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Isoconversional kinetic analysis of stoichiometric and off-stoichiometric epoxy-amine cures

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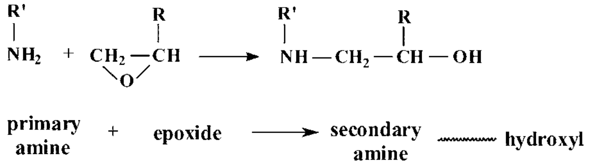
Abstract

The curing reaction of stoichiometric and off-stoichiometric diglycidyl ether of bisphenol A (DGEBA) and 1,3-phenylene diamine (*m*-PDA) mixtures was studied by differential scanning calorimetry, thermogravimetric analysis and rheological measurements. In order to highlight the side reactions such as etherification and homopolymerization, the neat DGEBA and DGEBA/DMBA (*N*,*N*-dimethylbenzylamine) mixture were examined. The classical model-fitting and the advanced isoconversional methods were used to determine the activation energy of the different reactions. The advanced isoconversional method leads to a good agreement between isothermal, nonisothermal and rheological results. The effective activation energies of primary amine epoxy reaction, etherification and homopolymerization were estimated to about 55–60, 104 and 170 kJ mol^{-1}, respectively.

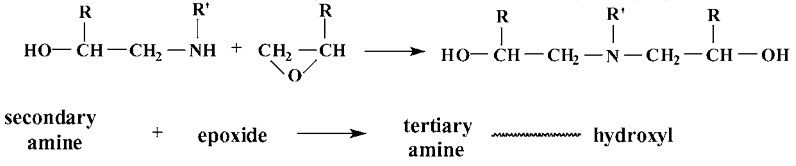
Keywords: Epoxy cure; Etherification; Homopolymerization; Isoconversional analysis; Model-free kinetics; Rheometry

1. Introduction

Elucidation of the reaction mechanisms of epoxy-amine cure is still a subject of great interest for both fundamental and applied reasons [1–3]. Reactions of epoxy prepolymer with amine are widely used for thermosettings but the curing mechanisms are still not completely understood. This complexity makes difficult the kinetic approach of the reactions. For these reasons, epoxies have been the subject of many theoretical and experimental investigations. These studies have a great importance by both, challenging questions about very basic knowledge of curing aspects, and also by giving useful information for the production of epoxy materials with improved properties. There is also a strong practical motivation for studying the reaction kinetics and correlating them with the chemical and physical factors that enable the better performances. Particularly, the influence of side reactions such as etherification or homopolymerization has been the subject of numerous contradictory studies. Competitive chemical reactions accompanied by complex physical phenomena occur during curing, when the system passes from a mixture of linear and branched oligo- and polymers into a single, three-dimensional, macromolecule. For an epoxy cure with a primary amine at least four reactions occur. The first reaction is between an epoxide ring (E) and a primary amine (PA) to produce a secondary amine (SA) and a hydroxyl group (OH):



The formed secondary amine can react also with an epoxide to produce a tertiary amine (TA) and a new hydroxyl group (OH):



Another possible reaction is the etherification between a hydroxyl group of secondary amine and an epoxide to form an

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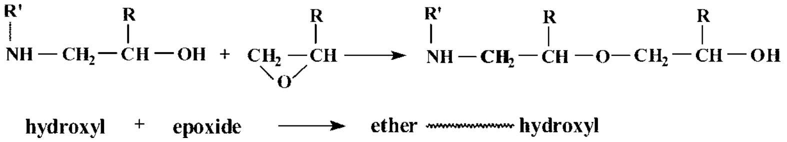
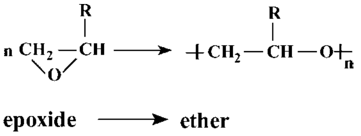
ether link and a new hydroxyl group:



Epoxide group polymerizes at high temperature, reaction that produces an ether link:

