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Investigation of the curing reactions of some multifunctional epoxy resins using differential scanning calorimetry

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Abstract

Curing reaction of three tetrafunctional epoxy resins in the presence of tetraethylene tetramine was examined by differential scanning calorimetry at different heating rates. The kinetic parameters of the curing reaction were determined using various computational methods (Barrett, Borchardt–Daniels and Kissinger). The heating rate shows a great influence on the curing process. The activation energy varied in the range 43–80 kJ/mol, and the order of the curing reaction is observed to be $\approx$1.0 with slight variations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cure kinetics; Epoxy resins; Differential scanning calorimetry; Kinetical model

1. Introduction

Epoxy resins are the most important thermosetting polymers, widely used as structural adhesives and matrices for fibre compositions [1]. Linear epoxy resins are converted into a three-dimensional cross-linked thermoset network during cure. These resins have good thermal, electrical and mechanical properties, but they are brittle and have poor resistance to crack propagation [2–6]. Various chemical reactions take place during cure, and for high performance applications it is necessary to understand the processes, which takes place during the cure reaction. The final properties for this materials depend on the kinetics of the curing reaction, and this is needed to establish relationships between processing and properties in the studied thermosetting systems, and to find the optimum curing conditions [7,8].

The use of differential scanning calorimetry (DSC) to investigate the cure of variations in the thermosetting polymers were previously reported [7–11]. Dynamic DSC measures the heat flow to the sample as a function of temperature, being rapidly and accurately, and the kinetic data are obtained in a relatively short period of time. The majority of the DSC studies on the cure reaction of epoxy resins refer to the bifunctional compounds. There are less investigations regarding the DSC applications to the study of the cure reactions of multifunctional epoxy resins [12]. In the present work the DSC technique is applied to study the curing kinetics of some multifunctional epoxy resins, in the presence of tetraethylene tetramine (TETA) as curing agent.

2. Experimental

2.1. Materials

The three tetrafunctional epoxy resins, namely, tetraglycidyl of diaminodiphenylmethane (TGDDM),

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tetraglycidyl of diaminodiphenylether (TGDDE), and tetraglycidyl of diaminobibenzyl (TGDBBz) were prepared starting from the amines, in the presence of an excess of epichlorohydrin, according to the method reported [13]. The amines, epichlorohydrin and organic solvents were chemically pure reagents, and were used without further purifications.

2.2. *Resins characterization*

The synthesized resins were characterized by IR and ^{1}H-NMR spectroscopy, rheological and thermal techniques [13]. The functionality of the tested tetrafunctional epoxy resins, theoretically equal to 4 epoxy groups/mol, was determined by Sander et al. [14] method. The epoxy equivalent weight was 114 g/eq of TGDDM resin, 111 g/eq of TGDDE resin, and 116 g/eq of TGDBBz resin. The curing agent was TETA in an $r = 0.75$, where r is defined as hydrogen from amine/epoxy group ratio.

2.3. *Measurements*

The extent of curing was evaluated by means of a Mettler 12 E type DSC. The instrument was calibrated using indium as a standard. Approximately 5–10 mg of the epoxy resins mixed with the curing agent, in the proposed ratio, were scanned from 20 to 200°C, with different heating rates (5, 10 and 20°C/min), in a nitrogen atmosphere. Runs were always carried out using an empty cell as a reference. The heat flow data, the relative fractional conversion and the rate of reaction were calculated using the area under the peak of the exotherm.

The degree of cure of the resins, as fractional conversion (α), was evaluated using the DSC thermograms, as the ratio of the heat recorded up to a time t (q) to the total heat (q_{tot}) recorded over all the reaction. These parameters are in a direct relationship to the partial area (a) at a particular temperature (T), as well as to the total area (A) of the peaks in the thermograms:

$$\alpha = \frac{q}{q_{\mathrm{tot}}} = \frac{a}{A} \qquad (1)$$

The rate constant (k) of the curing reaction was estimated from variation of α versus time (t), using Barrett's relation [15], as follows:

$$k = \frac{\mathrm{d}\alpha/\mathrm{d}t}{A-a} = \frac{\mathrm{d}H/\mathrm{d}t}{A-a} \qquad (2)$$

where dH/dt is the heat flow (J/min).

