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Studies on cure kinetics and thermal stability of liquid epoxy resin based on bisphenol-C and epichlorohydrin using different amines as curing agents

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Abstract

The curing reactions of liquid epoxy resin based on 1,1′-bis(4-hydroxyphenyl) cyclohexane (DGEBC) with different amine curing agents have been investigated by differential scanning calorimetry. The overall kinetics of curing have been found to follow a simple Arrhenius-type rate-temperature dependence, having an average overall activation energy of 40–97 kJ mol^{-1}. The kinetics of thermal degradation of the cured epoxy resins were studied by thermogravimetric analysis in static air atmosphere at a heating rate of 10 °C min^{-1}. The thermal degradation reactions were found to proceed in a single step with an activation energy in the range 30–56 kJ mol^{-1}.

INTRODUCTION

Despite their relatively high cost, epoxides are now firmly established in a number of important applications. They find use primarily in surface coating and in other applications including adhesives, castings and laminates.

The most common commercial epoxy resin is the diglycidyl ether of bisphenol-A (DGEBA). Extensive work has been reported on the cure kinetics and thermal stability of these resins under varied conditions. But not a single reference is available in the literature concerning such a study of the liquid epoxy resin DGEBC although the DSC curing kinetics of the solid DGEBC with phthalic anhydride as curing agent has been reported [1].

The present work reports the synthesis and characterisation of liquid epoxy resin based on bisphenol-C.

The resin was characterised by epoxy equivalent weight (EEW) and infrared (IR) analysis. The number-average molecular weight was established by vapour pressure osmometry. The curing reactions were studied by

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DSC using various amines as curing agents. The overall kinetic parameters of the curing reactions were estimated using a single dynamic DSC scan. The effect of the curing agents on the characteristic parameters of epoxy curing reactions were investigated. The thermal behaviour of DGEBC cured with amine curing agents was also studied.

EXPERIMENTAL

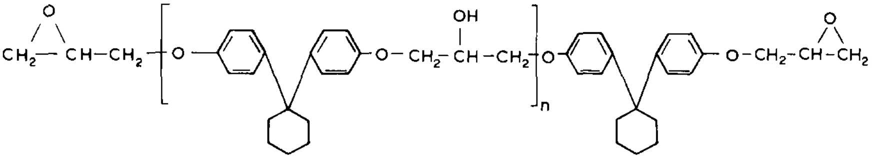
Materials

The sodium hydroxide used in the present work was commercial grade. Epichlorohydrin was distilled before use (b.p. 114–116 ° C). 1,1′-bis(4-Hydroxyphenyl) cyclohexane (Bisphenol-C, m.p. 186 ° C) was synthesised according to the reported method [2].

The various aliphatic and aromatic amines such as diethylene triamine (DETA) and triethylenetetramine (TETA), were laboratory grade reagents; *m*-phenylenediamine (MPD) was distilled under reduced pressure before use; *p,p′*-diaminodiphenyl methane (DDM) and *p,p′*-diaminodiphenyl-sulphone (DDS) were used after recrystallisation from appropriate solvents.

The resin was prepared using the following procedure. Biphenol-C (26.8 g, 0.1 mole) and epichlorohydrin (92.5 g, 1 mole) were placed in a 250 ml three-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a dropping funnel. The contents were brought to 100 ° C with stirring. A 40% aqueous sodium hydroxide solution (8.8 g, 0.22 mole) was added slowly to it over 2 hours, the temperature of the mixture being kept between 100 and 110 ° C. The reaction mixture was further stirred for another hour at the same temperature, cooled to room temperature, and the salt that had separated was removed by filtration. The organic layer was washed with distilled water to remove any alkali, and then stripped under reduced pressure, first at 100 ° C and 100 mmHg, and finally at 140 ° C and 5 mmHg. Upon cooling, a transparent liquid resin is was obtained (32 g). The structure of this resin is shown below in Scheme 1.

