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Cure kinetics of epoxy resins studied by non-isothermal DSC data

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Abstract

The curing kinetics of diglycidyl ether of bisphenol A (DGEBA) and diglycidyl ether of hydroquinone (DGEHQ) epoxy resins in presence of diglycidyl aniline as a reactive diluent and triethylenetetramine (TETA) as the curing agent was studied by non-isothermal differential scanning calorimetry (DSC) technique at different heating rates. The kinetic parameters of the curing process were determined by isoconversional method given by Málek for the kinetic analysis of the data obtained by the thermal treatment. A two-parameter (m, n) autocatalytic model (Šesták–Berggren equation) was found to be the most adequate selected to describe the cure kinetics of the studied epoxy resins. Reactive diluent decreases both the activation energy and the cure kinetic parameters. Non-isothermal DSC curves obtained using the experimental data show a good agreement with that theoretically calculated.

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

1. Introduction

Epoxy resins are the most important thermosetting polymers widely used as matrices in reinforced composites, adhesives in the aerospace industry, surface coatings, etc. [1–3]. Most of the commercially available epoxy resins are oligomers of diglycidyl ether of bisphenol A (DGEBA).

An epoxy resin becomes an insoluble thermosetting polymer when it reacts with a cross-linking agent. These resins have good thermal, electrical and mechanical properties, but they are brittle and have poor resistance to the crack propagation [4,5]. To alternate this deficiency, the epoxy resins are mixed with modifying agents, such as low molecular weight polymers, reactive oligomeric compounds, plasticizers, fillers, reactive diluents, etc. which modify the viscosity of the resin so that the processability of the system is not impaired [6–10].

It is known that the physical properties of the cured epoxy resins depend on their structure [10,11], the extent of cure [12], the curing conditions [13,14], and the time and temperature of cure [15]. For this reason, it is necessary to know and to understand the relationships between the structure of the networks and the final properties, in order to obtain resins with high performance applications [16,17].

Differential scanning calorimetry (DSC), which measures the heat flow of the sample as a function of temperature, has extensively used to study the cure kinetics of various thermosetting polymers [12,14,15,17].

The presence of reactive diluents modifies the properties of the epoxy systems [18–20]. In the previous paper [21], the behavior of the two epoxy resins with different structure, namely DGEBA and diglycidyl ether of hydroquinone (DGEHQ), cross-linked

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with triethylenetetramine (TETA), in presence of diglycidyl aniline (DGA), used as reactive diluent, was studied in isothermal conditions regarding their rheological and thermal properties. The present paper reports the cure kinetics of the two above-mentioned epoxy resins and determination of the kinetic parameters of the cure reaction from non-isothermal DSC measurements, applying the simple and consistent method of Málek [22,23] on kinetic analysis of the data obtained by the thermal treatment. The used method allowed us to select the most convenient model for the curing reaction (Šesták–Berggren equation) of the studied epoxy resins.

2. Experimental

2.1. Materials

DGEBA epoxy resin was a commercial product (supplied from Sintofarm SA-Bucharest, Romania), which was obtained by the reaction between bisphenol A and epichlorohydrin. It has an epoxy equivalent weight of 160 g (Eq. (1)), and was used as received. DGEHQ was synthesized in laboratory [24] starting from hydroquinone and epichlorohydrin. It has an epoxy equivalent weight of 345 g (Eq. (1)). DGA with an epoxy equivalent weight of 194 g (Eq. (1)) was obtained by a reaction between aniline and epichlorohydrin [21]. Aniline, epichlorohydrin, hydroquinone and TETA were of regent grade and used as received.

The studied epoxy resins were mixed with both the reactive diluent and with the curing agent at the weight ratios shown in Table 1. The mixture was stirred for 10 min at room temperature and then degassed in a vacuum oven to remove the air included during the mixing process.

