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THE CURING KINETICS OF BROMINATED EPOXY RESINS

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ABSTRACT

The influence of the amounts of dicyandiamide curing agent and benzyl-*N*,*N*-dimethylamine accelerator on the curing kinetics of a non-brominated epoxy resin and those of epoxy resins containing 20% and 46% bromine was studied by differential scanning calorimetry (DSC). The temperature of the maximal reaction rate (peak temperature), the heat of reaction, the activation energy, and the reaction order were measured or calculated. It was found that the peak temperature decreases with increasing amounts of curing agent and accelerator, but increases with an increasing amount of bromine in the resin. The heat of reaction and the activation energy also increase with increasing amount of bromine.

INTRODUCTION

In brominated epoxy resins, bromine atoms can be bonded at positions 2 and 6 of the benzene ring. The amount of bromine in the resin depends on the purpose for which the resin is to be used. Bromine-containing epoxy resins acquire excellent flame-retardant characteristics with little loss of other desirable properties. Nevertheless, bromine indirectly influences all the physical and chemical parameters connected with the synthesis and curing of the epoxy resin, in particular the kinetic parameters. Curing is a step-growth polymerization with different kinetics of individual reactions which depend on reaction conditions and on the type and amount of the curing agent and accelerator [1–4]. Differential scanning calorimetry (DSC) is an excellent method for studying epoxy resin curing [5–13].

In this work, a study of the curing (with dicyandiamide) of the diglycidyl ether of bisphenol A, of a partly brominated epoxy resin containing 20% of bromine, and of the diglycidyl ether of tetrabromobisphenol A, containing 46% of bromine, is reported. As accelerator, benzyl-*N*,*N*-dimethylamine was used. Using a DSC calorimeter, the peak temperature (T_{peak}), the heat of reaction (ΔH), the activation energy (E_a), and the reaction order (n) were studied as functions of the amounts of curing agent and accelerator and the content of bromine.

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EXPERIMENTAL

Materials

Three types of epoxy resin were used: (1) the diglycidyl ether of bisphenol A (DGEBA), epoxy equivalent weight (EEW) = 186; (2) an epoxy resin with 20% of bromine (ER/20), EEW = 478; and (3) the diglycidyl ether of tetrabromobisphenol A (DGETBBA), 46% of bromine, EEW = 330. Dicyandiamide (DICY), m.p. = 210 ° C, as curing agent. Benzyl-*N*,*N*-dimethylamine (BDMA), b.p. = 183° C, as accelerator.

The ratios between the components of the reaction mixtures are given as parts per 100 parts (by weight) of resin (phr).

At a constant amount of BDMA (0.25 phr), 2.0, 4.0, 8.0 or 10.0 phr of DICY, and a constant amount of DICY (10.0 phr), 0.25, 1.0 or 4.0 phr of BDMA were added to the samples of each epoxy resin. In both cases experiments without DICY and BDMA were performed as references. The samples were homogenized by dissolving them in 2-methoxyethanol at 75 ° C and then dried at 85 ° C.

The measurements were carried out in a Perkin–Elmer DSC-7 calorimeter, using the computer program DSC-Kinetics V-100, 1986 [14,15,16], in the temperature range between 40 and 280 ° C and at a heating rate of 5 ° C min^{-1}. Sealed aluminium pans were used. The sample weights were $\leqslant 5$ mg. Isothermal measurements were recorded in temperature intervals of 10 ° C in the range between 90 and 170 ° C for DGEBA and between 110 and 210 ° C for DGETBBA until the curve became horizontal, but not longer than 60 min.

RESULTS AND DISCUSSION

To enable the comparison between different epoxy resins, the heats of reaction were calculated per mol of epoxy rings.

The curing of epoxy resins is a heterogeneous step-growth exothermic reaction, depending on the type and amount of the reactive groups in the reaction mixture. The heat of curing is between -50 and -100 kJ mol^{-1}. The heat of the epoxy ring opening depends on steric hindrance, on epoxy ring resonance stabilization, and on dipolar interactions between neighbouring atoms. When the amounts of curing agent or accelerator are small or the reaction temperature is too low, curing is incomplete and the curing rate is low. The reaction rate depends also on the amount of bromine in the resin.