The epoxy equivalent weight (EEW) was determined by the acetone–hydrochloride method. It was found to be 255 g equiv^{-1}. The number-average



Scheme 1 ($n = 0.4$).

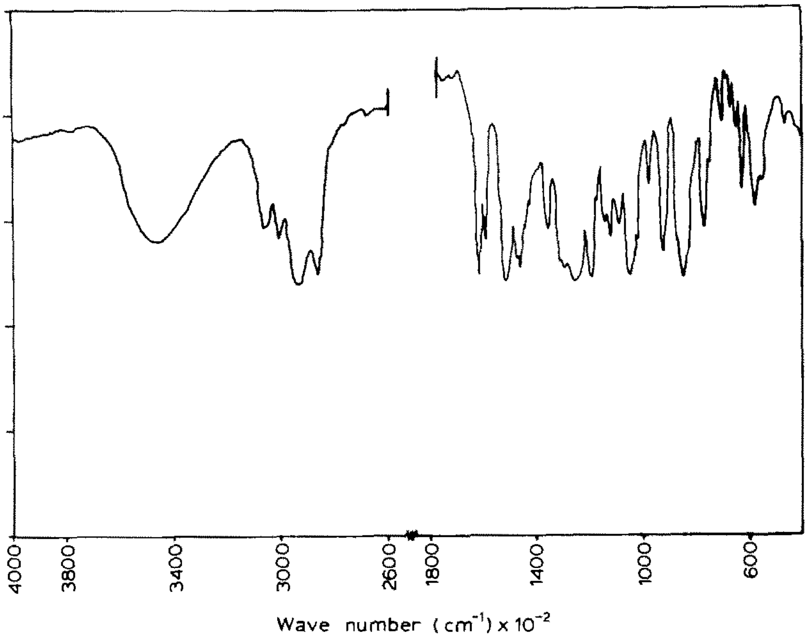


Fig. 1. IR spectra of DGEBC.

molecular weight as determined by vapour pressure osmometry was found to be 506.

The resin was also characterised by IR spectroscopy. Figure 1 shows a broad band at 3460–3520 cm^{-1} due to the presence of hydrogen-bonded hydroxyl species [3]. The bands at 3050 and 1190 cm^{-1} are due to the aromatic C–H stretching vibrations. The absorption bands at 2930, 2850 and 1360 cm^{-1} are due to the presence of ether methylene C–H vibrations. The bands in the region of 1255, 920 and 850 cm^{-1} are due to the presence of terminal epoxy groups. The bands at 735 and 765 cm^{-1} are due to the methylene groups.

Curing procedure

A Du Pont 9900 thermal analyser connected to a 910 DSC module was used to measure the heat flow as a function of temperature, after calibration with high purity indium (Du Pont thermometric standard), under nitrogen at a heating rate of 10 ° C min^{-1}.

The epoxy resin and amines were thoroughly mixed in stoichiometric ratio, i.e. one amine proton per epoxy group. The aliphatic amines were mixed with resin at room temperature and the solid diamines were heated with vigorous stirring for 5 minutes at the required temperature. The mixture was then placed in a vacuum oven for 5 minutes to remove bubbles of gas. The void-free mixture was then used for the DSC studies, using an empty cell as reference.

Thermogravimetric analysis (TGA) of the cured epoxy resins

The remaining samples were then cured and post-cured in a previously heated oven (about 180 °C) for around 3 hours. The cured resins were powdered and used for thermogravimetric analysis (TGA) on a Du Pont 951 thermogravimetric analyser attached to a Du Pont 990 thermal analyser, in static air at a heating rate of 10 °C min^{-1}.

Analysis of DSC and TGA data

DSC yields thermograms of the rate of heat absorption as a function of temperature. These thermograms were further analysed to obtain the rate of reaction and fractional conversion.