The Barrett method assumes that the temperature dependence of the reaction rate follows a relationship of Arrhenius type:

$$k = Z\,\mathrm{e}^{-E_{\mathrm{a}}/RT} \qquad (3)$$

where k is the rate constant, Z the frequence factor, E_{a} the activation energy, R the gas constant, and T the absolute temperature.

The kinetic parameters of the curing reaction were calculated and using the Borchardt–Daniels method [16], which gives the following general rate equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_{\mathrm{T}}(1-\alpha)^n \qquad (4)$$

where α is the fractional conversion, k_{T} the specific rate constant (s^{-1}), n the reaction order, and t the time.The E_{a} determined taking into consideration all the three heating rates, was evaluated by means of the Kissinger equation [17]:

$$\ln\frac{\beta}{T_{\mathrm{p}}^2} = \ln\frac{k_0}{\beta} - \frac{\beta}{T_{\mathrm{p}}} \qquad (5)$$

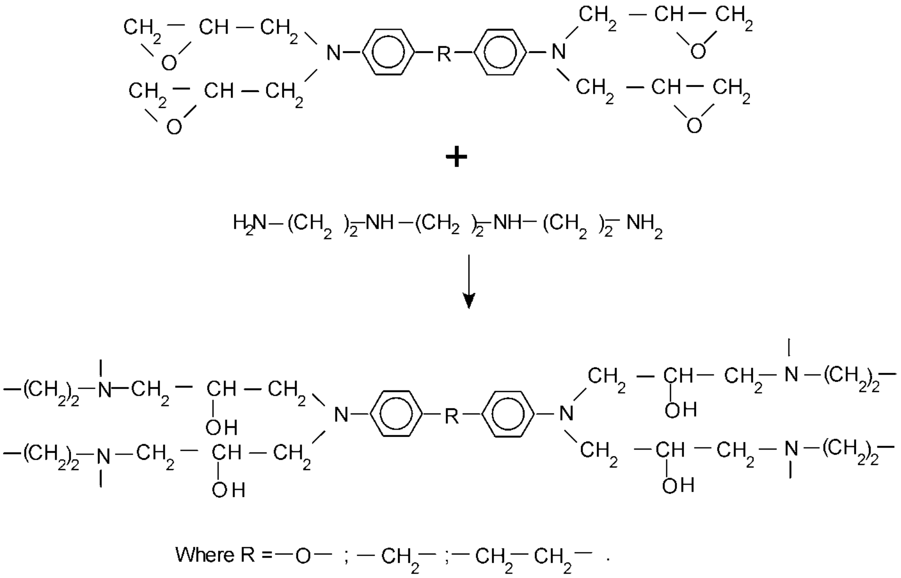
where β is the scan rate (°C/s), T_{p} the peak temperature in the DSC trace, k_0 the Arrhenius pre-exponential factor (s^{-1}) and $\beta = E_{\mathrm{a}}/R$.

3. Results and discussion

The chemical reactions involved in the curing reaction of the tested epoxy resins are shown in Scheme 1.

The crosslinked epoxy resins do not show bands in the IR spectra between 910 and 920 cm^{-1}, which are characteristics to the epoxy group. In exchange, they show a large band in the zone specific to the OH group, this being in favor of the curing process.

The curing reaction of the studied epoxy resins in the presence of TETA was investigated by DSC at three different heating rates. Fig. 1 shows a typical example of the DSC thermograms recorded for TGDDM epoxy resin at 5, 10 and 20°C/min heating rates, in the temperature range 40–250°C.



Scheme 1.