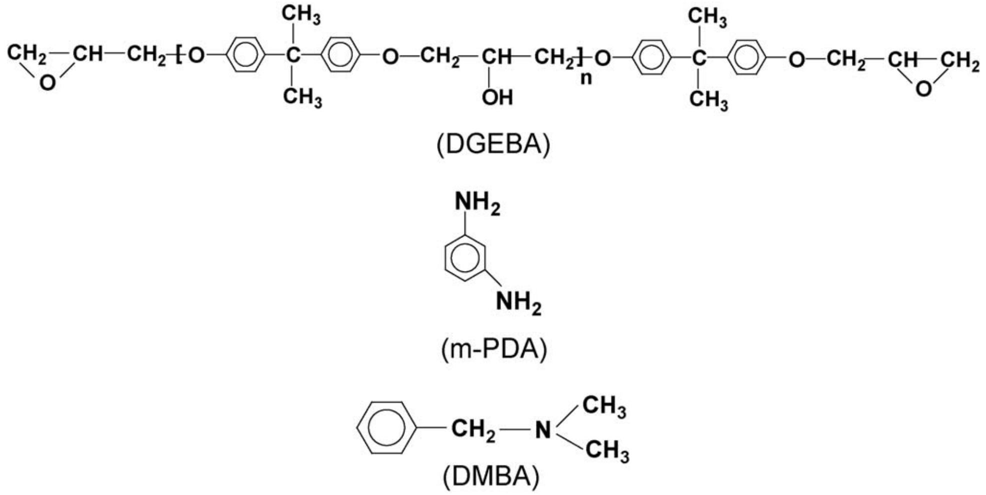


Epoxide to primary amine reaction becomes insignificant above $\alpha = 0.4$ conversion, whereas the secondary amine and hydroxyl addition to epoxide accelerate [4]. It is assumed that the reaction can be divided into several stages [5]. At the beginning of the cure the additions of epoxide to amines dominate, frequently the etherification and homopolymerization are supposed to be insignificant. At $\alpha = 0.6$ the primary amine with epoxide reaction is supposed to be negligible and at $\alpha = 0.8$ that of the secondary amine. At the end of the cure, the reaction tends to become simply first order to epoxide concentration (etherification). Cole et al. [5] identified a “turning point” around $\alpha = 0.45$. At this conversion over 90% of the primary amine has disappeared and the formation of the ether starting to becomes important. The secondary amine with epoxide reaction is significant both before and after this point, producing tertiary amine groups which catalyze the etherification reaction. Chiao [6] finds that etherification becomes important only above 150 °C, with a rate constant larger than that for the catalyzed secondary amine reaction but smaller with an order of magnitude than that for the catalyzed primary amine reaction. For Apicella et al.[7] etherification occurs once all the primary amine are exhausted, considering that below 200 °C the reaction does not play a relevant role in the cure. Many of authors consider that this reaction is negligible in stoichiometric systems but gradually becomes pronounced at high epoxy/amine ratios and high temperatures [8,9]. The apparent activation energies for the primary, secondary amine additions to epoxide and etherification were found [6] about 55.1, 71.6 and 97.2 kJ mol^{-1}. Regarding the homopolymerization reaction, the literature is very poor. Generally, it is considered that occurs only at high temperature, reaction being initiated by specific catalysts such as boron trifluoride, tertiary amine, impurities and so on [9–12]. A value of about 92 kJ mol^{-1} was reported by Barton [4] considering the homopolymerization of phenylglycidyl ether (PGE) or diglycidyl ether of bisphenol A in presence of tertiary amine. Generally, the homopolymerization and etherification reactions are treated both in literature as an etherification. In both cases an ether linkage is formed and there is no change in number of hydroxyl groups.