The activation energy (E), pre-exponential factor (Z) and order of reaction (n) were obtained from the DSC scans using the method of Borchardt and Daniels [4] by assuming that the reaction follows nth order kinetics and that the temperature dependence of the reaction rate follows the Arrhenius expression. In addition, the activation energy (E) and order of reaction (n) were determined from the Freeman–Carroll relation [5]. Using the Barrett relation [6], the kinetic parameters such as the activation energy (E) and pre-exponential factor ($\ln A$) were obtained.

The thermal stabilities of DGEBC with different amine curing agents were evaluated by thermogravimetric analysis. The relative thermal stability of the cured resin were analysed to give percentage weight loss as a function of temperature. The activation energy (E) of the degradation process was obtained using Broido's method [7]. Integral procedure decomposition temperature (IPDT) values were obtained by using Doyle's method [8].

RESULTS AND DISCUSSION

In order to understand the effect of the amine structure on the curing reaction and on the thermal behaviour of cured DGEBC, various amines such as DETA, TETA, MPD, DDM and DDS were used as curing agents. From the DSC scans, the temperature at which the curing started (T_i), the peak exothermic temperature (T_p) and the temperature of complete curing (T_f) were calculated and are presented in Table 1; selected DSC curves are shown in Fig. 2.

The curing characteristics listed in Table 1 show that T_i, T_p and T_f depend on the curing agent used. The values are lowest for DETA and highest for DDS. This indicates that the rate of curing of DGEBC–DETA

TABLE 1

Kinetic parameters of epoxy–amine systems

Epoxy resin–curing agent system [a]	T_i [b] (°C)	T_p [c] (°C)	T_f [d] (°C)	Borchardt–Daniels relation			Freeman–Carroll relation		Barrett relation	
				E [e] (kJ mol^{-1})	log Z	n	E [e] (kJ mol^{-1})	n	E (kJ mol^{-1})	ln A [e]
DGEBC–DETA	39.1	95.47	192	84.9	12.2	1.7	78.70	1.8	76.13	22.68
DGEBC–TETA	40.2	96.77	181	95.4	13.8	2.3	71.52	1.75	66.44	20.00
DGEBC–MPD	77.0	134.62	217	96.8	12.5	2.3	53.39	1.325	58.51	15.49
DGEBC–DDM	94.0	163.88	244	82.0	9.4	1.0	79.90	0.975	81.494	21.34
DGEBC–DDS	132.0	211.0	287	80.0	8.2	1.5	76.412	1.45	76.68	17.83

[a] Resin, diglycidyl ether of 1,1′-bis(4-hydroxyphenyl) cyclohexane (dGEBC); DETA, diethylene triamine; TETA, triethylene tetramine; MPD, *m*-phenylenediamine; DDM, *p*,*p*′-diaminodiphenyl methane; DDS, *p*,*p*′-diaminodiphenyl sulphone.

[b] T_i, temperature (°C) of the onset of curing.

[c] T_p, temperature (°C) of the peak of the exotherm.

[d] T_f, temperature (°C) of the completion of curing.

[e] Errors in E and ln A, ±2.