Table 1
Samples analyzed by DSC technique

Sample	Weight ratio of the components	
	DGEBA/DGA/TETA	DGEHQ/DGA/TETA
1	1/0/0.75	–
2	1/1/1.5	–
3	0/1/0.75	–
4	–	1/0/0.75
5	–	1/1/1.5

2.2. DSC measurements

The curing thermal data were obtained by means of a Mettler 12 E type differential scanning calorimeter, heated from 20 to 200 °C with different heating rates (5, 10 and 20 °C min^{-1}), in a nitrogen atmosphere. Pure indium was used as a standard for calorimetric calibration. Runs were carried out using an empty cell as a reference. The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm. These data were processed further to obtain the fractional conversion (α) and the rate of reaction.

The basic assumption for the application of DSC technique to the cure of the thermoset polymers is that the rate of the kinetic process ($d\alpha/dt$) is proportional to the measured heat flow ϕ [22,25].

$$\frac{d\alpha}{dt} = \frac{\phi}{\Delta H} \tag{1}$$

ΔH being the enthalpy of the curing reaction.

The rate of the kinetic process in kinetic analysis can be described by Eq. (2)

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \tag{2}$$

where $K(T)$ is a temperature-dependent reaction rate constant, and $f(\alpha)$ a dependent kinetic model function [22,26].

The rate constant $K(T)$ is dependent on temperature as in Eq. (3)

$$K(T) = A\exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where A is the pre-exponential factor and E_a is the apparent activation energy.

The kinetic parameters of the curing reaction, with special reference to E_a, can be calculated using various computational methods [27–29]. The E_a was determined by the isoconversional method [23], using the logarithmic form of the kinetic (Eq. (2))

$$\ln\frac{da}{dt} = \ln[Af(\alpha)] - \frac{E_a}{RT} \tag{4}$$

The slope of $\ln d\alpha/dt$ versus $1/T$ for the same value of α gives the value of E_a. The values of E_a can then be used to find the appropriate kinetic model which best describes the conversion function of the studied

process. For this, it is necessary to appeal to the special functions $y(\alpha)$ and $z(\alpha)$ [22,23].

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) e^{x} \quad (5)$$

$$z(\alpha) = \pi(x)\left(\frac{d\alpha}{dt}\right)\frac{T}{\beta} \quad (6)$$

where x is reduced activation energy (E_a/RT), β the heating rate (K min^{-1}), T absolute temperature (K) and $\pi(x)$ is the expression of the temperature integral. As was pointed out [26], $\pi(x)$ function can be well approximated using the 4th rational expression of Senum and Yang [30] as in Eq. (7)

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (7)$$

The $y(\alpha)$ function is proportional to $f(\alpha)$ function, being characteristic for a given kinetic model. The shape and the maximum of both $y(\alpha)$ and $z(\alpha)$ functions for several models, normalized within the (0, 1) interval, give valuable informations for determination of the most suitable kinetic model characterizing the process studied.

Using the value of E_a and knowing the kinetic model, the pre-exponential factor A is calculated according to Eq. (8)

$$A = -\frac{\beta x_p}{Tf'(\alpha_p)}\exp x_p \quad (8)$$

where, $f'(\alpha_p)$ is the differential form of the kinetic model [$df(\alpha)/d\alpha$], α_p is the conversion corresponding to the maximum on DSC curve and p is the maximum of DSC curve.

3. Results and discussion

The curing reaction of the studied epoxy resins in presence of TETA and DGA was investigated by DSC at three different heating rates. Fig. 1 shows a typical example of the DSC thermograms for DGEBA/DGA/

