

Material Behaviour

Cure kinetics of a liquid-crystalline epoxy resin studied by non-isothermal data

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Abstract

The curing kinetics of diglycidyl ether of 4,4'-bisphenol (DGE BP) epoxy mesogenic resin in the presence of sulphanimide (SAA) was studied by non-isothermal differential scanning calorimetry (DSC) at different heating rates. At low heating rates ($2\text{--}5\text{ }^{\circ}\text{C min}^{-1}$), the curing reaction takes place by two processes evidenced by the presence of a double peak on the DSC thermograms. The first process is due to the reaction of primary amine with epoxy, while the second one corresponds to the formation of the crosslinked network with liquid crystalline (LC) properties by the attack of the secondary amine previously formed onto the epoxide groups unreacted in the first stage of the reaction. An activation energy ($E_a = 59\text{ kJ mol}^{-1}$) was evaluated for the second process and an autocatalytic kinetic model (Šesták–Berggren equation) was proposed to better describe the cure kinetics of the studied system. The theoretical DSC curves calculated using the kinetic parameters determined in non-isothermal conditions show good agreement with those experimentally determined.

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1. Introduction

Epoxy resins are the most important thermosetting polymers, widely used as adhesives and composite materials [1]. These resins have good thermal, electrical and mechanical properties, but they are brittle and have poor resistance to crack propagation [2,3]. In order to obtain resins for high performance applications, numerous works have been done in the last decade on the networks obtained by curing reaction of epoxy resins with polyfunctional amines [4–9].

The properties of epoxides can be much enhanced if liquid crystalline (LC) like structures are incorporated into epoxy networks [10–12]. One way to synthesize the

LC epoxy resins is the curing reaction of some functionalized potentially mesogenic rigid molecules with a suitable curing agent. In that case, the introduction of some mesogenic groups into the epoxy structure leads to compounds that combine the properties which are specific to epoxies with those characteristic to LC compounds.

As known, the curing reaction is a very complex process, because many reactive processes occur simultaneously. The final properties of the crosslinked epoxy resins depend on the kinetics of the curing reaction. The study of the cure kinetics contributes both to a better knowledge of the process development and to improving the quality of the final product. Unfortunately, very few kinetic studies have been reported on the curing reaction and phase transition of LC epoxy compounds [10,12–14].

The present paper reports the cure kinetics of an epoxy resin displaying a LC structure, namely, the diglycidyl ether of 4,4'-bisphenol (DGE BP), in the presence of sul-

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phanilamide (SAA) as the curing agent. The cure kinetics of the studied system were examined by non-isothermal differential scanning calorimetry (DSC) at different heating rates.

2. Experimental

2.1. Materials

4,4'-bisphenol, SAA, epichlorohydrin and benzyltrimethylammonium bromide were commercial grade products (Aldrich) and used without further purification. The DGE BP epoxy compound was synthesized as reported previously [15]. A mixture constituted from 0.16 mol 4,4'-bisphenol, 3.35 mol epichlorohydrin and 0.005 mol benzyltrimethylammonium bromide was introduced in a flask (500 ml) provided with a stirrer, thermometer and a reflux condenser. The mixture was heated at reflux for a duration of 40 min. Then, an aqueous solution of 15% wt. NaOH (0.33 mol) was added to the flask and the mixture was again heated for 45 min. The reaction was completed at ambient temperature after an additional 2 h. The DGE BP obtained was purified by multiple recrystallization processes using a mixture constituted from isopropylalcohol/chloroform (2:1).

2.2. DSC measurements

DSC, which measures the heat flow of the sample against temperature, was used to study the cure kinetics of the epoxy resin in the presence of SAA. The curing thermal data were obtained using a Perkin-Elmer DSC 7 type calorimeter, which was heated from 25 up to 300 °C with different heating rates (2 up to 5 and 10 °C min⁻¹), in a nitrogen atmosphere. Pure indium was used as a standard for calorimetric calibration. The study of the curing reaction was carried out using a molar ratio of 2:1 DGE BP/SAA.

A small quantity of the sample (8–12 mg) was used for the DSC studies in an aluminium cell. An identical empty cell was taken as reference. The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm. They were processed further to obtain a fractional conversion (α) and the rate of the reaction $d\alpha/dt$.