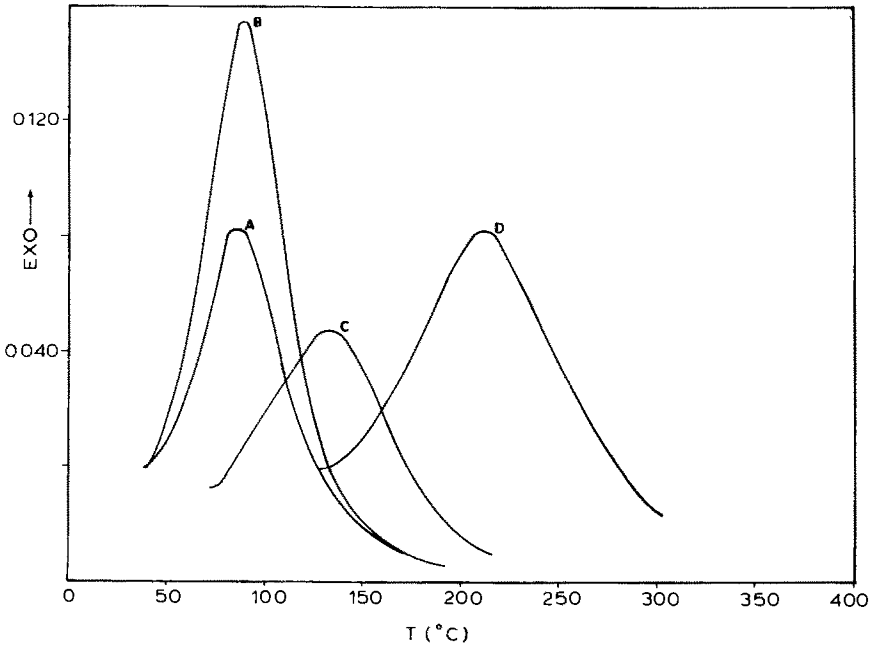


Fig. 2. Dynamic DSC scans at 10 °C min^{-1} for the systems: A, DGEBC–DETA; B, DGEBC–TETA; C, DGEBC–MPD; and D, DGEBC–DDS.

is highest among the systems used. The trend revealed for the ease of curing for the epoxy system is DGEBC–DETA ≈ DGEBC–TETA > DGEBC–MPD > DGEBC–DDM > DGEBC–DDS.

The ease of curing depends on the reactivity of the amines. The highest reactivity of DETA may be attributed to the fact that DETA is a purely aliphatic system; in the case of DDS, the reactivity is lowest because of the presence of the electron-withdrawing sulphonyl group.

In order to evaluate the kinetic parameters associated with the curing reaction, such as activation energy (E), order of reaction (n) and pre-exponential factor, the DSC data were treated in terms of three different methods. Analyses of the data using the method of Freeman and Carroll [5] and of Barrett [6] are shown in Figs. 3 and 4 respectively. The data obtained from the plots using the above two methods are listed in Table 1. The activation energy values for the five epoxy systems differ significantly, indicating the difference in the relative reactivities; this is also evident from the characteristic temperatures.

The kinetics of the epoxy–amine reaction is rather complex, as both the hydrogen atoms take part in the addition reaction with the epoxide. However, the rates of the two reactions are close but not identical and it can be safely stated that the primary and secondary hydrogens take part simultaneously in the reaction with epoxide, as shown from the single DSC