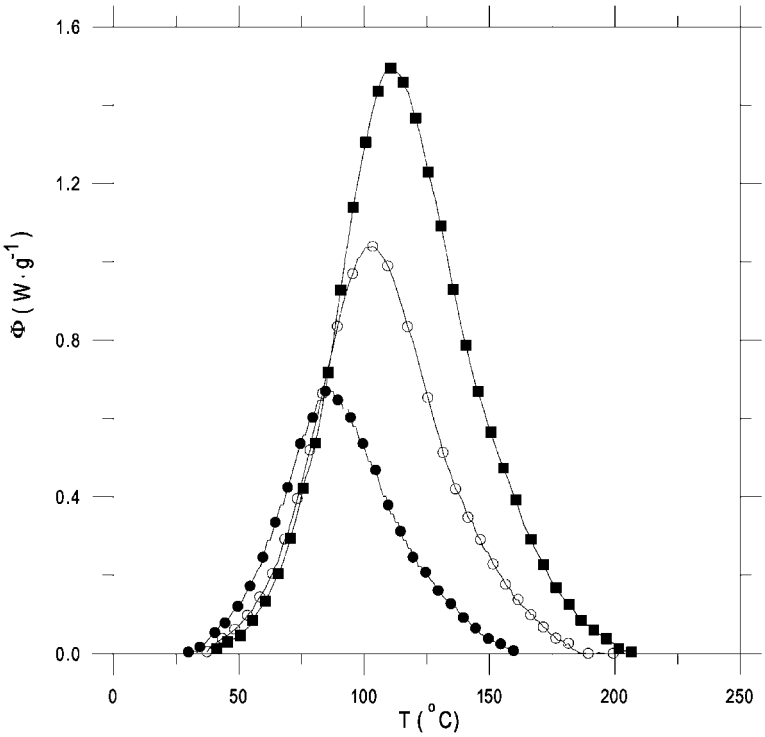

Fig. 1. Typical DSC curves recorded for DGEBA/DGA/TETA system at different heating rates: (●) 5 °C min^{-1}; (○) 10 °C min^{-1}; (■) 20 °C min^{-1}.

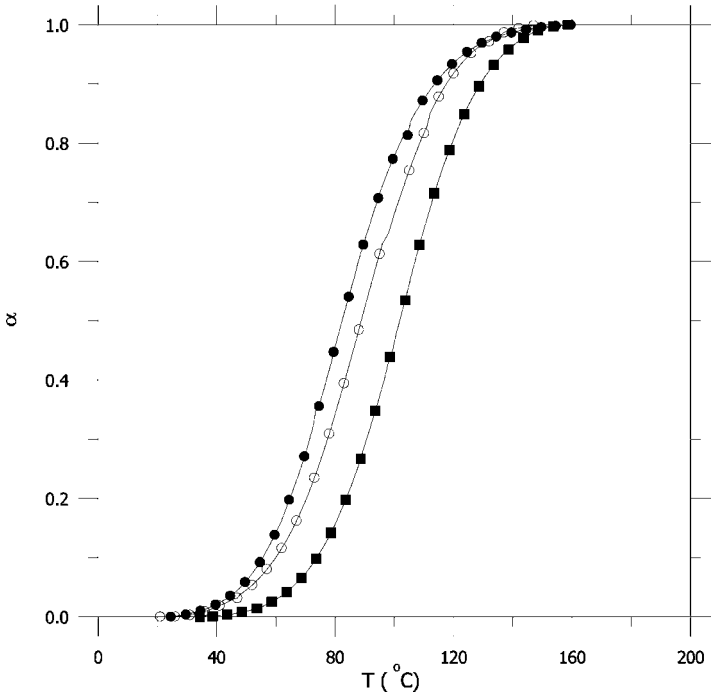

Fig. 2. Fractional conversion as a function of temperatures for DGEBA/DGA/TETA system: (●) 5 °C min^{-1}; (○) 10 °C min^{-1}; (■) 20 °C min^{-1}.

TETA sample 1 recorded at 5, 10 and 20 °C min^{-1}, while Fig. 2 shows the variation of the fractional conversion as a function of temperature for the same sample 1.

