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THERMOANALYTICAL STUDY OF AN EPOXY RESIN CROSSLINKED WITH AN ALIPHATIC POLYAMINE*

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ABSTRACT

Samples of the cured resins were prepared in the form of cast sheets. The concentration of the amine curing agent (triethylenetetramine) in the epoxy resin (bisphenol-A diglycidylether) was varied between 25 and 100% of the stoichiometric quantity. The cured resins were examined by differential scanning calorimetry, penetration under load as a function of temperature, and dynamic mechanical analysis. It is found that all of these methods provide a useful means of monitoring crosslinking through changes in the glass transition temperature. The dependence of some characteristic secondary relaxation temperatures, and the change in heat capacity at the glass transition, on the concentration of the amine were also investigated.

INTRODUCTION

Epoxy resins are increasingly being used in load bearing structures particularly in the form of fibre-reinforced composites. It is necessary to have firmly based tests for monitoring the extent of reaction and degree of crosslinking in such materials, as the mechanical and physical properties are dependent on these parameters. In the present work various thermoanalytical techniques are applied to a series of cured epoxy resins in which the concentration of curing agent is varied, to assess the utility of these techniques for monitoring the cure of similar resin systems.

EXPERIMENTAL

Materials

The epoxy resin was Shell Epikote 825 which is essentially (~ 97%) the diglycidylether of bisphenol-A (DGBA), or 2,2-bis [*p*-(2,3 epoxypropyloxy) phenyl] propane.

TABLE 1

PREPARATION OF SAMPLES

Sample	*[TETA]*		*Cure*
	Weight %	*% Stoichiometry*	
1	3.4	25.1	16 h at ambient/ 24 h at 120°C
2	6.5	50.4	48 h at ambient/ 20 h at 100–110°C
3	9.5	75.8	17 h at ambient/ 2 h at 120°C 2 h at 160°C
4	12.3	100.7	17 h at ambient/ 8 h at 160°C

The epoxide equivalent weight was 175. The curing agent was Ciba-Geigy HY 951 which is triethylenetetramine (TETA) or 1,2-bis (2 aminoethylamino) ethane. The equivalent weight of TETA for stoichiometric reaction with epoxide is MW/6 = 24.3. Four samples were prepared with different proportions of TETA, as shown in Table 1. In each case the resin and TETA were mixed at room temperature and then degassed in vacuum for about 5 min. The mixture was poured into a mould consisting of two polished aluminium plates coated with a fluorocarbon mould release agent and separated by a rubber spacer approximately 0.3 cm thick.

The oven cure schedules are given in Table 1. It was necessary to postcure samples 3 and 4 at 160°C to complete the curing reaction. In each case the cure cycle was established experimentally to achieve the maximum T_g without causing significant oxidative degradation.

Instruments

The differential scanning calorimeter (DSC) was the DuPont 990/DSC cell. In addition to the normal recorder readout the DSC temperature and heat flow signals were also recorded on punched tape for computer processing, through a digital voltmeter and an interface. The penetration-under-load tests were done with a DuPont thermomechanical analyser (TMA). The quartz probe was cylindrical with a flat-ended tip of 0.064 cm diameter. The samples were placed on the quartz platform, the probe was lowered to touch the surface of the sample, and was loaded with the required weight, and the penetration was recorded as a function of temperature at constant heating rate. For the dynamic mechanical tests a DuPont 980 dynamic mechanical analyser (DMA) was used. The purge gas and thermal transfer medium was nitrogen.

RESULTS

DSC measurements

Heat capacity (c_p) and enthalpy difference data were obtained from experiments

TABLE 2

DSC RESULTS

Sample	Quenched (Q) or Annealed (A)	T_g (°C)	Heat capacity at T_g $c_p(l)$ ($J\ K^{-1}\ g^{-1}$)	$c_p(g)$	Δc_p	$\Delta c_p\ (T_g + 273)$ $J\ g^{-1}$
1	Q	56	1.800	1.395	0.405	133
	A	45	1.625	1.210	0.415	132
2	Q	98	2.016	1.679	0.337	125
	A	96	2.040	1.687	0.353	130
3	Q	126	1.766	1.578	0.188	75
	A	122	1.698	1.471	0.227	90
4	Q	128	1.743	1.529	0.214	86
	A	120	1.863	1.662	0.201	79

