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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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J. M. Barton[a]
[a] Materials Department, Royal Aircraft Establishment, Farnborough, Hants, England

To cite this Article Barton, J. M.(1974) 'Monitoring the Cross-Linking of Epoxide Resins by Thermoanalytical Techniques', Journal of Macromolecular Science, Part A, 8: 1, 25 — 32
To link to this Article: DOI: 10.1080/00222337408065810
URL: http://dx.doi.org/10.1080/00222337408065810

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J. MACROMOL. SCI.—CHEM., A8(1), pp. 25-32 (1974)

Monitoring the Cross-Linking of Epoxide Resins by Thermoanalytical Techniques

J. M. BARTON

Materials Department
Royal Aircraft Establishment
Farnborough, Hants., England

ABSTRACT

The curing reaction of bisphenol A diglycidylether with 4,4'-diaminodiphenylmethane (DDM) was studied by thermoanalytical methods. The overall reaction was monitored through the exothermic heat of reaction by differential scanning calorimetry (DSC), and a method is developed for predicting isothermal conversion-time curves over a wide temperature range from the results of two dynamic DSC scans. The reaction mechanism is not specified but it is assumed not to change with conversion, and the rate is assumed to be controlled by a single rate constant of the Arrhenius form. A series of fully cured resins prepared with varying DDM concentration is characterized by penetrometer, thermal expansion, and DSC methods. The T_g's of these resins are compared with those obtained using the stoichiometric quantity of DDM and reacted to different calorimetric degrees of cure. The T_g of the resin increases by about 70°C in the final 10% of the curing reaction where ΔH measurements are least sensitive, so that the final stages of cure are best monitored by T_g measurements.

The value of thermoanalytical techniques for investigating the curing reactions of epoxide resins has been demonstrated previously [1-4]. From a study of the curing reaction of the diglycidyl ether of bisphenol-A (DGEBA) with hexahydrophthalic anhydride, Fava [1] has shown that isothermal cure curves can be predicted from dynamic differential scanning calorimetry (DSC) experiments without any assumptions being made about the form of the kinetic equations or reaction mechanism. A disadvantage of the method is that data from a large number of DSC scans over a wide range of heating rates are required.

In this paper a method is developed for obtaining a profile of resin cure characteristics, and predicting isothermal cure curves, from two dynamic DSC experiments at different heating rates. The method is evaluated for the system DGEBA/4,4'-diaminodiphenylmethane (DDM). The relative sensitivities of different thermoanalytical techniques for assessing extent of cure are also discussed.

It is assumed that the overall rate of cure is given by

$$d\alpha/dt = kf(\alpha) \tag{1}$$

where α is the fractional conversion which for a calorimetric experiment equals $\Delta H_t/\Delta H_0$, ΔH_t being the heat of reaction up to time t and ΔH_0 the overall heat of reaction. For a DSC experiment, therefore, the rate of cure $d\alpha/dt = (dH/dt)(1/\Delta H_0)$. The quantity $f(\alpha)$ is unspecified and depends on the reaction mechanism. The rate constant k is assumed to have the usual Arrhenius form: $k = A\exp(-E/RT)$. If the activation energy, E, is known, then the rate, $r = d\alpha/dt$, determined at one temperature and conversion can be reduced to a corresponding rate at a different temperature and the same conversion:

$$\ln(r_1/r_2) = (E/R)(T_2^{-1} - T_1^{-1}) \tag{2}$$

In this way a rate vs conversion plot obtained from a dynamic DSC experiment can be reduced to corresponding plot at a single temperature. Fava [1] has shown that the area under a plot of 1/r, for a fixed temperature, against α is the time for a given conversion at that temperature,

$$\int_{\alpha_0}^{\alpha}(dt/d\alpha)d\alpha = t_\alpha - t_{\alpha_0}$$

An isothermal cure curve can thus be built up from the reduced rate vs α data, and using the activation energy this can be transformed into a family of isothermal curves at different temperatures.

E can be obtained from two dynamic DSC scans at different heating rates by the use of Eq. (2) since a given degree of conversion in each of the scans will correspond to different reaction rates and temperatures.