From DSC thermograms obtained for all the five studied samples information about the curing reaction were obtained as follows: the initial curing temperature (T_i), the peak temperature (T_p), the finishing temperature (T_f) and the curing range of the studied systems. Some data on the curing reactions are summarized in Table 2.

As can be noted, with some exceptions, the increase of the reactive diluent content in the studied samples leads to increase of the cure range, the cure duration, as well as the ΔH, especially. This behavior can be related to the more comprehensive cure of the tested resins in presence of the reactive diluent, due to both the decrease of the viscosity and increase of the number of the epoxy groups which react with the reactive diluent.

Arrhenius plots from DSC scans recorded for the cured samples using Eq. (4) and the same α value are

Table 2
Curing characteristics of both DGEBA/DGA/TETA and DGEHQ/DGA/TETA samples evaluated from DSC thermograms recorded at 10 °C min^{-1} heating rate

Sample	T_i (°C)	T_p (°C)	T_f (°C)	Cure range (%)	Cure duration (min)	ΔH (J g^{-1})
1	28	92	150	122	12.0	373
2	37	104	187	150	15.0	680
3	49	110	158	109	11.0	718
4	41	90	146	105	10.5	519
5	44	107	197	153	15.0	1158

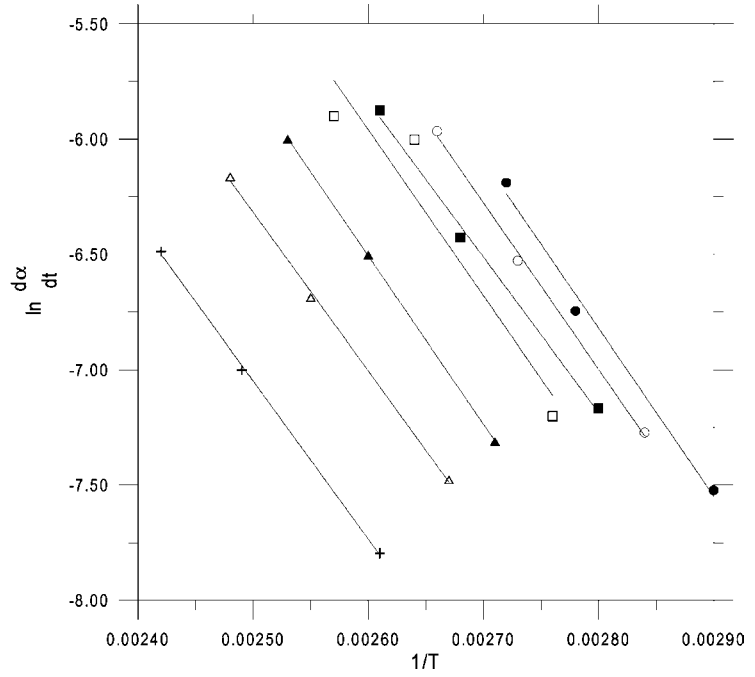

Fig. 3. Arrhenius plots for sample 3 in the interval $0.2 < \alpha < 0.8$: (●) $\alpha = 0.2$; (○) $\alpha = 0.3$; (■) $\alpha = 0.4$; (□) $\alpha = 0.5$; (▲) $\alpha = 0.6$; (△) $\alpha = 0.7$; (+) $\alpha = 0.8$.

