of amine to epoxide in the formulations used is one that gave an optimum strength for single lap joints. They contained a slight excess of epoxide, which would be expected to plasticize the cured resin and so probably strengthen the resistance of the joints towards peeling forces[2-4]. A cold curing matrix resin, Shell Epikote 828/Epikure 114, has also been examined.

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EXPERIMENTAL

Materials

Two epoxides were used: the diglycidyl ether of bisphenol A (DGEBA) in the form of Shell Epikote 828; and an epoxide-isoprene copolymer prepared by reacting DGEBA with isoprene and sodium, in tetrahydrofuran as solvent[5-7] The copolymer consists of two phases which separate into two layers on standing. The isoprene-rich upper layer accounts for about 10% of the total volume; the lower layer consists of unreacted DGEBA. The upper layer consists of short polyisoprene chains, terminated at both ends by DGEBA units. Dr. D. H. Richards and his co-workers, who kindly provided the epoxide-isoprene copolymer, demonstrated that optimum adhesive properties are obtained with this same ratio of the two phases which fortuitously arose from the synthesis. In order that the effects of each component can be evaluated, our experiments have been carried out on separate layers of the adhesive and on the mixture of both.

Three hardeners have been employed: di-(1-amino-propyl-3-epoxy) ether (DAPEE), Ajicure B001 and Shell Epikure 114. Ajicure B001 was obtained from Albright and Wilson Ltd., and has an amine equivalent weight of 135. A major component[8] of Ajicure B001 is:

Shell Epikure 114 consists of a solution of cycloalkylamines in benzyl alcohol and its amine molar mass is 72.

We have previously reported the use of the epoxide-isoprene copolymer as an adhesive for carbon fibre com-

Table 1   Epoxide hardener formulations

Epoxide	Hardener			Ratio— NH$_2$/epoxide
Epoxide—isoprene copolymer	100 g	DAPEE	25.2 g	0.47
Top layer	100 g	DAPEE	7.3 g	0.47
DGEBA	100 g	DAPEE	27.2 g	0.47
Epoxide—isoprene copolymer	100 g	Ajicure	30 g	0.45
Top layer	100 g	Ajicure	8.7 g	0.45
DGEBA	100 g	Ajicure	32.4 g	0.45
DGEBA	100 g	Epikure 114	38 g	1.00

(a) For purposes other than i.r. spectroscopy, 40 g aluminium powder (240-dust) was added to formulations with DAPEE and Ajicure hardeners. (b) Shell Epikote 828 has epoxide molar mass of 182-194. A value of 188 was assumed
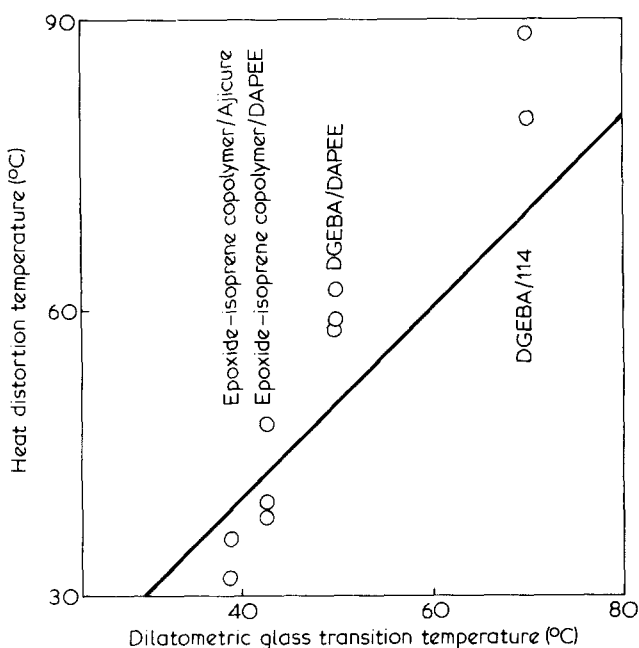

Figure 1   Comparison of heat distortion temperatures with dilatometric glass transition temperatures for some cured epoxides

~ sites[1] and given details of the formulation of the copolymer with Ajicure B001 and DAPEE hardeners. The same optimum formulations, including the aluminium filler, were used here In formulations using the separate layers of the adhesive, the same epoxide-to-amine ratio was used as with the complete material. Formulations are in *Table 1*. Where appropriate, samples were cured at room temperature or postcured in an oven at 80°C.