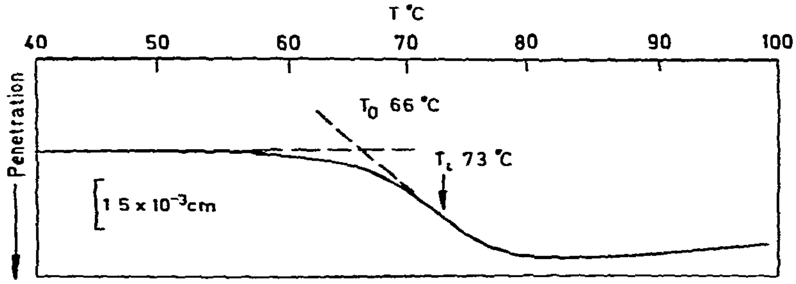

Fig. 1. TMA penetration–temperature curve for sample 1. Heating rate 10 K min^{-1}, load 10 g; probe: flat-ended 0.06 cm diameter.

at a heating rate of 10 K min^{-1}. Each sample was conditioned by holding at about $T_g + 50$ K for 30 min and then either quenching to room temperature by placing it on a metal plate at room temperature, or for the second run by cooling it to room temperature at 0.5 K min^{-1}. From these data the T_gs were determined by the method of Richardson and Savill[1], in which the T_g is calculated as the intersection point of enthalpy–temperature curves extrapolated from well above and below the transition region. Also the heat capacity increment at T_g, Δc_p, was obtained for each sample by extrapolating the experimental c_p data from the regions above and below T_g where c_p shows an approximately linear dependence on temperature ($\sim T_g \pm 50$ K). The results are given in Table 2, in which c_{pl} and c_{pg} are the heat capacity data extrapolated to T_g from above and below T_g, respectively, and $\Delta c_p = c_{pl} - c_{pg}$.

Penetration under load (TMA)

A penetration–temperature curve is shown in Fig. 1 for sample 1. The heating rate was 10 K min^{-1}, the load was 10 g (309.7 kPa) and the sample was a piece of cast sheet about 0.14 cm thick. The sigmoidal shape of the curve in the glass transition region is typical of all the samples and is characterised by an extrapolated onset temperature, T_0, and an inflection temperature, T_i, as shown in Fig. 1. The results for

TABLE 3

TMA PENETRATION UNDER LOAD AT 10 K MIN^{-1} HEATING RATE

Sample	*Load*		*T_o(°C)*	*T_i(°C)*	*No. of repeat runs*
	g	*kPa*			
1	10	310	66 (1.5)	72 (1.7)	5
2	10	310	97	103	1
3	10	310	122 (3.1)	131 (3.6)	5
	20	620	123 (3.9)	132 (2.9)	5
	50	1550	125 (2.5)	132 (2.1)	3
	100	3100	127 (2.1)	134 (1.2)	3
4	50	1550	121 (0.9)	133 (1.5)	5

Standard deviation of T_o and T_i given in parentheses.