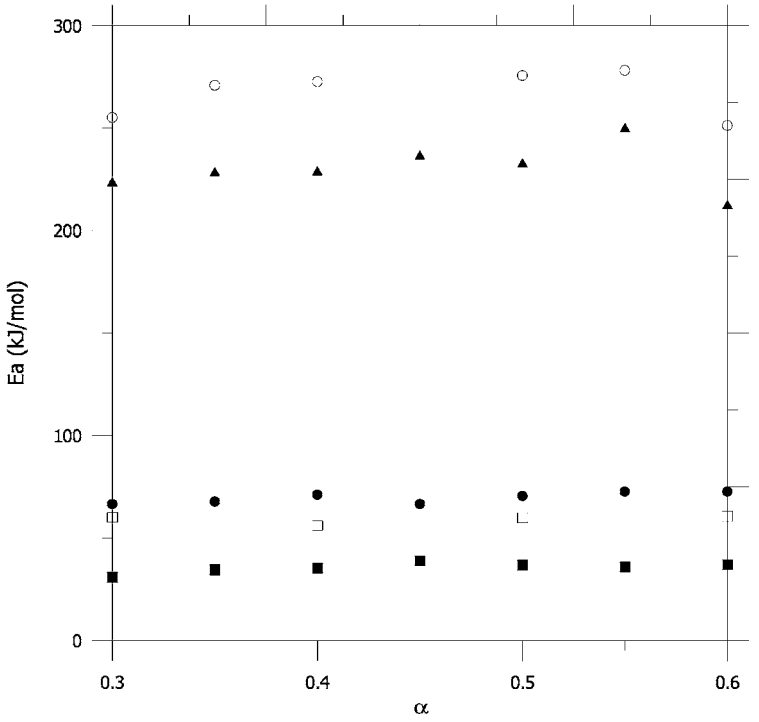

Fig. 4. Variation of E_a versus conversion: (●) sample 1; (○) sample 2; (□) sample 3; (▲) sample 4; (■) sample 5.

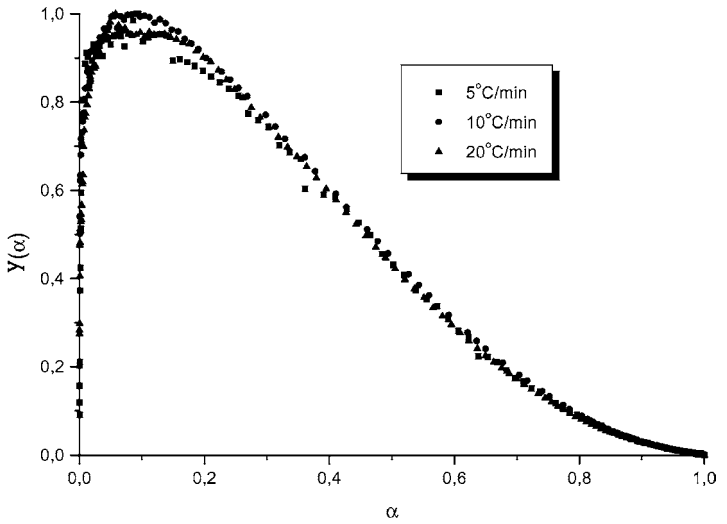

Fig. 5. Variation of $y(\alpha)$ function versus conversion for DGEBA/DGA/TETA system.

straight lines, the slope of which gives the value of E_a.

Fig. 3 shows a plot obtained for the sample 3, in the interval $0.2 < \alpha < 0.8$, while Fig. 4 shows the variation of E_a for all the studied samples as a function of the fractional conversion.

It can be observed that E_a determined from DSC scans is practically constant in the conversion interval $0.3 < \alpha < 0.6$, with the slight tendency to increase for α values out of the above-mentioned interval. These deviations are probably due to the errors in base line approximation for peak tails [22].

The value of E_a determined from DSC data was used to calculate both $y(\alpha)$ and $z(\alpha)$ functions using Eqs. (5) and (6), respectively. Figs. 5 and 6 show the variation of $y(\alpha)$ (Fig. 5) and $z(\alpha)$ (Fig. 6) values with