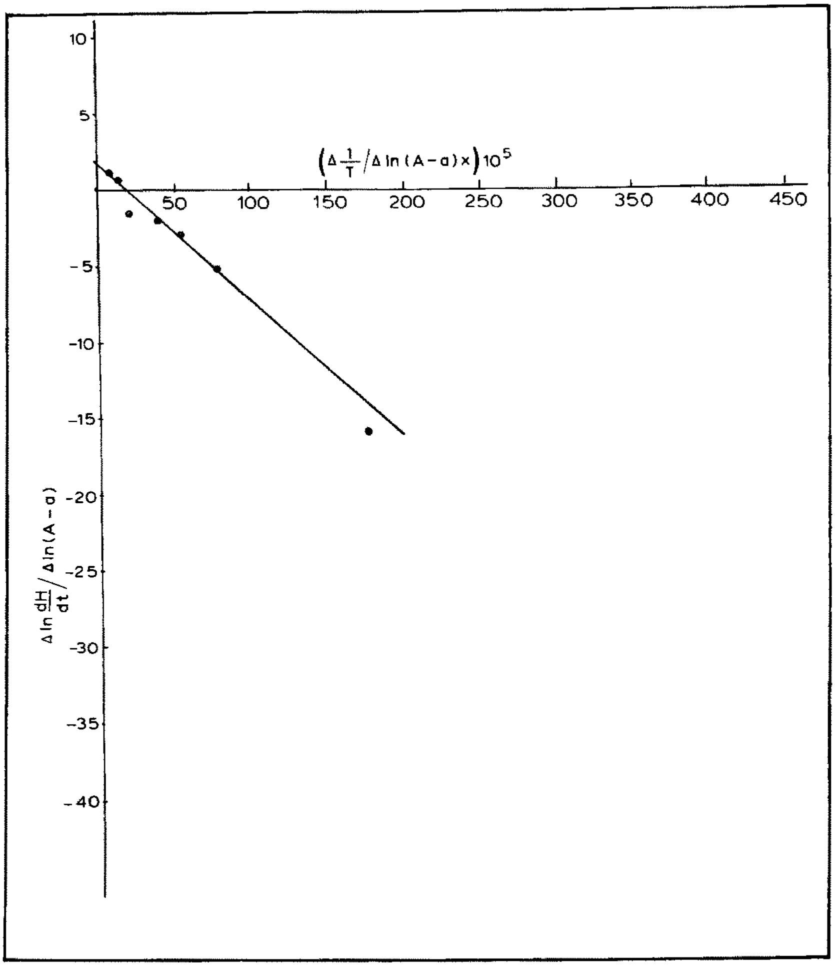


Fig. 3. A plot of [Δ ln(dH/dt)]/[Δ ln($A-a$)] vs. Δ(1/T)×10^5/[Δ ln($A-a$)] for DGEBC–DETA using the Freeman–Carroll relation.

peak in Fig. 2. The overall activation energy of the kinetic curing is in the range of 40–97 kJ mol^{-1}.

In order to investigate the effect of the amine structure on the thermal stability of the cured epoxy resins, selected thermograms obtained under dynamic conditions at a heating rate of 10 °C min^{-1} are reproduced in Fig. 5. The temperature characteristics such as T_0 (temperature of onset of decomposition), T_{10} (temperature for 10% weight loss), T_{20} (temperature for 20% weight loss), T_{max} (temperature of maximum rate of degradation), *IPDT* (integral procedure decomposition temperature) and the activation energy (E) of the degradation process were calculated and are presented in Table 2.

T_0 and T_{10} are the two main criteria for the heat stability of the polymers. The higher the values of T_0 and T_{10} the higher the heat stability

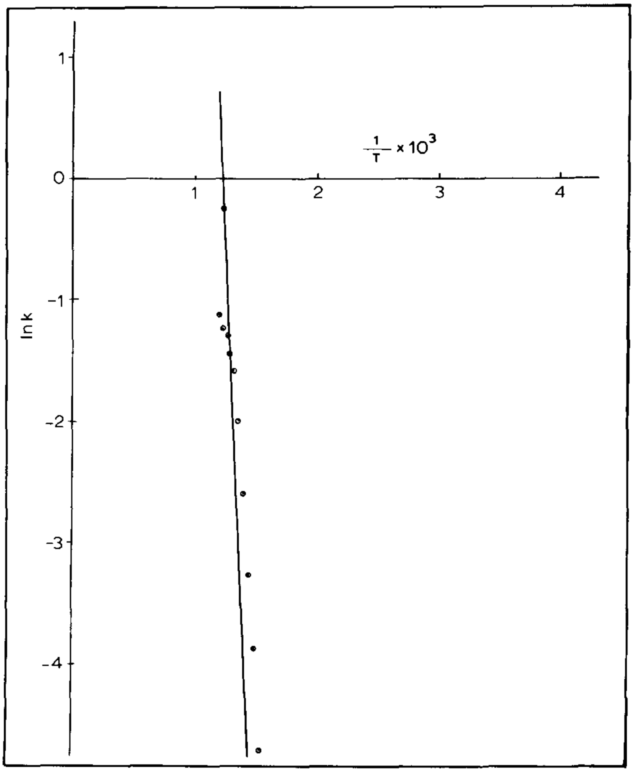


Fig. 4. A plot of ln K vs. $1/T \times 10^3$ for DGEBC–DETA using the Barrett relation.,

of the system [9]. To obtain a quantitative assessment of the relative stabilities, the IPDT values can be regarded as having significant importance, as they represent the overall nature of the TGA curves.