The rate of the kinetic process can be described by Eq. (1) [16,17]

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (1)$$

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

There is an Arrhenius type dependence between $K(T)$ and temperature according to Eq. (2).

$$K(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

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

For non-isothermal conditions, when the temperature varies with time with a constant heating rate $\beta = dT/dt$, Eq. (2) is modified as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (3)$$

Usually, E_a values are determined using the integral forms of Eq. (3), the most popular derivative modes being those proposed by Ozawa [18], Flynn and Wall [19], and Doyle [20], which give E_a from the plot $\ln\beta_i$ against $T_{\alpha,i}^{-1}$ (i is the ordinal number of DSC runs performed at different heating rates, β_i). Generally, the E_a values found by these equations require further corrections [21], which can be avoided using the methods suggested by ASTM E 698-79 [5,22], according to which the E_a is evaluated from the plot $\ln(\beta_i/T_{m,i}^2)$ against $T_{m,i}^{-1}$, where $T_{m,i}$ are the temperatures corresponding to peak maxima at different heating rates. The latter has been used in present computations of E_a at different values of α . The experimentally evaluated values of E_a were used to find the appropriate kinetic model which best describes the conversion function of the process studied.

The kinetic parameters of the curing process were determined by the isoconversional method given by Málek [16,23]. Once E_a has been determined, the special functions $y(\alpha)$ (4) and $z(\alpha)$ (5) must be evaluated:

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right) \cdot e^x \quad (4)$$

$$z(\alpha) = \pi(x) \cdot \left(\frac{d\alpha}{dt}\right) \frac{T}{\beta} \quad (5)$$

where x is reduced activation energy (E_a/RT), β the heating rate (K min⁻¹), T the absolute temperature (K) and $\pi(x)$ the expression of the temperature integral, which was approximated using the fourth rational expression of Senum and Yang [24].

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (6)$$

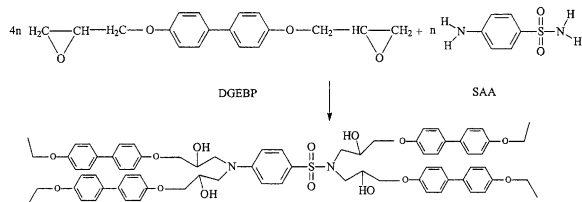
For practical reasons, the $y(\alpha)$ and $z(\alpha)$ functions are normalized within (0,1) range. The maximum α_M of the $y(\alpha)$ function and α_p^∞ of the $z(\alpha)$ function suggest the choice of the most suitable kinetic model characterizing the curing process studied. Once the kinetic model has been determined, and using the value of E_a , other kinetic parameters can be determined, such as the pre-exponential factor and the kinetic exponents. The pre-exponential factor A was calculated according to Eq. (7):

$$A = \frac{\beta x_p}{T f'(\alpha_p)} \exp x_p \quad (7)$$

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 thermoset LC epoxy monomer (DGEBP) in the presence of SAA was investigated by DSC using different heating rates. The chemical reactions involved are shown in Scheme 1.



The diamine SAA has two different amine functions of unequal reactivity and leads to the formation of a smectic phase when it is used as a curing agent [25]. Concerning the LC behaviour of the epoxy monomers, polarized optical microscopy showed that DGEBP does not display a LC phase [15]. Initially, the melting of the DGEBP/SAA mixture does not show the LC properties since an isotropic liquid is formed above the melting point. Then, as the reaction between epoxy and amine proceeds, a LC texture is developed, which is locked in the crosslinked network by the nematic arrangement.

Depending on the heating rate, the DSC thermograms of the curing process show two endothermal peaks and one or two exothermal peaks. Generally, the exothermal peaks appear, together with endothermal peaks, when the samples are cured at very low heating rates (2 up to 5 °C min⁻¹). Fig. 1 shows a typical example of the DSC thermograms for DGEBP/SAA mixture recorded at 2 °C min⁻¹.

The first two endothermal peaks observed in the temperature range between 120 and 140 °C are assigned to the melting of the individual components of the mixture studied. With increase of temperature above 140 °C, the DSC curve in Fig. 1 shows two exothermic peaks. The latter correspond to the smectic phase, as noted previously using polarized optical microscopy [15].

The heating rate shows a great influence on the curing process. This can be observed in Fig. 2, where the DSC thermograms for DGEBP/SAA sample are recorded at different heating rates. As can be noted, at very low heating rates (2 up to 5 °C min⁻¹), two exothermal peaks appear, while at higher heating rate (10 °C min⁻¹), the thermal phenomenon is superposed in a single exothermal signal.