EXPERIMENTAL

The epoxide resin was Shell Epikote 825 which is essentially (96 to 99%) DGEBA. The epoxide equivalent weight is 175. The DDM was recrystallized twice from acetone/toluene. The required amount of DDM was dissolved in the resin using a small quantity of dichloromethane as cosolvent. The dichloromethane was removed under vacuum at 70 to 80° C, and the resin was either used in the DSC curing experiments or was fully cured as a cast sheet (0.5 to 1.5 mm thick) in an oven using the cure schedules given in Table 2.

DSC measurements were made on resin samples of about 20 to 30 mg with the Du Pont 900/DSC instrument, operating in a nitrogen atmosphere. Pure Sn, In, and Hg were the calorimetric standards.

The Du Pont 941 instrument was used for the thermomechanical tests. Any surface oxidized layer on the cast resin samples was removed with fine emery for the penetrometer tests, which were made with a cylindrical quartz probe, 0.025 in. diameter, and a 20-g load. A quartz probe of 0.100 in. diameter was used for the thermal expansion measurements.

RESULTS AND DISCUSSION

The DSC curing experiments were all on the stoichiometric mixture of diepoxide and diamine (28.3 phr of DDM). The total exothermic heat of reaction was found from scans at 20° C/min to be 97.1 cal/g. Data from two DSC scans at heating rates of 10 and 20° C/min are shown in Table 1. The activation energies derived using Eq. (2) at different values of α are also included in the table. Apart from the values for $\alpha = 0.1$ and 0.8, the scatter in E is small. The average value for E, with 95% confidence limits, is 12.6 ± 1.4 kcal/mole, and this is close to the value determined from isothermal experiments: 11.9 kcal/mole.

The data from a DSC scan (10° C/min) were reduced to 100° C using Eq. (2) for E = 12.6 kcal/mole. The original and reduced data are shown in Fig. 1 as plots of r_T (T = 120 to 230° C) and r_{100} against α. The plot of $1/r_{100}$ against α is shown in Fig. 2. Integration of the area under this plot with a lower limit $\alpha_0 = 0.0025$ gave the predicted 100° C isothermal cure curve. These data were transformed into a family of isothermal curves at different temperatures using

TABLE 1. Determination of Activation Energy (E) from DSC Scans at 10 and 20°C/min

α	T_{20} (°C)	T_{10} (°C)	$10^2 r_{20}$ (min^{-1})	$10^2 r_{10}$ (min^{-1})	E (kcal/mole)
0.1	168	150	17.0	8.1	15.29
0.2	179	159.5	28.4	15.7	11.82
0.3	185	165	41.6	23.2	11.66
0.4	189	169	51.0	28.8	11.62
0.5	192.5	172	54.0	30.9	11.23
0.6	196	175.5	51.4	28.7	11.90
0.7	200.5	179.5	42.6	23.1	12.12
0.8	206.5	190	28.4	15.5	16.22
0.9	216.5	194.5	13.6	7.9	11.25

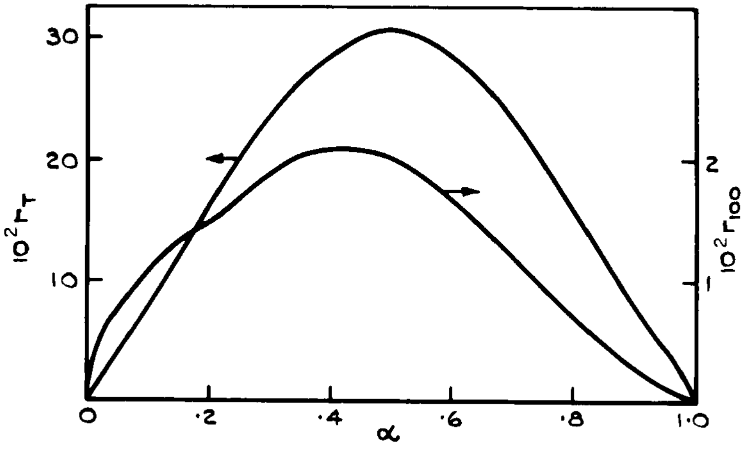

FIG. 1. Dependence of dynamic rate (r_T) and 100°C reduced rate (r_{100}) on conversion for 10°C/min DSC scan.