Differential scanning calorimetry (DSC) is a very instructive technique because it allows the direct measurement of the heat flow which is considered to be directly proportional to the reaction rate [13,14]. In this study, the cure kinetics of diglycidyl ether of bisphenol A (DGEBA) in the presence of 1,3-phenylene diamine (*m*-PDA) were explored by isothermal and non-isothermal DSC measurements.

In this paper, we proposed the evaluation of the cure kinetics in a comparative manner applying two kinds of approaches: the classical model-fitting methods and the advanced model-free kinetics analysis.

For obtaining completely cured thermosets, stoichiometric amounts of the two reactants (DGEBA, *m*-PDA) were used. In order to realize an investigation of the complex reactions that occur during crosslinking, off-stoichiometric systems have also been analyzed. For these systems, DGEBA/*m*-PDA mixtures containing a five-fold excess of amine were investigated.



Scheme 1. Molecular structure of the reactants.

Complementary DSC studies have been proposed whose objective was to characterise the homopolymerization of DGEBA epoxy chains. Preliminary experiments were conducted on the neat DGEBA, to highlight a possible homopolymerization reaction of epoxies groups with temperature effects. Another study of this reaction has been realized using a tertiary amine, the *N*,*N*-dimethylbenzylamine (DMBA), as catalyst.

2. Experimental section

2.1. Materials

A liquid bifunctional epoxy resin, diglycidyl ether of bisphenol A (DGEBA), has a molecular weight of about 355 g mol^{-1}, a viscosity of 50–65 P at 25 °C, a glass transition temperature T_g of about −20 °C (midpoint DSC) and an epoxy equivalent of about 176. An aromatic tetrafunctional diamine, 1,3-phenylene diamine (*m*-PDA) is more than 99% pure and its amino hydrogen equivalent is ∼27. A tertiary amine, *N*,*N*-dimethylbenzylamine (DMBA) (M_w = 135.21 g mol^{-1}, mp −75 °C, d = 0.900 g cm^{-3}) was employed as initiator to perform homopolymerization of DGEBA. All the reagents were purchased from Aldrich Chemical Co. and used as received, i.e. without further purification. The molecular structures of DGEBA (n = 0–1), *m*-PDA and DMBA are shown in Scheme 1.

2.2. Preparation of samples for DSC crosslinking studies

To study the crosslinking reactions two type of molar ratios mixtures were prepared: DGEBA/*m*-PDA 1:1 and DGEBA/*m*-PDA 1:5. Samples were obtained by vigorously mixing the DGEBA, melted at 70 °C, with the *m*-PDA until reaching room temperature. The mixtures were then stored at temperatures below the glass transition temperature of the unreacted material ($T_{g,0}$) at −30 °C, for no more than two days. Crosslinking reactions were directly performed in DSC aluminum pans, by simple heating. Samples of about 5–10 mg were sealed under air in aluminum pans and cured by heating in a Mettler-Toledo DSC 821^e apparatus [15]. All the computations were done on new fresh samples. We used a new set of new same sample each time the experimental conditions were changed to perform computations from a same set of sample.

2.3. Preparation of samples for DSC homopolymerization studies

To try to characterize the thermal effect associated with homopolymerization, also referred as self-curing in the literature, neat DGEBA was heated in aluminum pans (25–300 °C) at a heating rate of 5 °C min^{-1}.

Etherification and homopolymerization reactions are operative in presence of tertiary amines. Mixtures for studies were prepared using DMBA as catalyst, in an amount of 0.078 mol of DMBA per mole of epoxide group. Samples of about 5–10 mg were sealed in glass pans and heated in a static atmosphere.

2.4. Experimental techniques

Regular DSC runs were carried out on a Mettler-Toledo DSC 821^e. The apparatus has a ceramic sensor FRS5 (heat-flux sensor with 56 thermocouples Au–Au/Pd), which affords high sensitivity and short time constant. Temperature and power calibrations were performed by using indium and zinc standards.