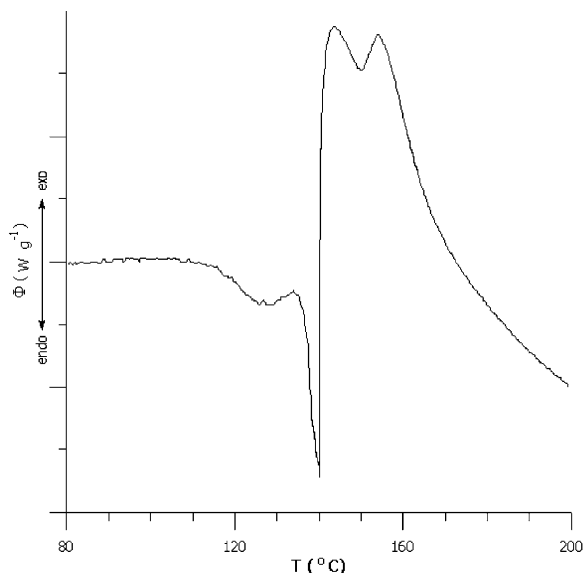


Fig. 1. Typical DSC curve recorded for DGEBP/SAA system at 2 °C min⁻¹.

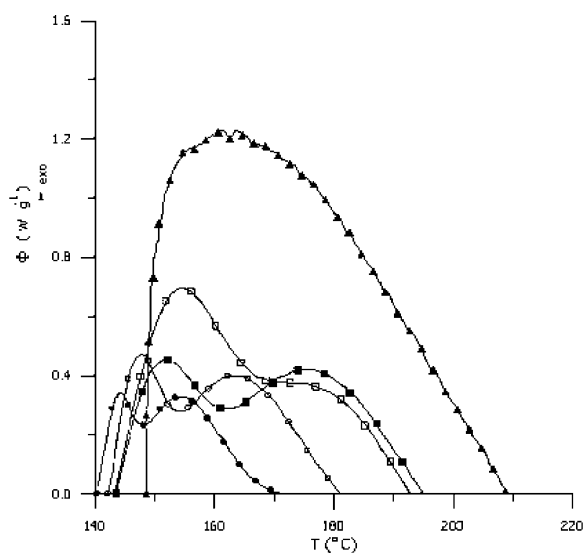


Fig. 2. Typical exothermal peaks recorded for DGEBP/SAA system at different heating rates (●) 2 °C min⁻¹; (○) 3 °C min⁻¹; (■) 4 °C min⁻¹; (□) 5 °C min⁻¹; (▲) 10 °C min⁻¹.

From Fig. 2, information about the curing reaction was obtained as follows: the initial temperature (T_i), the peak temperature (T_p), the finishing temperature (T_f), the cure time (min) and the reaction enthalpy (ΔH). The data obtained are summarized in Table 1.

It can be observed that the increase of the heating rate leads to decrease of the cure time. Simultaneously, on increasing the heating rate, the curing curves for the tested mixture are shifted to the higher temperatures. The

Table 1
Curing characteristics of DGEBP/SAA mixture at various heating rate

Heating rate (β , °C min ⁻¹)	T_i (°C)	T_{p1} (°C)	T_{p2} (°C)	T_f (°C)	Cure time (min)	ΔH (J g ⁻¹)
2	140	143	153	172	16	286.2
3	142	145	162	181	13	348.2
4	143	147	173	195	13	298.6
5	144	149	181	193	10	331.8
10	149	163	—	209	6	292.6

mean thermal exothermic effect (ΔH), which characterizes the reaction between DGEBP and SAA, lies at a value of 307.5 J g⁻¹. The maximum deviation of 13% from this value can be due to the errors connected with methods used to estimate the baseline. The mean value of ΔH is placed between values obtained for the curing reaction of other LC epoxy resins (304–370 J g⁻¹) [12].

The kinetic analysis of the DSC curves at the heating rates between 2 and 5 °C min⁻¹ was carried out by separation of the two exothermic peaks (Microcal Origin 6.0 programme) and the distinct characterization of them. As an exemplification of this, Fig. 3 shows a typical example of the DSC thermograms recorded for the curing reaction of the DGEBP/SAA sample at 3 °C min⁻¹.