The thermal stability of amine-cured epoxy systems is most affected by the structure of the amine used as curing agent. The following trend of thermal stability for amine-cured epoxy resins is revealed from Table 2: DGEBC–DDS > DGEBC–DDM > DGEBC–MPD > DGEBC–TETA > DGEBC–DETA.

The lowest stability observed in the case of DGEBC–DETA is due to the purely aliphatic structure of DETA in the cured product. The thermal stability of the product obtained by curing DGEBC with MPD is better than that of DGEBC–DETA, which is due to the aromatic nature of MPD. The curing agents DDM and DDS gave relatively more stable cured resins because of the thermally stable linkage present within the aromatic nuclei [10,11]. The greater stability of the DDS-cured resin than the DDM-cured resin may be ascribed to the great heat resistance of the sulphur linkage compared with that of the carbon linkage [11].

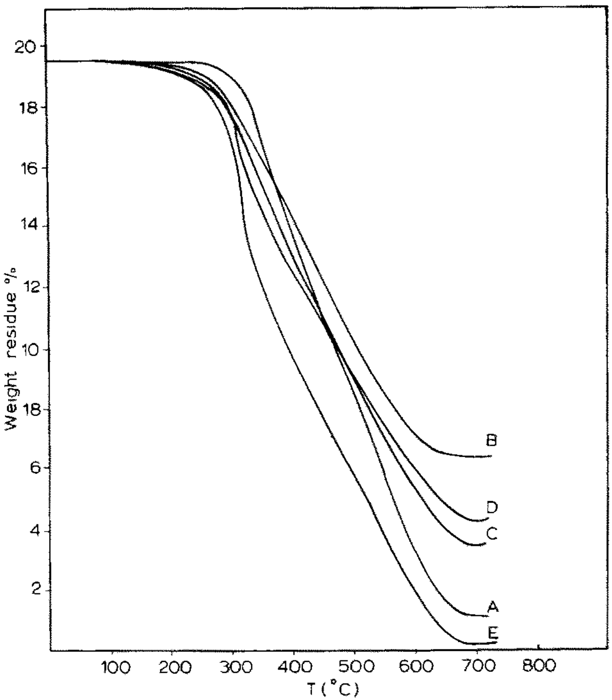


Fig. 5. TG curves for cured epoxy systems in static air at a heating rate of 10 °C $\min^{-1}$: A, DGEBC–DDS; B, DGEBC–DDM; C, DGEBC–MPD; D, DGEBC–TETA; and E, DGEBC–DETA.

The activation energy values also give a trend for the thermal stability of the cured resins. The values of E are higher for resin systems with higher heat stabilities: DGEBC–DDS > DGEBC–DDM > DGEBC–MPD > DGEBC–TETA > DGEBC–DETA.

TABLE 2

Temperature characteristics and kinetic parameters of cured epoxy resins

Epoxy resin–curing agent system [a]	T_0 (°C)	T_{10} (°C)	T_{20} (°C)	$T_{\max}$ (°C)	IPDT [b] (°C)	E [c] (kJ mol^{-1})
DGEBC–DETA	120	300	318	325	442.55	30.54
DGEBC–TETA	125	303	325	337.5	449.48	31.50
DGEBC–MPD	150	309	343	325	472.46	35.14
DGEBC–DDM	172.5	312.5	369	500	482.32	40.25
DGEBC–DDS	250	340.5	387.5	437.5	535.64	55.37

[a] See Table 1 for the abbreviations used in the epoxy resin–curing agent systems.
[b] IPDT, integral procedure decomposition temperature.
[c] Error, ±2.

CONCLUSIONS

The dynamic DSC, cure kinetics study of DGEBC with different amine curing agents revealed that the systems follow simple *n*th order Arrhenius-type kinetics, having an activation energy in the range of 40–97 kJ mol^{-1}. The thermogravimetric study of DGEBC–amine-cured systems shows that the thermal stability depends on the structure of the curing agent used. The activation energy of the degradation process is in the range of 30–56 kJ mol^{-1}.

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