Measurement of transition temperatures

Heat distortion temperatures of samples cured overnight prior to postcuring were measured using a DuPont Thermomechanical Analyser as a penetrometer. Samples were in the form of discs (2 mm thick, 4 mm radius). The scan rate was 10 K min^{-1} and ranges were usually from 0 to 80°C, although in a few cases they were from liquid nitrogen temperature. A 10 g probe weight was employed. At the heat distortion temperature large vertical displacements of the probe were recorded, and T_d was taken as the intersection of the extrapolated baseline and the line drawn through the region of maximum slope. It is estimated that T_d can be measured to ± 2K by this method.

Glass transition temperatures (T_g) were measured by a dilatometric technique. Glass dilatometers incorporating 1 mm bore precision capillary were used with mercury as the containing fluid. A vacuum technique was employed in filling the dilatometers, which were then heated in a water bath at a rate of 2 K h^{-1}. Meniscus positions were measured using a travelling microscope, and plots of this against temperature showed clear changes in slope, which permitted the estimation of T_g to ± 1 K.

Infrared spectroscopy

Samples of the formulations were spread between two potassium bromide discs, and cured or postcured in this location. Spectra were recorded using a Perkin Elmer 337 i.r. spectrophotometer. The absorbance at 910 cm^{-1} has been assigned to the epoxide ring[9,10], and can provide values of the relative concentration of this group. This was evaluated by comparing the absorbance at 910 cm^{-1} with that at 1610 cm^{-1} which is due to phenyl groups[9,11] and so acts as an internal standard. A baseline correction[12] was applied to each absorbance.

RESULTS AND DISCUSSION

In *Figure 1* T_d and dilatometric T_g are compared for some postcured epoxides. The line is drawn at $T_d = T_g$ to assist comparison. There is some scatter in T_d values but it seems that the difference between T_d and T_g does not exceed about 5°C. However the trend for (T_d-T_g) to increase with temperature seems significant. The small differences between T_d and T_g are readily accounted for by the different heating rates (600 K h^{-1} for T_d and 2 K h^{-1} for T_g). Thus there is reasonable justification in equating T_d with T_g for the epoxides used here.

Fava[13] has similarly compared T_g measured by differential scanning calorimetry with T_d measured according to a standard test method (ASTM D 648—56) for a resin prepared from DGEBA, hexahydrophthalic anhydride and tris-2,4,6-dimethylaminophenol and found that T_d exceeds T_g by about 7 deg. C.

Our earlier communication[1] demonstrated that when DAPEE is the hardener for the epoxide-isoprene copolymer, T_d increases during postcuring at 60°C or 80°C for roughly 12 h. After this time T_d does not increase. Maximum T_d values are 41°C for an 80°C postcure and 46°C for a 60°C
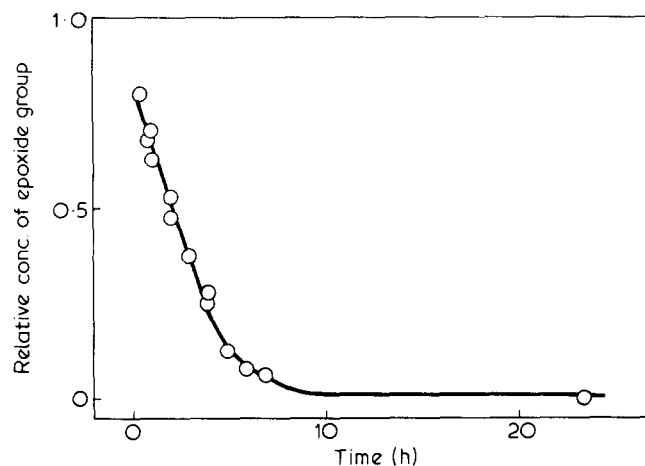