The experimentally recorded thermogram (solid line) in Fig. 3 with two partially superposed peaks was deconvoluted into two distinct peaks (peak I—black circles and peak II—white circles). The presence of the two peaks in Fig. 3 is in accordance with the well known kinetic scheme of the epoxy–amine reaction, in which

the reaction of a primary amine function with an epoxy group leads to a secondary amine, which can further react with another epoxy group. Peak I in Fig. 3 corresponds to the beginning of the reaction between the primary amine group and epoxy with the formation of some secondary amine structures and obtaining some linear or slightly branched mers [12]. Further, with extension of the reaction by the addition of the secondary amine to the epoxy monomer, a tridimensional network is formed (peak II).

For each peak, E_a was evaluated from the plot of $\ln(\beta_i/T_i^2)$ against T_i^{-1} [22], where T_i are the temperatures corresponding to different values of α . The variation of E_a with conversion α for the two processes (peak I and peak II) is shown in Fig. 4.

For process I, it can be noted that E_a varies with conversion with important values. If in the initial stages ($\alpha = 0.01$ – 0.1), E_a has values between 260 and 230 kJ mol⁻¹, in the final stages ($\alpha = 0.95$ – 1.0), E_a values vary between 87 and 74 kJ mol⁻¹. This behaviour reflects the complexity of process I, which proceeds through a nucleophilic attack of the primary amine onto the epoxy ring. The low reactivity of -NH₂ group in SAA can be an explanation of a high value of E_a in the first stage of the curing reaction. The hydroxyls appearing from the opening of the epoxy ring by the amine has an autocatalytic effect on the reaction and this explains the drastic decrease of E_a with conversion.

Regarding process II, a lower variation of E_a with conversion can be observed. In this stage, E_a is modified from values between 79 and 75 kJ mol⁻¹ for low conversions ($\alpha = 0.05$ – 0.1) to values between 49 and 47 kJ mol⁻¹ for higher conversions ($\alpha = 0.85$ – 0.95). Simultaneously, it can be noted that for the conversions between 0.3 and 0.6, there is very low variation of E_a with conversion (mean value of $E_a = 59$ kJ mol⁻¹).

The mean value of E_a estimated for process II was used to calculate $y(\alpha)$ and $z(\alpha)$ functions, using Eqs. (4) and (5), respectively. Figs. 5 and 6 show the variation of $y(\alpha)$ (Fig. 5) and $z(\alpha)$ (Fig. 6) values with conversion. The values of both $y(\alpha)$ and $z(\alpha)$ were normalized within the (0,1) interval using different heating rates for the curing reaction of DGEBP/SAA samples. These functions exhibit maxima at α_M and α_p^∞ , respectively. Both α_M and