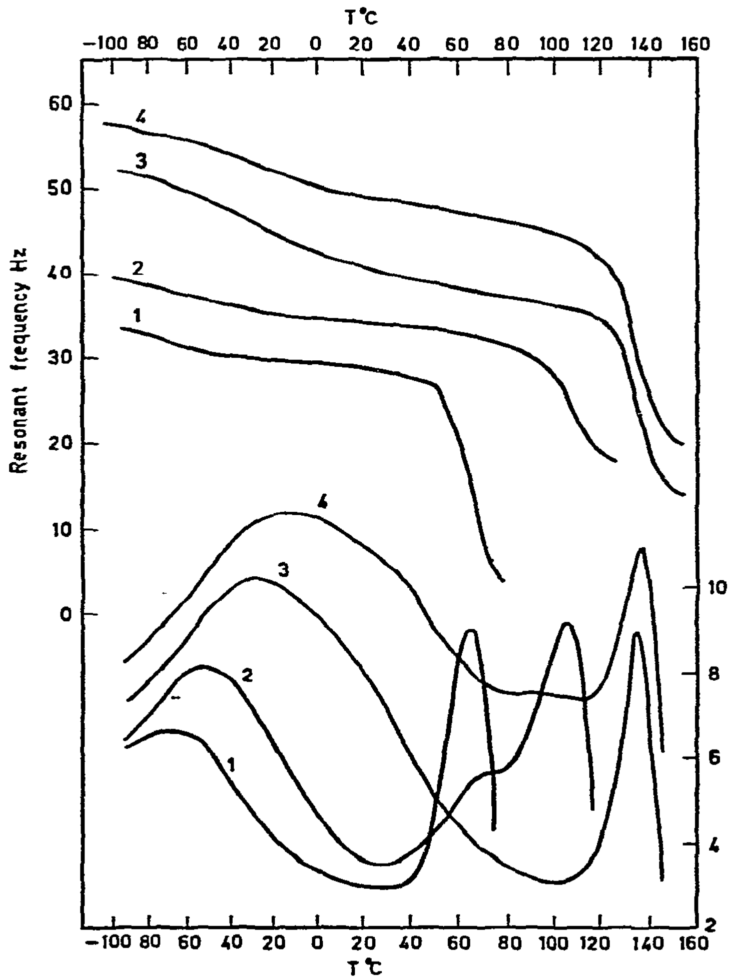

Fig. 2. DMA results. For clarity the resonant frequency and relative damping curves are displaced vertically as follows: sample 2, +15 Hz, +2 dB; sample 3, +10 Hz, +3 dB; sample 4, +15 Hz, +4 dB.

the four samples are summarised in Table 3. All of the tests were at a heating rate of 10 K min^{-1} on samples of about 0.14 cm thickness which had been rapidly cooled to room temperature after equilibration above T_g. For sample 3 the tests were done at four different loads and although there are small increases in both T_0 and T_i with increasing load, these are probably not significant as they are within the standard deviation of the replicate values at each load.

DMA measurements

Samples cut from the cast resin sheets, approximately 0.2 × 1.0 × 1.2 cm, were tested in the DMA instrument at a heating rate of 5 K min^{-1}. Before each run the samples were rapidly cooled from above T_g as described previously. The curves of resonant frequency and relative damping as a function of temperature are plotted in Fig. 2. The characteristic drops in resonant frequency, corresponding to a reduction in modulus, and the peaks in relative damping can be seen in the glass transition regions. A low temperature damping peak is also observed for each sample and is seen to move to higher temperatures with increasing concentration of TETA. The presence of a further transition is also seen for two of the samples. For sample 2 this is observed as a shoulder at about 70°C on the damping peak associated with the glass transition. For sample 4 this occurs at about 90°C. The transition temperatures, T_α, determined from the inflections in the resonant frequency–temperature curves and from the corresponding sampling maxima, are given in Table 4. Also shown are the lower temperature transitions T_β and T_γ determined from the damping maxima.

For the DMA, Young's modulus, E, of the sample is given by the expression[2]