Figure 2   Relative concentration of the epoxide group in epoxide—isoprene copolymer cured with DAPEE at room temperature
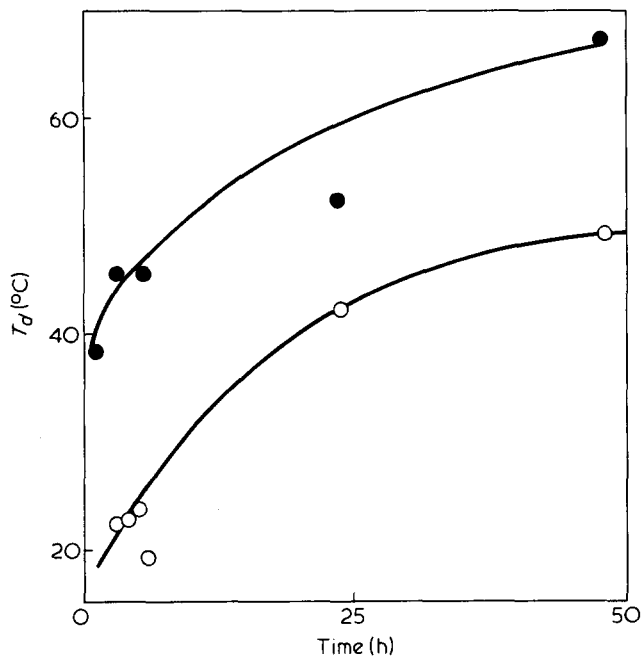
Figure 3 Dependence of heat distortion temperature upon duration of postcure at 80°C for epoxides cured with Ajicure. ●, DGEBA; ○, top layer of copolymer
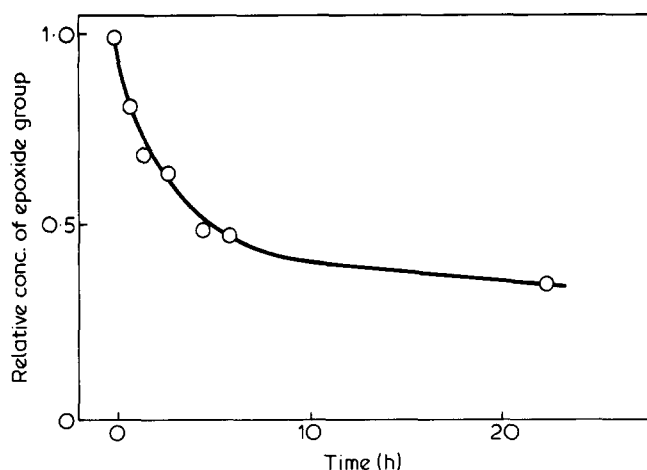

Figure 4 Relative concentration of epoxide group upon curing isoprene—epoxide copolymer with Ajicure at room temperature.

postcure: the difference in values is probably insignificant. Formulations using separate layers of the copolymer with DAPEE hardener show similar behaviour on postcuring at 80°C, reaching maximum T_d values of 30°C for the top layer and 45°C for DGEBA. These changes in T_d during postcure are not dependant upon any chemical reaction of the epoxide group: i.r. spectroscopy results (*Figure 2*) clearly show total consumption of the group after only 10 h of cure at room temperature, leaving none available for reaction in the later postcuring stage. The data fit 1st order kinetics; a good straight line (not shown) was obtained for log (concentration) vs time, with first order rate constant k_1 = (4.91 ± 0.29) × 10^{-5} s^{-1}.