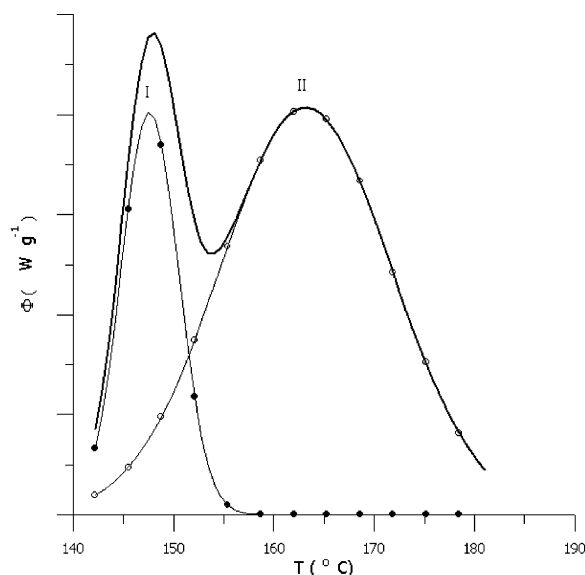
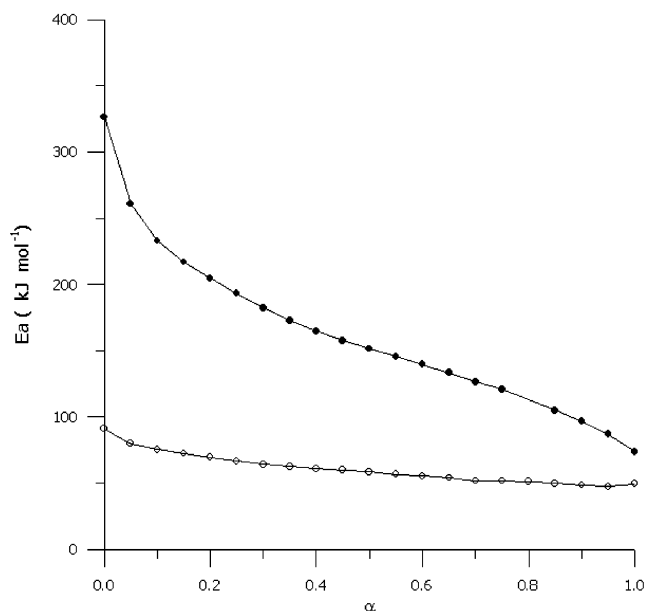
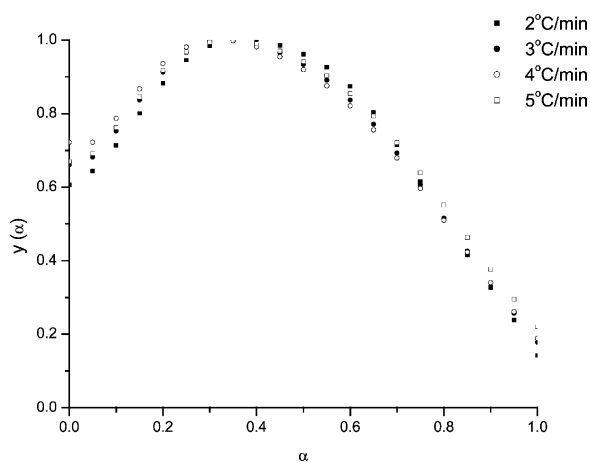
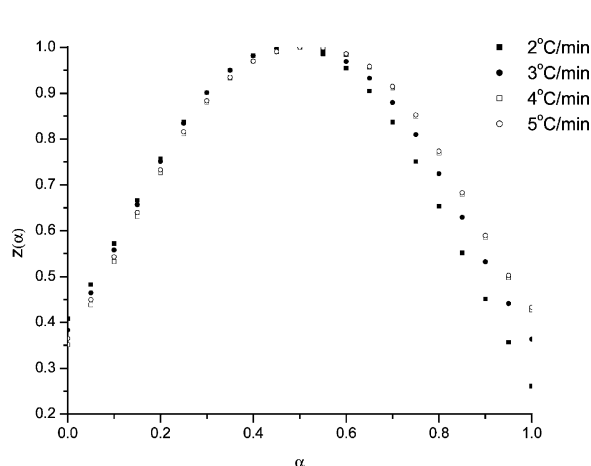


Fig. 3. DSC spectra of DGEBP/SAA recorded at 3 °C min⁻¹: the DSC thermogram (solid line) and the two peaks, peak I—black circles and peak II—white circles.

Fig. 4. Variation of E_a vs. conversion: (●) process I; (○) process II.Fig. 5. Variation of $y(\alpha)$ function vs. conversion for DGEBP/SAA sample cured at different heating rates: (■) 2 °C min⁻¹; (●) 3 °C min⁻¹; (○) 4 °C min⁻¹; (□) 5 °C min⁻¹.Fig. 6. Variation of $z(\alpha)$ function vs. conversion for DGEBP/SAA sample cured at different heating rates: (■) 2 °C min⁻¹; (●) 3 °C min⁻¹; (□) 4 °C min⁻¹; (○) 5 °C min⁻¹.

α_p^∞ help to choose the kinetic model which is correct for the system studied [23].

Table 2 lists the values of maxima α_M and α_p^∞ corresponding to the functions $y(\alpha)$ and $z(\alpha)$, together with the α_p value taken as the maximum of the DSC peak for the stage when the smectic phase is formed.