$$E = \frac{(4\pi^2 f^2 J - K)(L/B)^3}{2W\left(\frac{L}{2} + L_c\right)^2}$$

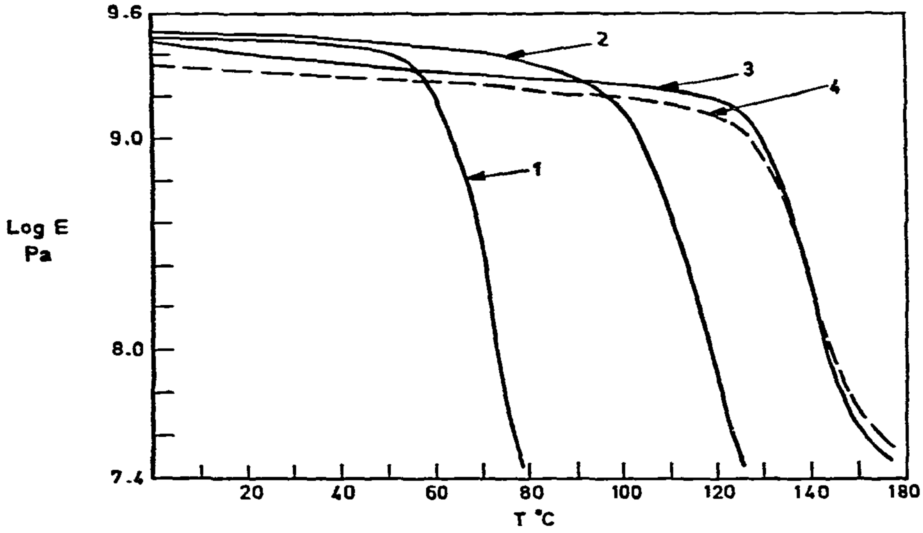

Fig. 3. DMA: Young's Modulus–temperature plots.

TABLE 4

DMA TRANSITION TEMPERATURES

Sample	T_α(°C)		T_β(°C)	T_γ(°C)
	a	*b*	*b*	*b*
1	67	65		−66
2	106	105	~70	−52
3	135	135		−25
4	136	136	~90	−11

a Inflection in resonant frequency–*T* curve.
b Damping maxima.

where f is the resonant frequency, J is the moment of inertia of the DMA arm, K is the spring constant of the pivot, L is the exposed width of the sample between the clamps, B and W are the sample thickness and width, respectively, and L_c is the clamping distance (from the centre of the arm to the end of the clamp). Calibration of the instrument gave $J = 1.830 \times 10^4$ g cm^2, $K = 4.094 \times 10^6$ dyne. cm rad^{-1} (40.94 N cm rad^{-1}).

The moduli, E, calculated from the equation above, are plotted logarithmically against temperature in Fig. 3.

It can be seen that all of the samples undergo a reduction in modulus by a factor of approximately 100 through the glass transition region. An equivalent drop in shear modulus of the same order has been observed in a similar resin system by Pogany[3].

DISCUSSION

The T_g values from the DSC measurements are derived from the heat capacity and enthalpy data outside the transition region, they are also corrected for temperature lag in the specimen, and they should not be dependent on the heating rate[1]. The T_g is, however, dependent on the thermal history of the sample prior to the DSC scan. The annealed (slowly-cooled) samples will be closer to equilibrium below T_g than the quenched samples, and this is reflected in the lower T_gs in Table 2 for the annealed samples.

The results of T_g measurements on the quenched samples by the different methods are compared in Table 5. The most consistent correlation is that between the DSC and DMA methods, the DMA data will be dependent on heating rate and frequency, as well as on the thermal history of the sample, and the observed higher values for T_g are consistent with these effects. The apparent T_gs determined from the TMA, penetration under load, are within ± 5 K of the DMA values and they follow the same trend of increasing T_g with increasing concentration of TETA.

If it is assumed that the resin network is formed simply by the nucleophilic addition of primary and secondary amine groups to epoxide then the molecular

TABLE 5

COMPARATIVE T_g DATA ON QUENCHED SAMPLES

Sample	*T_g(°C)*			
	a	*b*	*c*	*d*
1	56	66	72	67
2	98	97	103	106
3	126	122	131	135
4	128	121	133	136

a DSC, T_g; b TMA, T_0; c TMA, T_1; d DMA (frequency–T inflection).

weight between crosslinks should decrease with increasing amine concentration to reach a minimum at the stoichiometric proportion of amine. It is known that, in general, the T_g of a polymer network increases with decreasing molecular weight between crosslinks but the quantitative relationship is not simple[4, 5]. The present results show that T_g increases with increasing TETA concentration up to the 75% stoichiometric level. There is however no significant difference between T_g at the 75 and 100% stoichiometric levels, implying that the degree of crosslinking is approximately the same at these levels. This could be due to additional crosslinking at the lower TETA concentrations through epoxide etherification reaction catalysed by amine groups[6]. It is interesting that this does not appear to occur to the same extent with the amine of similar structure, diethylenetriamine. For the reaction of this amine with essentially the same epoxy resin, Pogany[3] found a steady decrease in T_g and increase in molecular weight between crosslinks as the amine concentration used reduced below the stoichiometric quantity.