Using Ajicure hardener and the component layers, no limiting value of T_d was obtained after 50 h postcure at 80°C (*Figure 3*). Our earlier communication[1] observed an identical lack of limiting T_d for the complete copolymer when cured with Ajicure hardener at 60°, 80° or 100°C. The plots of T_d against postcure time at 80°C for the whole and for the

component parts are closely parallel, i.e. the change in T_d due to the different components is independent of the extent of postcure. The disappearance of the epoxide group is more complex than in the case of DAPEE hardener. *Figure 4* shows that the epoxide group is not all consumed on curing. Some 40% of the group remains unreacted after 24 h. Upon subsequent postcuring at 80°C, further consumption of the group occurs (*Figure 5*) but even after 144 h at 80°C, about 10% of the epoxide groups remain. Neither of these epoxide removal reactions fits either first or second order kinetics, and so complex kinetic processes are probable. The continuously increasing T_d is likely to be due in part at least to slow crosslinking during postcure, involving the chemical reaction of epoxide groups. By accurate weighings we have ascertained that this increase is not due to the slow volatilization of a plasticizing component.

Figure 6 shows that no maximum T_d is reached by DGEBA/Epikure 114 on postcuring at 80°C, although the rate of increase is less than with Ajicure hardener. It might be possible to draw a plateau through the last four points, particularly if the last point is ignored. I.r. absorbance data for the DGEBA/Epikure 114 system are shown in *Figure 7*. Treatment of this data as a second order reaction with equimolar reactants showed it to be a good fit with a relative second order rate constant of (2.5 ±0.1) × 10^{-5} s^{-1}. Rather surprisingly, in view of the amount of amine hydrogen present, some epoxide remains after curing which is not removed by subsequent postcuring at 80°C for 72 h.

In summary distinctly different curing behaviour occurs with the three hardeners used. With DAPEE 1st order consumption of epoxide groups goes to completion during cure, and T_d has a maximum value. With Ajicure, kinetics of epoxide consumption is complex, but the group is consumed during cure *and* postcure. No upper limit to T_d has been observed. With Epikure 114 removal of epoxide is second order
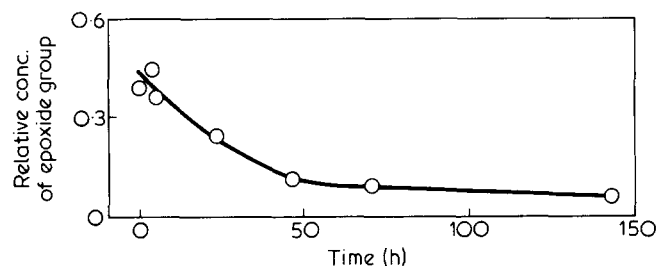

Figure 5 Relative concentration of epoxide group on postcuring isoprene—epoxide copolymer with Ajicure at 80°C
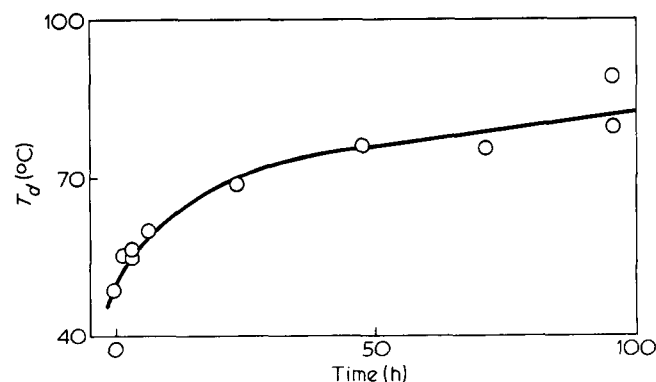