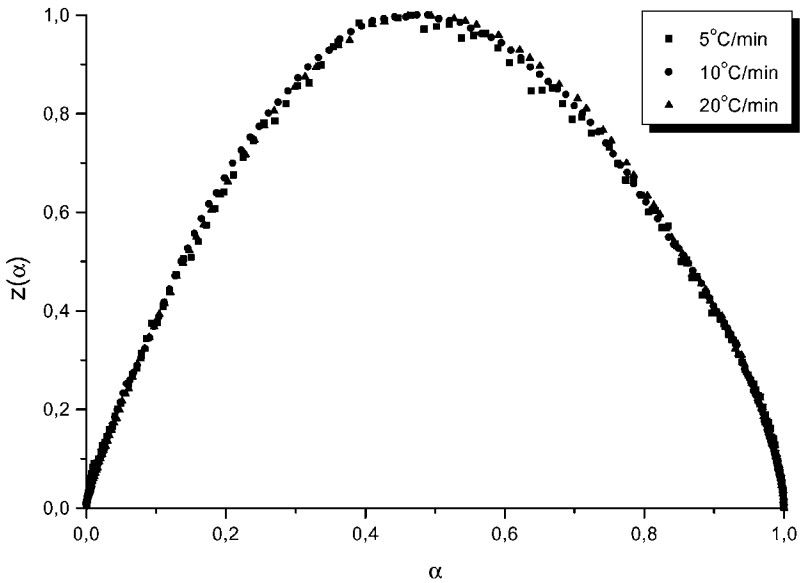

Fig. 6. Variation of $z(\alpha)$ function versus conversion for DGEBA/DGA/TETA system.

conversion. The values of both $y(\alpha)$ and $z(\alpha)$ were normalized within the (0, 1) interval of DGEBA/DGA/TETA systems for various heating rates. These functions exhibit maxima at α_M and α_p^∞, respectively. Both α_M and α_p^∞ help to decide the choice of the kinetic model [23].

Table 3 lists the values of maxima α_M and α_p^∞ corresponding to the functions $y(\alpha)$ and $z(\alpha)$ for all the studied samples, together with α_p taken as the maximum of the DSC peak.

As was noted, data in Figs. 5 and 6, respective in Table 3, show that α_M, α_p^∞ and α_p values are independently of the heating rate. Simultaneously, the values of α_M are lower against the values of α_p, while α_p^∞ exhibits values lower than 0.632. These remarks indicate that the studied curing process can be described using the two-parameter autocatalytic kinetic model Šesták–Berggren (Eq. (9)) [31].

$$f(\alpha) = \alpha^m(1-\alpha)^n \quad (9)$$

where m and n are the kinetic exponents [23].

The kinetic parameter n is obtained by the slope of the linear dependence $\ln[(d\alpha/dt)\, e^x]$ versus $\ln[\alpha^p\,(1-\alpha)]$ (from Eq. (2)), and $m = pn$, where $p = \alpha_M/(1-\alpha_M)$.

Table 4 lists some kinetic parameters evaluated for the proposed Šesták–Berggren kinetic model. As it is shown in Table 4, the variation of the kinetic parameter values with the heating rate is placed in the experimental errors limit (within 10% of the average value).

Table 3
The values of α_p, α_M and α_p^∞ obtained from DSC thermograms analysis

Sample	Heating rate (°C min^{-1})	α_p	α_M	α_p^∞
DGEBA/TETA	5	0.74	0.01	0.540
	10	0.54	0.01	0.540
	20	0.52	0.03	0.533
DGEBA/DGA/TETA	5	0.43	0.10	0.460
	10	0.46	0.09	0.480
	20	0.42	0.06	0.480
DGEHQ/TETA	5	0.781	0.00088	0.601
	10	0.598	0.00078	0.598
	20	0.549	0.00039	0.607
DGEHQ/DGA/TETA	5	0.403	0.0003	0.450
	10	0.495	0.0004	0.408
	20	0.408	0.0003	0.448

The correctness of the kinetic model proposed using the Šesták–Berggren equation was verified by plotting $d\alpha/dt$ versus temperature (experimental curves), using the data listed in Table 4, with the curves obtained by computational processing of the thermograms (calculated curves). An example is given in Fig. 7 for the DGEBA/TETA system. It is observed that the two-parameter Šesták–Berggren model well describes the studied curing process.