In Fig. 1, the dynamic curing thermograms of DGEBA and DGETBBA are shown. The T_{peak} value depends on the amounts of DICY (Fig. 2) and BDMA (Fig. 3): the resins without DICY or BDMA have the highest T_{peak}, and T_{peak} then decreases with increasing amount of both reagents up to 4.0

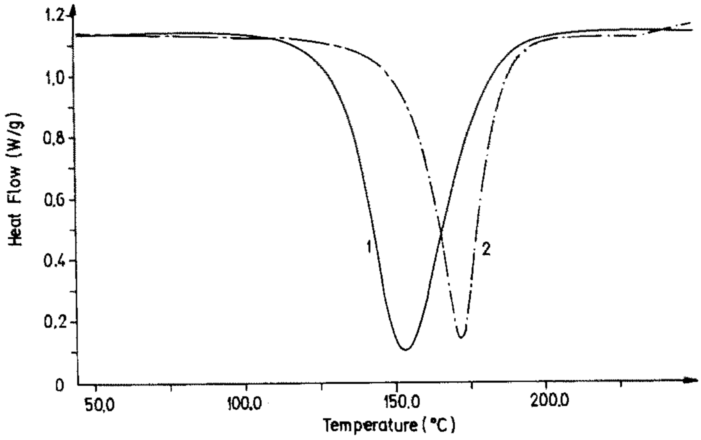

Fig. 1. Dynamic DSC thermograms of epoxy resin curing; resin : DICY : BDMA = 100 : 10 : 0.25 phr. (1) DGEBA, (2) DGETBBA.

phr of DICY and up to 1.0 phr of BDMA. The decrease of T_{peak} is more obvious for the non-brominated resin than for DGETBBA.

The heat of curing as a function of DICY amount at 0.25 phr of BDMA reaches a maximum with 4.0 phr of DICY and then slowly decreases (Table 1). The reason for this is the commencement of the curing reaction before starting the measurements of ΔH owing to the higher concentrations of DICY. A similar phenomenon is observed for the dependence of ΔH on the

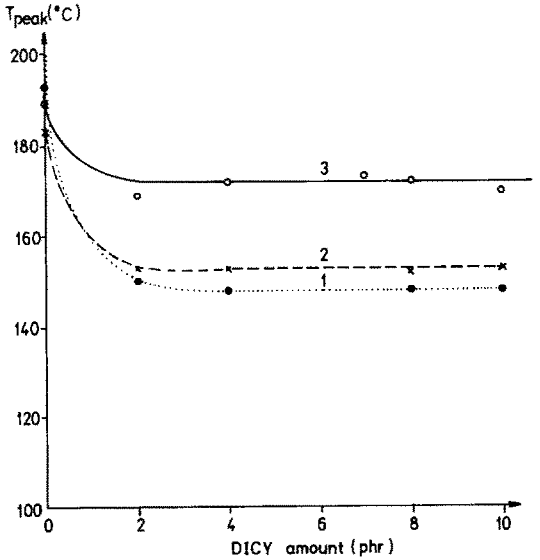

Fig. 2. Peak temperature as a function of DICY amount (BDMA amount = 0.25 phr). (1) DGEBA, (2) ER/20, (3) DGETBBA.

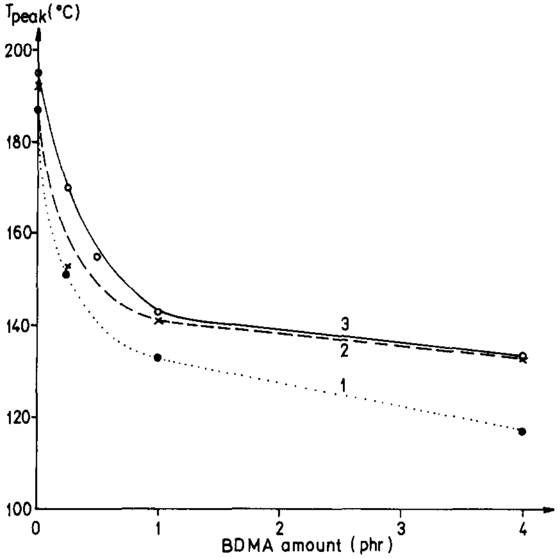

Fig. 3. Peak temperature as a function of BDMA amount (DICY amount = 10 phr). (1) DGEBA, (2) ER/20, (3) DGETBBA.

TABLE 1

Heats of curing reactions in kJ mol^{-1} for different epoxy resins as a function of DICY amount (BDMA amount = 0.25 phr)

DICY (phr)	DGEBA	ER/20	DGETBBA
0	−14.9	−39.0	−17.0
2	−21.6	−59.0	−57.7
4	−51.8	−77.0	−98.6
8	−80.5	−70.0	−87.8
10	−68.6	−75.0	−81.7

TABLE 2

Heats of curing reactions in kJ mol^{-1} for different epoxy resins as a function of BDMA amount (DICY amount = 10 phr)

BDMA (phr)	DGEBA	ER/20	DGETBBA
0	−29.0	−48.0	−37.7
0.25	−68.6	−75.0	−81.7
1	−60.1	−45.0	−62.0
4	−6.9	−41.0	−30.2

amount of BDMA at 10 phr of DICY. The maximal ΔH is obtained with 0.25 phr of BDMA (Table 2).