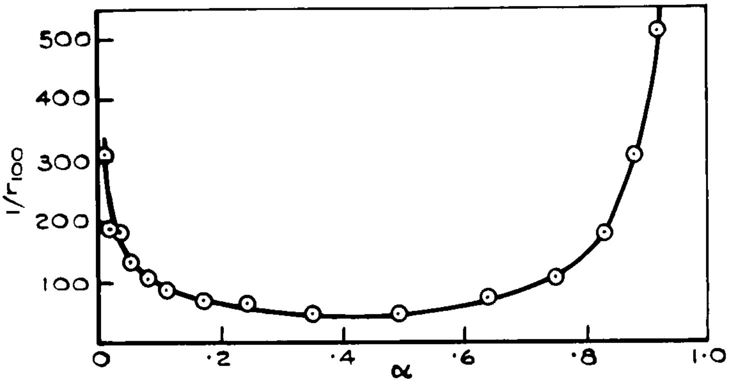

FIG. 2. Dependence of $1/r_{100}$ on conversion.

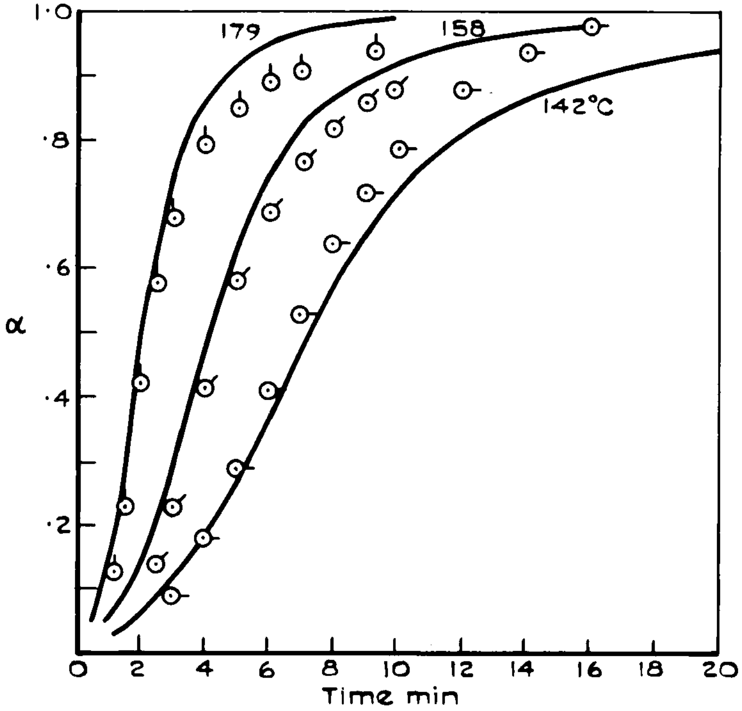

FIG. 3. Isothermal cure curves predicted from dynamic data (solid curves) and corresponding isothermal experimental points.

Eq. (2) and the relationship $(t_2/t_1)_\alpha = (r_2/r_1)_\alpha$ for temperature T_1 and T_2. The predicted curves are compared with experimental isothermal data in Fig. 3. While exact agreement is not obtained, the predicted curves do provide a fair approximation to those observed. The discrepancies are greater at higher conversions, and this is the region where rate controlling diffusion processes become significant. When the T_g of a cross-linked resin approaches the cure temperature, the curing reaction is retarded and appears to be controlled by segmental relaxation processes [1, 5]. Horie et al. [3] found that the cure of DGEBA by aliphatic diamines became subject to diffusion control at about 60% conversion. These factors are not allowed for in the simple empirical model used, so that discrepancies would be expected at high degrees of conversion. From this standpoint it is perhaps surprising that the activation energy appears not to increase with increasing conversion.