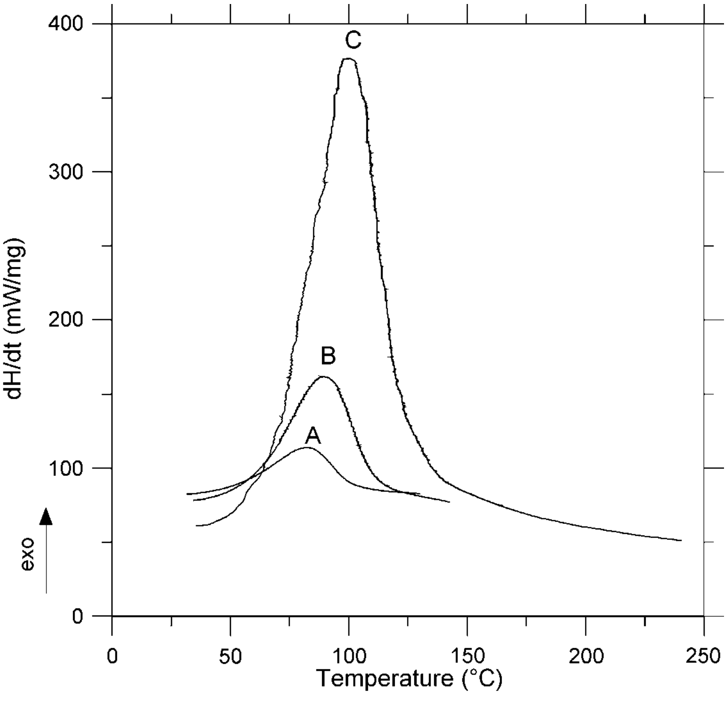


Fig. 1. Typical DSC curves recorded for TGDDM/TETA system at different heating rates: (A) 5°C/min; (B) 10°C/min; (C) 20°C/min.

Table 1
Curing characteristics of the epoxy resin/TETA mixtures at various heating rates

System	Heating rate (°C/min)	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	Cure range (%)	Cure time (min)
TGDDM/TETA	5	30	84	137	65.05	107	21.4
	10	31	95	142	416.2	111	11.1
	20	53	103	146	327.3	93	4.7
TGDDE/TETA	5	31	81	130	283.06	99	19.8
	10	34	89	143	374.3	109	10.9
	20	35	99	240	700.06	205	10.2
TGDBBz/TETA	5	30	75	132	259.3	101	20.2
	10	40	83	145	348.2	105	7.5
	20	46	94	195	419.7	149	6.5

The main characteristics of the DSC scans taken into consideration in obtaining information about the curing reaction were as follows: the initial curing temperature (T_i), peak temperature (T_p), finishing temperature (T_f), the area under the curve (a and/or A), and the heat flow (dH/dt) evolved in the time of curing. These data were fitted to all the methods mentioned above for the calculation of the kinetic parameters of the curing process, and the results obtained are summarized in Table 1.

As was noted, on increasing heating rate, all the samples tested showed a continuous increase in T_i, T_p, and T_f, a very high increase of ΔH (exception the sample DGDDM), and a decrease of the cure time.

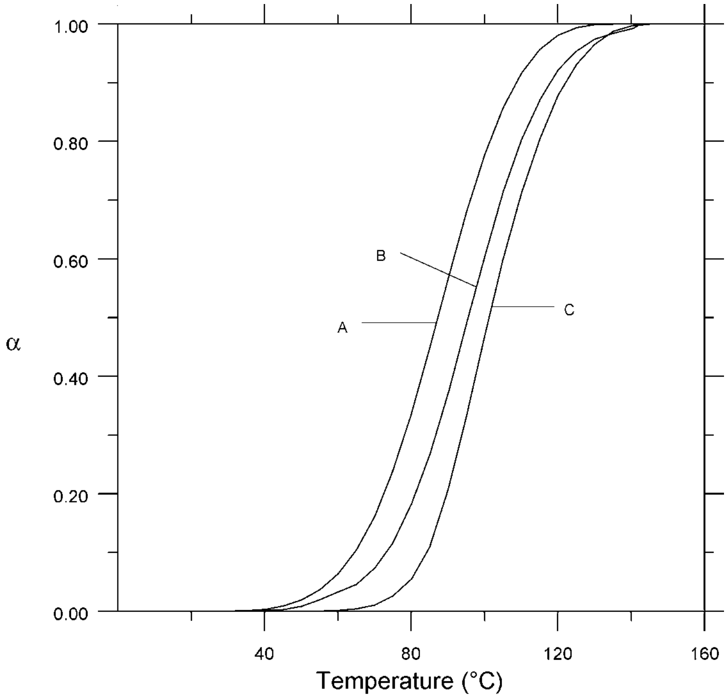


Fig. 2. Fractional conversion as a function of temperatures for TGDDM/TETA system: (A) 5°C/min; (B) 10°C/min; (C) 20°C/min.