The ΔH value increases with the increasing amount of bromine in the resin. The maximal ΔH is -80.5 kJ mol^{-1} for DGEBA and -98.6 kJ mol^{-1} for DGETBBA. To explain the differences in ΔH for the two resins, the heats of ethylene oxide and propylene oxide polymerization were considered [17]: the former (no steric hindrance or other dipolar influences) is -94.5 kJ mol^{-1} and the latter (in which the epoxy ring is sterically hindered and resonance stabilization does not take place) is -75.0 kJ mol^{-1}. By comparing the ΔH values, it can be concluded that the curing behaviour of DGEBA is similar to that of propylene oxide. The ΔH value for DGETBBA is higher by 18.1 kJ mol^{-1} than that for DGEBA. Evidently, the bromine atoms on the benzene rings are too far away from the epoxy rings to cause steric hindrance. The high ΔH value can be attributed to strong resonance stabilization of the epoxy rings due to the high electronegativity of bromine atoms, which raises the heat of curing of DGETBBA. The ΔH value for ER/20 lies between the values for DGEBA and DGETBBA.

The activation energy and the reaction order were calculated from the dynamic DSC thermograms using the following equation [18]:

$$\frac{\ln(d_2/d_1)}{\ln[(A-a_2)/(A-a_1)]} = \frac{E_a}{R} \cdot \frac{(1/T_2 - 1/T_1)}{\ln[(A-a_2)/(A-a_1)]} + n \qquad (1)$$

where T_1 and T_2 are any two temperatures within the temperature range of the reaction, a_1 and a_2 are the corresponding areas, d_1 and d_2 are the

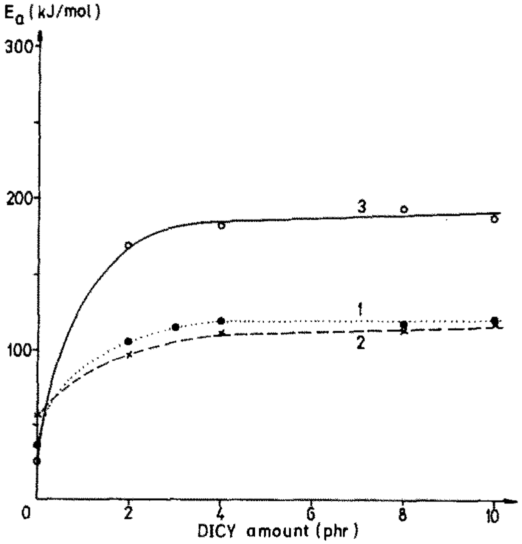

Fig. 4. Activation energy as a function of DICY amount (BDMA amount = 0.25 phr). (1) DGEBA, (2) ER/20, (3) DGETBBA.

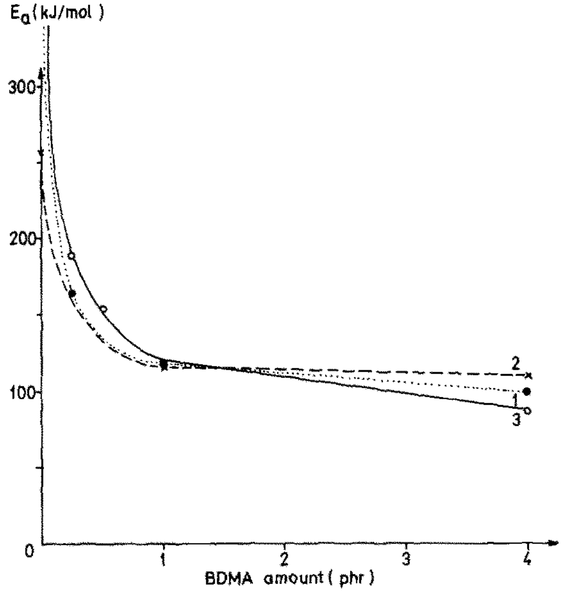

Fig. 5. Activation energy as a function of BDMA amount (DICY amount = 10 phr). (1) DGEBA, (2) ER/20, (3) DGETBBA.