Figure 6 Heat distortion temperature of DGEBA — Epikure 114 on postcuring at 80°C
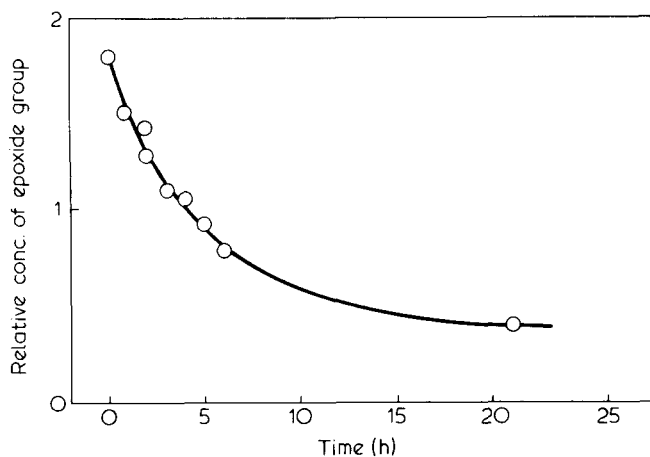
Figure 7 Relative concentration of the epoxide group in DGEBA/ Epikure 114 on curing at room temperature. The relative concentration shown by the last point remained unaltered on subsequent postcuring at 80°C for 72 h

but does not go to completion. Any delayed increase in T_d is slight.

There have been indications that amine cured DGEBA resins have T_g much higher than those reported here. Pogany[14] reported a value of $T_g = 104°C$ for fully cured DGEBA/diethylene tetramine and also showed[15] that departure from stoichiometry caused either by excess amine or excess epoxide caused a depression in T_g. The resins used in our work would all have T_g reduced by this effect.

With DAPEE and Ajicure hardeners there is about 0.5 of an amine group per epoxide group (the exact amounts are 0.47 for DAPEE and 0.45 for Ajicure) so it might be expected that chemical curing here involves reaction of both primary amine hydrogens with epoxide. However with 114 hardener the formulation is equimolar in epoxide and amine groups: this is in accord with the observation of equimolar second order kinetics for the removal of epoxide groups. Explanation of the observed first order kinetics for DAPEE is not so clear.

Second order kinetics have previously been observed for the reaction of amines with epoxides. During reaction of aromatic amines with epoxides, Dobas and Eichler[16] observed and measured 2nd order rate constants for the sequential reaction of each amine hydrogen. The ratio of rate constants for each amine was in the range 3–5, so showing the two hydrogens to have similar reactivities. Smith concluded that the frequently observed 2nd order kinetics may not be diagnostic of a bimolecular mechanism, and demonstrated that a termolecular process, involving a hydrogen-bonded transition state was consistent with observed 2nd order kinetics[17]. Dusek, Bleha and Lunak[18] used gel permeation chromatography to examine the reaction of phenyl glycidyl ether with 1,6-diaminohexane or the phenylglycidyl ether dodecylamine 1:1 adduct. When amine is present in at least stoichiometric quantities, ring opening proceeds from attack by either a primary or secondary amine. However when the epoxide is in excess, hydroxyl groups from earlier curing cause further ring opening. This reaction could only be detected after all amine had virtually disappeared, and was much slower than the reactions with amine.

In two cases, DAPEE and Epikure 114, chemical cure is complete before postcuring, but in postcuring large increases can occur in T_d. It seems reasonable to suggest that the changes which account for the increase in T_d in these circumstances are of a physical rather than a chemical nature.

This supports the development of supermolecular structure in epoxides which has recently been demonstrated by Racich and Koutsky[19] and Aspbury and Wake[20]. The former observed structures 10–60 nm in size on the free fracture surfaces of epoxides, but no consistent relationship between cure and size was observed. Aspbury and Wake, however, found that aggregate size increased on postcuring, and attributed the increase of postcured adhesive joint strengths to this phenomenon. Similar postcuring phenomena have been observed by others. Luttgert and Bonart[21] worked with an acid anhydride hardener at 150°C, and observed using i.r. that the epoxide group disappears within 1 h, but T_g reaches a maximum over a period of about 14 h. In contrast Dobas and Eichler[16] reacted epoxides with 4,4'-diamino diphenyl methane and compared the increase of T_g at 150°C with the amount of uncured material which could be extracted. Here the indication was that postcuring could be fully ascribed to chemical reaction.