Table 4
The kinetic parameters evaluated for the curing of the tested epoxy resins

Sample	Heating rate (°C min^{-1})	E_a (kJ mol^{-1})	ln A	Mean	m	Mean	n	Mean
DGEBA/TETA	5		17.973		0.0147		1.948	
	10	69.5	18.061	17.953	0.0259	0.0284	1.770	1.755
	20		17.837		0.0447		1.549	
DGEBA/DGA/TETA	5		13.842		0.194		1.880	
	10	59.1	13.727	13.783	0.156	0.155	1.732	1.826
	20		13.779		0.114		1.865	
DGEHQ/TETA	5		86.204		0.00044		5.002	
	10	267.0	86.646	86.459	0.00380	0.00206	4.841	4.937
	20		86.527		0.00196		4.967	
DGEHQ/DGA/TETA	5		68.024		0.00016		3.920	
	10	230.5	68.533	68.446	0.00092	0.00092	4.770	4.772
	20		68.842		0.00169		5.626	

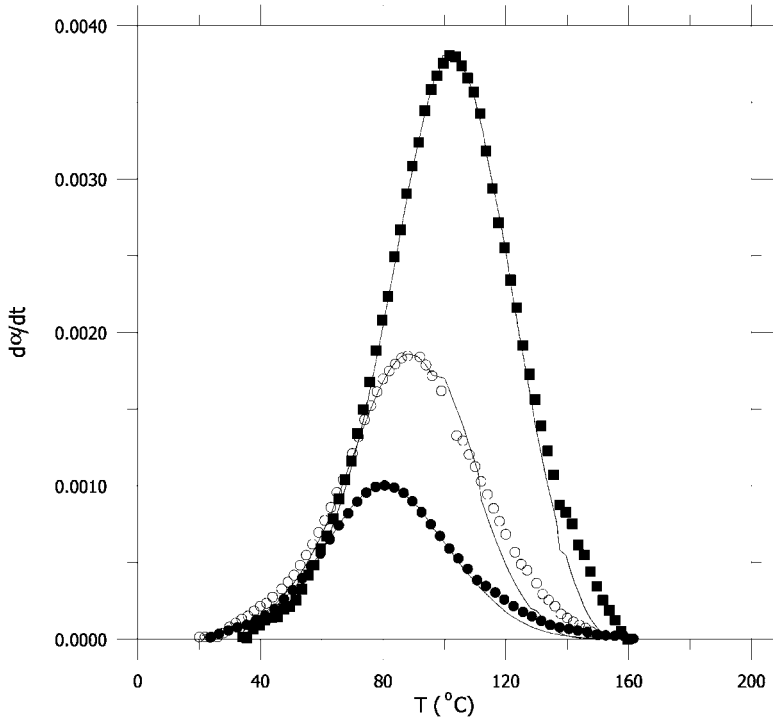

Fig. 7. Comparison of experimental (symbols) and calculated (full lines) DSC curves for DGEBA/TETA system: (●) 5 °C min^{-1}; (○) 10 °C min^{-1}; (■) 20 °C min^{-1}.

4. Conclusions

The cure kinetics of two epoxy resins with different structures (DGEBA and DGEHQ), in presence of DGA, as a reactive diluent, and TETA, as hardener, was examined by DSC technique at various heating rates. The E_a determined by isoconversional method was 69.5 kJ mol^{-1} for DGEBA/TETA system, and 267.0 kJ mol^{-1} for DGEHQ/TETA system. The presence of the reactive diluent leads to decrease of the E_a for both the studied epoxy resins. The values of E_a in the conversion interval between 0.3 and 0.6 is relatively constant and independent of the experimental working conditions.

It was established that the two-parameter autocatalytic model (Šesták–Berggren equation) is the most suitable for description of the studied curing process. The kinetic parameters which were experimentally determined were used to calculate the theoretically DSC curves. These show a good agreement with that experimentally determined.