This behavior can be related to the instrumental factors (high initiation temperatures at higher heating rates), structural factors (a more complete curing at higher heating rates due to the presence of a great number of epoxy groups in the reaction), and kinetical factors (heating rates increase with increase of temperature, this makes as the cure time to decrease).

Fig. 2 shows the variation of the fractional conversion as a function of temperature for TGDDM/TETA mixture at different scan rates, as an exemplification.

The plots recorded in Fig. 2 showed that the curing curves shifted to higher temperatures with higher scan rates. The curves of fractional conversion against temperature, as well as the curves of fractional conversion against time, were used to evaluate the kinetic parameters which characterize the curing reaction of the epoxy resin, using the three different computational methods. Table 2 lists the values of E_a, n, and the frequency factor ($\ln A$), along with the least squares regression coefficients.

The kinetic data listed in Table 2 showed important differences in the value of E_a for the calculated method used, as well as the heating rate. The parameters calculated on the basis of the three methods mentioned above support the assumption of the presence of the different reaction mechanisms, with various order of magnitude.

As it is well known, the reaction between epoxies and amines involves several steps [18–20], and hence the kinetics may be rather complex.

The analysis of both E_a and pre-exponential factor ($\ln A$) using the Barrett method shows the greater influence of the heating rate on the heating process . This leads to the conclusion that the unitary reaction order assumed by the Barrett equation does not characterize the cure kinetics in the systems studied.

The Borchardt–Daniels equation allowed the evaluation both of $E_{a.}$, $\ln A$ and n. As in the case of the Barrett equation, these kinetic parameters are influenced by the heating rate. The other kinetic parameters (E_a and $\ln A$) were higher than those calculated by Barrett method.

The correctness of the kinetic model using the Borchardt–Daniels equation was verified by plotting in the curves fractional conversion versus temperatures using the data listed in Table 2, and their comparison with the curves obtained by computational processing of the thermograms. An example is reported in Fig. 3 for the TGDBBz/TETA system.

It is observed a better fit, especially for the fractional conversions higher than 0.15.

Because both the Barrett and Borchardt–Daniels methods show a great influence of the heating rate on the E_a and $\ln A$, the latter were evaluated taking into consideration all the three heating rates used in this study. The data evaluated using the Kissinger method are just on the line with the Barrett and Borchardt–Daniels methods.

Table 2
DSC kinetic parameters of the studied epoxy resin/TETA mixtures

System	Heating rate (°C/min)	Method								
		Barrett			Borchardt–Daniels			Kissinger		
		E_a (kJ/mol)	$\ln A$ ($\min^{-1}$)	Regression coefficient	E_a (kJ/mol)	$\ln A$ ($\min^{-1}$)	n	E_a (kJ/mol)	$\ln A$ ($\min^{-1}$)	Regression coefficient
TGDDM/TETA	5	60.1	12.0	0.983	58.9	17.6	0.86			
	10	77.8	14.9	0.962	72.3	22.3	1.04	74.5	9.2	0.996
	20	72.6	12.5	0.952	76.0	24.4	1.06			
TGDDE/TETA	5	46.9	6.7	0.975	77.5	23.7	1.39			
	10	45.1	2.3	0.964	78.1	26.1	1.98	78.1	19.8	0.997
	20	43.5	1.9	0.995	76.2	25.0	2.02			
TGDBBz/TETA	5	60.8	10.3	0.982	80.4	26.2	1.18			
	10	59.4	13.5	0.916	64.3	17.3	1.26	71.1	17.8	0.969
	20	67.9	25.7	0.974	76.8	45.4	1.28			