As can be noted, α_M , α_p^∞ and α_p values are independent of the heating rate. The α_M values are lower against the α_p values and α_p^∞ exhibits values lower than 0.632 (a characteristic value for the kinetic model determination) [17]. In accordance with the papers of Málek [16,17,23] on the kinetics of the curing reaction

Table 2

The values α_p , α_M and α_p^∞ evaluated for the curing of the DGEBP/SAA system in the second process

Heating rate (β , °C min ⁻¹)	α_p	α_M	α_p^∞
2	0.38	0.34	0.50
3	0.36	0.35	0.50
4	0.45	0.32	0.50
5	0.45	0.35	0.50

Table 3

The kinetic parameters evaluated for the curing of the DGEBP/SAA system (second process)

Heating rate (β , °C min ⁻¹)	E_a (kJ mol ⁻¹)	$\ln A$	Mean	m	Mean	n	Mean
2	59	15.55	15.24	0.50	0.44	0.93	0.87
3		15.27		0.49		0.91	
4		14.91		0.35		0.82	
5		15.25		0.44		0.81	

of epoxy resins under non-isothermal conditions, data in Table 2 show that the curing process of the DGEBP/SAA system can be well described using the two parameter autocatalytic kinetic model of Šesták–Berggren (Eq. (8)) [26]

$$f(\alpha) = \alpha^m(1-\alpha)^n \quad (8)$$

where m and n are the kinetic exponents.

The kinetic parameter n is obtained by the slope of the linear dependence $\ln[(d\alpha/dt) \cdot e^v]$ vs. $\ln[\alpha^p \cdot (1-\alpha)]$, and $m = p \cdot n$, where $p = \alpha_M / (1-\alpha_M)$.

Table 3 lists the kinetic parameters evaluated for the formation of the smectic liquid phase in the DGEBP/SAA system.

Experimental curves (full lines) and curves (symbols) calculated using the kinetic parameters corresponding to each heating rate 4 (see Table 3) are compared in Fig. 7. A good agreement can be seen between the calculated theoretical curves and those experimentally determined. This means that the two-parameter Šesták–Berggren

(m,n) model gives a good description of the curing process for DGEBP/SAA system.

4. Conclusions

The curing reaction of the epoxy resin DGEBP with amine SAA leads to a polymeric network with LC properties. The DSC studies showed that the curing of DGEBP/SAA system is a complex phenomenon. The reactions starts immediately after the melting of the two components of the mixture. At low heating rate (2–5 °C min⁻¹), the curing reaction takes place by two processes, as evidenced by the presence of a double peak on the DSC thermograms. The first process can be attributed to the nucleophilic attack of the primary amine onto the epoxy ring, when some linear or slightly branched mers are obtained [12]. The second process corresponds to the formation of the tridimensional network structure, with LC properties by the attack of the secondary amine previously formed onto the epoxide groups which do not react in totality in the first stage. The two processes are superposed.

The curing studies carried out with DGEBP/SAA system showed that the kinetics of the first process is complex, when E_a decreases with high values against conversion. The second process proceeds by a constant E_a ($E_a = 59$ kJ mol⁻¹) in the conversion interval $\alpha = 0.3$ – 0.6 .

The two-parameter (m,n) autocatalytic model of Šesták–Berggren was found to be the most adequate to describe the cure kinetics of the studied system. Non-isothermal curves obtained using the experimental data showed good agreement with those theoretically calculated.

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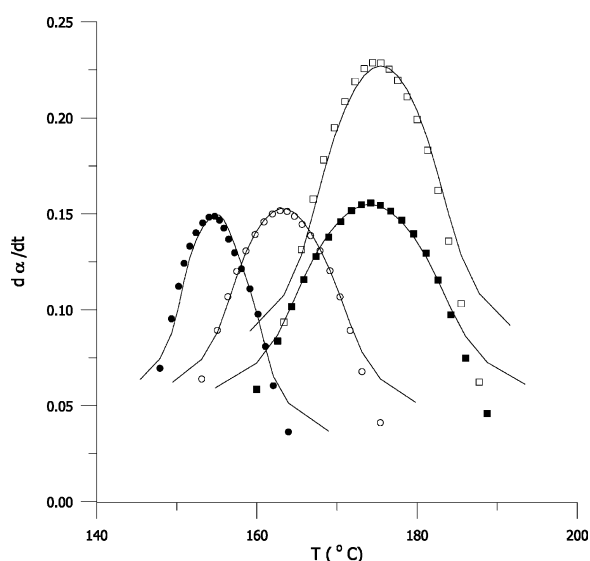


Fig. 7. Experimental (full lines) and calculated (symbols) DSC peaks corresponding to the curing second process for DGEBP/SAA samples; (●) 2 °C min⁻¹; (○) 3 °C min⁻¹; (■) 4 °C min⁻¹; (□) 5 °C min⁻¹.

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