References

[1] C.A. May, Epoxy Resins: Chemistry and Technology, 2nd Edition, Marcel Dekker, New York, 1988.
[2] T.M. Goulding, in: A. Pizzi, K.L. Mattal (Eds.), Handbook of Adhesive Technology, Marcel Dekker, New York, 1994, p. 531.
[3] M. Chen, A.S. Ren, J.F. Wang, M.S. Lee, L.R. Dalton, H. Zhang, G. Sun, W.H. Steirer, Polym. Prepr. 40 (1999) 162.
[4] T. Iijima, S. Miura, W. Fukuda, M. Tomoi, Eur. Polym. J. 29 (1993) 1103.
[5] U.M. Vaskil, G.C. Martin, J. Appl. Polym. Sci. 46 (1992) 2089.
[6] M.E. Frigione, L. Mascia, D. Acierno, Eur. Polym. J. 31 (1995) 1021.
[7] Y.G. Won, J. Galy, J.F. Gerard, J.P. Pascault, V. Bellenger, J. Verdu, Polymer 31 (1990) 1787.
[8] J. Thakkar, R.D. Patel, R.G. Patel, V.S. Patel, Brit. Polym. J. 22 (1990) 143.
[9] F. Mustata, I. Bicu, C.N. Cascaval, J. Polym. Eng. 17 (1997) 491.
[10] S. Suvarna, S.Y. Ambekar, M. Saletori, C. Biswas, A.V. Rajanna, J. Appl. Polym. Sci. 77 (2000) 2097.
[11] D.J. Liaw, W.C. Shen, Polym. Eng. Sci. 34 (1994) 1297.

[12] S. Montserrat, J. Málek, Thermochim. Acta 228 (1993) 47.
[13] D. Rosu, F. Mustata, C.N. Cascaval, Thermochim. Acta 370 (2001) 105.
[14] S. Montserrat, J. Thermal. Anal. 40 (1993) 553.
[15] C.N. Cascaval, D. Rosu, A. Stoleriu, Polym. Deg. Stab. 55 (1997) 281.
[16] Z. Cao, J. Galy, J.F. Gerard, H. Sautereau, Polym. Networks Blends 4 (1993) 15.
[17] R. Thiagarajan, P.V. Reddy, S. Sridhar, M.C. Ratra, J. Thermal. Anal. 36 (1990) 277.
[18] R.D. Patel, R.G. Patel, V.S. Patel, British Polym. J. 19 (1987) 37.
[19] E. Urbaczewski, J.P. Pascault, H. Sautereau, C.C. Riccardi, S.S. Moschiar, R.J.J. Williams, Macromol. Chem. 191 (1990) 943.
[20] E. Urbaczewski-Espuche, J. Galy, J.F. Gerard, J.P. Pascault, H. Sautereau, Polym. Eng. Sci. 31 (1991) 1572.
[21] F. Mustata, I. Bicu, Polym. Testing 20 (2001) 533.
[22] J. Málek, Thermochim. Acta 355 (2000) 239.
[23] J. Málek, Thermochim. Acta 200 (1992) 257.
[24] F. Mustata, I. Bicu, Polymer 45 (2000) 258.
[25] B.D. Park, B. Riedl, E.W. Hsu, J. Shields, Polymer 40 (1999) 1689.
[26] S. Montserrat, J. Málek, Thermochim. Acta 228 (1993) 47.
[27] K.E.J. Barret, J. Appl. Polym. Sci. 11 (1967) 1617.
[28] H.J. Borchardt, F.Y. Daniels, J. Am. Chem. Soc. 79 (1956) 41.
[29] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[30] G.I. Senum, R.T. Yang, J. Thermal. Anal. 11 (1977) 445.
[31] J. šesták, G. Berggren, Thermochim. Acta 3 (1971) 1.