In order to provide standards of comparison for calorimetric degree of cure and fixed degrees of cross-linking, a series of resins was prepared in which the DDM concentration was varied between 74 and 100% of the stoichiometric level. These resins were fully cured and their glass transitions (T_g's) were determined by DSC, penetrometer and thermal expansion measurements. From the DSC and penetrometer data the inflection points in scans at 20°C/min were taken as the T_g. The effect of heating rate on apparent T_g (DSC) was small, a reduction in heating rate from 20 to 50°C/min caused a reduction in T_g of only 3.5°C for the 100% stoichiometric sample. In the thermal expansion measurements the samples were equilibriated at about T_g + 50°C and the contraction was then observed at a cooling rate of 2°C/min. The T_g was obtained as the intersection of the approximately linear contraction curves extrapolated from above and below T_g. The results are shown in Table 2. The penetrometer T_g's are 2 to 20°C lower than those determined by DSC, with the greatest differences arising in the most highly cross-linked samples. This can be ascribed to the known stress activation of relaxation processes in polymers. It has been observed that heating experiments tend to show higher T_g's than those using a cooling mode because of nonequilibrium in the molecular relaxation processes [6], and this is shown in the lower T_g's obtained from contraction during cooling from above T_g compared to the DSC specific heat transitions obtained by heating from below T_g. A monotonic decrease in apparent T_g with decreasing degree of cross-linking is observed with all three methods used, and each would therefore be useful

TABLE 2. Effect of DDM Concentration on Resin Properties

DDM % stoichiometric	Cure time (hr) 150°C	200°C	T_g (°C) DSC	Penetrometer	Expansion
99.9	4	3	184	172	163
94.9	20	2	174	154.5	158
90.1	20	2	166	160.5	160
87.5	20	-	153	146.5	140
80.3	20	-	132	125.5	120
74.2	20	-	119.5	117.5	113

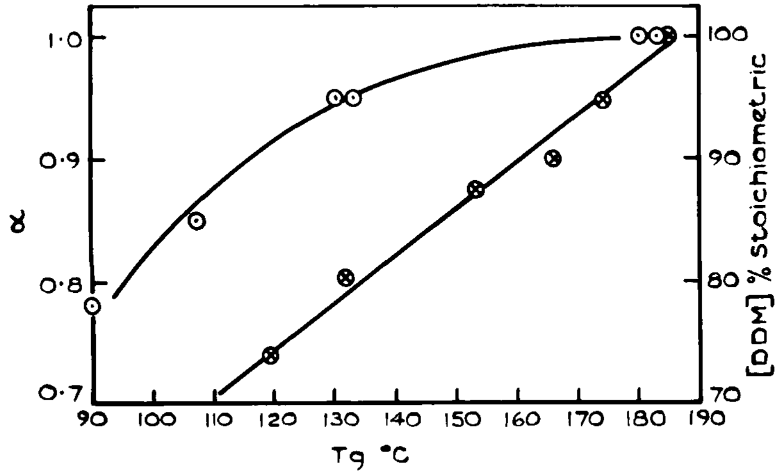

FIG. 4. Dependence of T_g on conversion and DDM concentration.

for monitoring the relative degree of cross-linking in the present system. For routine work the penetrometer test would be very useful as it is experimentally simple and generally yields the most clearly defined transitions. The approximately linear dependence of T_g on DDM concentration is shown in Fig. 4.

From isothermal experiments at various cure temperatures and times, samples were obtained of known calorimetric fractional conversion, α. The T_g's of these samples determined by DSC are also shown in Fig. 4. It is seen that T_g is a very sensitive index of the degree of cure and that there is a large increase of about 70°C in T_g during the final 10% of the curing reaction where ΔH measurements are least sensitive. Comparison with the plot of T_g of the fully cured samples against initial DDM concentration shows that the T_g for a given fractional conversion is lower than that corresponding to the same fractional stoichiometric quantity of DDM except in the last few percent of conversion. These differences may be ascribed to the plasticizing effect of unreacted diamine in the undercured stoichiometric compositions.

In conclusion, the early part of the curing reaction may be quantitatively described to a fair approximation using data from only two DSC scans. This method should be useful for other systems where Eq. (2) applies, k is of the Arrhenius form, and the reaction mechanism does not change during the reaction. Large increases in T_g occur during the final 10% of the curing reaction, and this phase is best monitored by T_g measurements.

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