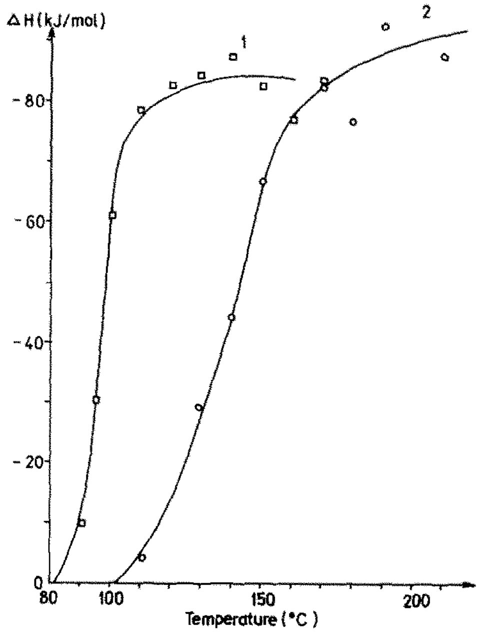

Fig. 6. Heat after 1 h of reaction as a function of isothermal curing temperature; resin : DICY : BDMA = 1 : 0.5 : 0.035 mol. (1) DGEBA, (2) DGETBBA.

corresponding distances from curve to baseline, and A is the total area between the curve and the baseline. By plotting the left-hand side of eqn. (1) versus $(1/T_2 - 1/T_1)/\ln[(A - a_2)/(A - a_1)]$, the activation energy is obtained from the slope of the resulting straight line. Its intersection with the ordinate axis gives the reaction order. The activation energies for the studied systems were also calculated by using the DSC-7 Kinetics Software Kit. The energies calculated by both methods agree to within ±2.4%.

The activation energies increase with increasing amount of DICY up to 4.0 phr (Fig. 4) and remain constant even at higher amounts of DICY. DGETBBA has the highest and DGEBA the lowest activation energy. The activation energies for all three resins decrease with increasing amount of BDMA up to 1.0 phr (Fig. 5).

The reaction orders lie between 1 and 2 and depend on the amounts of DICY and BDMA. Values calculated by both methods agree to within ±5.4%.

For isothermal measurements, the weight ratio between the resin, DICY, and BDMA was 100 : 6.4 : 0.72 and the temperature intervals were 10 ° C. Up to 120 ° C, the curing reaction of DGETBBA is slow. Most of the resin reacts between 130 and 170 ° C (Fig. 6). The highest heat of curing of DGETBBA is -85 kJ mol^{-1} at 180 ° C, which is lower, as compared with that from dynamic measurements. For DGEBA the reaction occurs earlier and the heat of curing is -82 kJ mol^{-1} at 120 ° C.

CONCLUSIONS

The kinetic parameters of the epoxy resin curing depend strongly on the amounts of curing agent, of accelerator and of bromine in the resin, which all influence the complexity of individual reactions. Bromine atoms on positions 2 and 6 of the benzene ring stabilize the epoxy ring with dipolar interactions which cause higher heats of the curing reactions compared to non-brominated resins.

REFERENCES

1 A.C. Grillet, J. Galy, J.P. Pascault and I. Bardin, Polymer, 30 (1989) 2094.

2 N.S. Schneider, J.F. Sprouse, G.L. Hagnauer and J.K. Gillham, Polym. Eng. Sci., 19 (1979) 304.

3 J.M. Barton and D.C.L. Greenfield, Br. Polym. J., 18 (1986) 196.

4 H.H. Naé, J. Appl. Polym. Sci., 33 (1987) 1173.

5 R.B. Prime and E. Sacher, Polymer, 13 (1972) 455.

6 E. Sacher, Polymer, 14 (1973) 91.

7 T. Malavašič, A. Može, I. Vizovišek and S. Lapanje, Angew. Makromol. Chem., 44 (1975) 89.

8 P. Peyser and W.D. Bascom, J. Appl. Polym. Sci, 21 (1977) 2359.
9 R.L. Miller and M.A. Oebser, Thermochim. Acta, 36 (1980) 121.
10 J.N. Leckenby, Br. Polym. J., 15 (1983) 45.
11 J. Sickfeld and W. Mielke, Prog. Org. Coat., 12 (1984) 27.
12 R.D. Patel, R.G. Patel and V.S. Patel, Br. Polym. J., 19 (1987) 37.
13 Cui Guo-Liang and Wang Wen-Ju, Thermochim. Acta, 134 (1988) 313.
14 E.S. Freemann and B. Carroll, J. Phys. Chem., 62 (1958) 394.
15 A.P. Gray, Anal. Calorim., (1968) 209.
16 DSC-7 Kinetics Software Kit N 519-0705, 1988, Perkin–Elmer.
17 J.B. Brandrup and E.H. Immergut, Polymer Handbook, Wiley, New York, 1975, II-421.
18 A. Šebenik, I. Vizovišek and S. Lapanje, Eur. Polym. J., 10 (1974) 273.