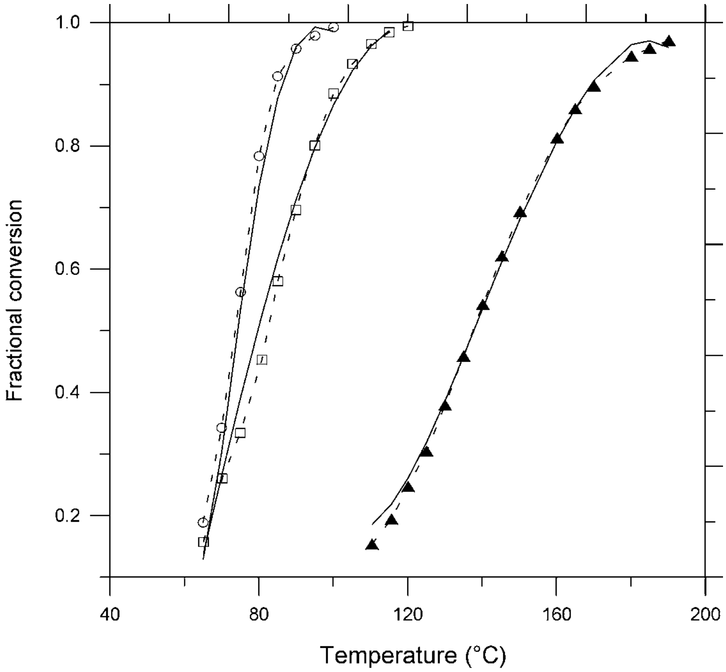


Fig. 3. Comparison of experimental values (- - -) and computed ones (——) for TGDBBz/TETA system cured at various heating rates: (○) 5°C/min; (□) 10°C/min; (▲) 20°C/min.

4. Conclusions

The curing reaction of some tetrafunctional epoxy resins in the presence of TETA is a complex process, due to the high functionality of the epoxy compounds, especially.

The kinetic parameters (E_a, ln A and n) determined using three different computational methods show the great influence of the heating rate on the curing process. The E_a determined at three heating rates (5, 10 and 20°C/min) show values between 43 and 80 kJ/mol, which are in good agreement with the reported values for various epoxy-amine systems [12,21].

References

[1] C.A. May, Epoxy Resins: Chemistry and Technology, 2nd Edition, Dekker, New York, 1988.
[2] E.B. Stark, J.C. Seferis, Thermochim. Acta 77 (1984) 19.
[3] D.J. Liaw, W.C. Shen, Polym. Eng. Sci. 34 (1994) 1297.
[4] A. Schiraldi, V. Wagner, G. Samanni, P.J. Rossi, J. Therm. Anal. 21 (1981) 299.
[5] T. Iijima, S. Miura, W. Fukuda, M. Tomoi, Eur. Polym. J 29 (1993) 1103.
[6] U.M. Vaskil, G.C. Martin, J. Appl. Polym. Sci. 46 (1992) 2089.
[7] Z. Cao, J.F. Galy, J.F. Gerard, H. Sauteren, Polym. Netw. Blends 4 (1993) 15.
[8] S.J. Montserrat, Polym. Sci. B 32 (1994) 509.
[9] R. Thiagarajan, P.V. Reddy, S. Sridhar, M.C. Ratio, J. Therm. Anal. 36 (1990) 277.
[10] G. Sánchez, Z. Brito, V. Mujica, G. Perdomo, Polym. Deg. Stab. 40 (1993) 109.
[11] C.N. Cascaval, D. Rosu, A. Stoleriu, Polym. Deg. Stab. 55 (1997) 281.
[12] R.D. Patel, R.G. Patel, V.S. Patel, Brit. Polym. J. 19 (1987) 37.
[13] F. Mustaţă, I. Bicu, J. Appl. Polym. Sci. 77 (2000) 2430.
[14] B. Sander, H.J. Ziegler, C. Bishof, Angew. Makromol. Chem. 181 (1990) 171.
[15] K.E.J. Barrett, J. Appl. Polym. Sci. 11 (1967) 1617.
[16] H.J. Borchardt, F.J. Daniels, J. Am. Chem. Soc. 79 (1956) 41.
[17] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[18] E. Urbaczewski, J.P. Pascault, H. Sautreau, C.C. Riccardi, S.S. Moschiar, R.J.J. Williams, J. Makromol. Chem. 191 (1990) 943.
[19] J. Mijovic, J. Kim, J. Slaby, J. Appl. Polym. Sci. 29 (1984) 1449.
[20] C.C. Riccardi, R.J.J. Williams, J. Appl. Polym. Sci. 32 (1986) 3445.
[21] R. Jenkins, L.J. Karre, J. Appl. Polym. Sci. 10 (1966) 303.