The DMA data in Fig. 2 and Table 4 show the low temperature transition, occurring at T_γ, as the temperature of a secondary maximum in relative damping. T_γ has an approximately linear dependence on TETA concentration, as indicated by Fig. 4. Thus T_γ would be a useful analytical indicator of the composition of a cured specimen of this system. The γ-relaxation in cured epoxy resins has been reported previously and it appears to be associated with the $-CH_2CH(OH)CH_2O-$ group[3, 7].

Arridge and Speake[8] studied specimens made from DGBA cured with TETA (7% excess over the stoichiometric quantity). From loss tangent measurements made with a torsion pendulum at a frequency of 0.67 Hz, T_γ was found to be about −40°C. Ultrasonic measurements at frequencies in the range 10 KHz to 2 MHz and the torsion pendulum data indicated that the activation energy for the γ-relaxation was[8] 23 kcal mole^{-1} (96 kJ mole^{-1}). For this activation energy T_γ would be shifted from −40°C at 0.67 Hz to −20°C at 35 Hz, which is in fair proximity to the observed DMA damping maximum of −11°C at 35 Hz.

The increase in heat capacity at T_g, Δc_p, is given for each sample in Table 2. It is seen that Δc_p tends to decrease with increasing degree of crosslinking, from about

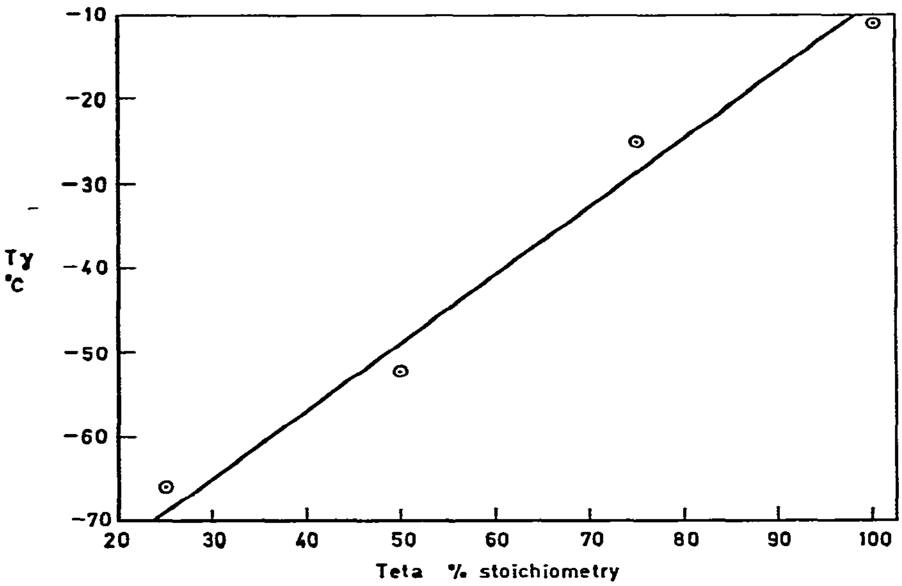

Fig. 4. Dependence of T_γ on TETA concentration.

0.41 J K^{-1} g^{-1} for sample 1 to about 0.21 J K^{-1} g^{-1} for samples 3 and 4. For linear amorphous polymers it has been claimed that the product Δc_p T_g is a constant[9]. The values of this product for the present system are given in Table 2. A downward trend in Δc_p T_g is seen with increasing degree of crosslinking.

CONCLUSIONS

The apparent glass transition temperatures measured by heat capacity and enthalpy change (DSC), penetration under load (TMA), and dynamic mechanical damping (DMA) all show the same trend of increasing with the degree of crosslinking. The samples with TETA concentrations of 75 and 100% stoichiometry have similar T_gs, implying similar levels of crosslinking.

The apparent T_gs derived by the DMA method are 8 to 11 K greater than those obtained by DSC, which is consistent with heating rate and frequency effects. All of the methods are suitable for monitoring the cure of the resin system. The DSC method has the advantage of internal corrections for heating rate effects, while the DMA method gives useful additional data on modulus changes and low temperature relaxations. The low temperature transition, T_γ, increases with increasing TETA concentration. The change in heat capacity at T_g, Δc_p, and the product Δc_p T_g decrease with increasing degree of crosslinking.

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