When postcured with DAPEE, the isoprene-rich upper layer has T_d of 30°C, whilst postcured DGEBA/DAPEE has the higher value of T_d at 45°C. Comparable values (after 50 h postcure) using Ajicure hardener are 49°C and 66°C, showing the depression of T_d by the isoprene component to be the same (within experimental accuracy) with both hardeners. These data can be examined in relation to theories of glass transition of copolymers, regarding polyisoprene as a plasticizing component. The upper layer consists of short polyisoprene chains (about 6 units) terminated at both ends by DGEBA units. With such short chains it seems unlikely that phase separation of the two components could occur at the same time as crosslinking. The cured material would thus consist of a single phase. It is to such homogeneous mixtures of two components A and B that the *Fox equation*[22], which is based on the free volume theory of the glass transition, and an appropriate equation from the *Gibbs-DiMarzio chain stiffness approach to glass transition*[23] apply:

Fox equation

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}$$

Gibbs--DiMarzio equation

$$T_g = n'_A T_{gA} + n'_B T_{gB}$$

Here T_g is the glass transition temperature of the copolymer and T_{gA} and T_{gB} are those of the constituent homopolymers. W_A and W_B are the weight fractions of the comonomers. n'_A is the fraction of rotatable bonds in component A, and n'_B is the fraction of rotatable bonds in component B. Some discussion has taken place as to whether only those bonds whose rotation could change the configuration of a polymer molecule should be counted here, or whether *all* rotatable bonds should be counted[24]. Here all rotatable bonds have been considered. In this case the homopolymers under consideration are DGEBA crosslinks with an appropriate hardener and polyisoprene. However there is a problem in applying these equations in that T_g of polyisoprene depends upon its isomerisation. We have applied these equations to predict the value of T_g of the type of polyisoprene contained in the copolymer. The predicted values from the *Fox equation* are 280K and 296K when DAPEE and Ajicure are hardeners, and from the *Gibbs--DiMarzio equation* the appropriate values are 289K and 308K. Uncertainty in these values is

fairly high (about ± 10K), whence agreement of these values with each other is good. The polyisoprene within the copolymer has been shown by n.m.r. spectroscopy[5-7] to contain 70% of the 3,4-units, 18% of the 1,2-units and 12% of 1,4-units (mostly *trans*). Ikeda, Wallach and Angelo[25] have reported glass transition temperatures for a polyisoprene prepared under conditions resembling the preparation of the DGEBA — isoprene copolymer, using anionic polymerization with sodium counterion in tetrahydrofuran. As expected the reported isomer contents (mainly 3,4- and 1,2- with only 10% of 1,4-units) are very similar to those in the copolymer. T_g was measured by differential scanning calorimetry, and after extrapolation to zero heating rate the measured value was 284K. Some similar values were also obtained for polyisoprene blocks within styrene copolymers. A further point of interest is that T_g of polydienes seemed only weakly dependent upon heating rates.

Agreement between T_g values for the polyisoprene given above is encouraging: it demonstrates the success with which the *Fox* and *Gibbs—DiMarzio theories* can be applied to these epoxides. The success of this analysis supports the view that the upper layer of the epoxide-isoprene copolymer forms a single phase when cured with aliphatic amines.

CONCLUSIONS

(1) Heat distortion temperatures measured using a thermomechanical analyser are close to dilatometric glass transition temperatures.
(2) Physical rearrangements as well as chemical reactions may lead to large increases in heat distortion temperatures.
(3) The systems studied show quite different kinetics of chemical cure.
(4) The epoxide terminated polyisoprene (upper layer) forms a single phase on curing, and the plasticizing effect of the isoprene units can be accounted for using the *Fox* and *Gibbs—DiMarzio* theories of the glass transition of copolymers.

ACKNOWLEDGEMENTS

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