The stoichiometric DGEBA/*m*-PDA 1:1 mixture was cured under isothermal conditions at 100, 120, 140, 160 and 180 °C, and under nonisothermal conditions at 1, 2, 3, 4, 5, 6, 8, 10 and 12 °C min^{-1}. The excess of amine, DGEBA/*m*-PDA 1:5, system was studied by DSC at the heating rates of 1, 2, 4, 6, 8, and 12 °C min^{-1}and under isothermal conditions at 70, 90, 100, 120, 140 and 160 °C. The DGEBA/DMBA system was cured at the heating rates of 0.75, 1, 1.25, 1.5, 1.75, and 2 °C min^{-1}.

Rheological measurements were conducted on oscillating mode with parallel plate geometries (25 mm diameter and 1 mm gap) of a Bohlin C-VOR rheomether with strain convection heating. The tests were carried out by heating the stoichiometric epoxy-amine mixtures from 0 to 200 °C at 2 °C min^{-1}. The frequency was 1 Hz on auto stress mode and the deformation 0.05%. Isothermal time to gelation for isothermal curing were estimated from rheological measurements as the point where storage (G') and loss modulii (G'') intersect.

Thermogravimetry (thermobalance Setaram, model 92-12) was used to monitor the weight loss associated with decomposition of samples. Measurements were carried out by heating 20 mg of sample from 25 to 800 °C at 5 °C min^{-1} under a 20 mL min^{-1} flow of nitrogen.

2.5. Theoretical calculations

The heat flow measured in DSC is proportional to both the overall heat release and the cure rate [14]:

$$\frac{dQ}{dt} = Q_{thr}\frac{d\alpha}{dt} = Q_{thr}k(T)f(\alpha) \tag{1}$$

where dQ/dT is the heat flow, Q_{thr} is the total heat released when an uncured material is brought to complete cure, $d\alpha/dT$ is the cure rate, α is the extent of reaction, $k(T)$ is the rate constant, T is the temperature, and $f(\alpha)$ is the reaction model. For epoxy cures, $f(\alpha)$ is usually taken in the form of $(1-\alpha)^n$ (reaction order kinetics) or of $\alpha^m(1-\alpha)^n$ (autocatalytic reaction). The explicit temperature dependence of the rate constant is introduced by replacing $k(T)$ with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, and R is the gas constant. When a sample is heated at a constant rate, the explicit temporal dependence in Eq. (2) is eliminated through the transformation

$$\frac{d\alpha}{dt} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{3}$$

where $\beta = dT/dt$ is the heating rate. For both isothermal and nonisothermal conditions, the extent of cure, α is estimated by integrating DSC peaks.

2.6. Isothermal model-fitting methods

2.6.1. n^{th} order model

Taking the logarithm of Eq. (1) and introducing the form of the reaction model $f(\alpha) = (1-\alpha)^n$:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln k(T) + n\ln(1-\alpha) \tag{4}$$

A linear regression applied to Eq. (4) will give $\ln k(T)$ and n for each temperature. The plot of $\ln k(T)$ versus $1/T$ gives E and $\ln A$, if the reaction obeys the same mechanism for the whole interval of temperature and conversion, i.e. $f(\alpha)$ constant.

2.6.2. Two-step autocatalytic models

Kamal and Sourour [16] developed a cure model

$$\frac{d\alpha}{dt} = [k_1(T) + k_2(T)\alpha](1-\alpha)(B-\alpha) \tag{5}$$

where B equals 1 for a stoichiometric mixture of an epoxy monomer with an initiator. Then, for isothermal conditions, a simple transformation

$$\frac{(d\alpha/dt)}{(1-\alpha)^2} = k_1(T) + k_2(T) \tag{6}$$

allows the rate constants to be evaluated as parameters of a linear regression which usually holds up to $\alpha = 0.3$–0.4 [16,17]. The rate constants $k_1(T)$ and $k_2(T)$ were determined for different temperatures and then used to evaluate Arrhenius parameters. A more general autocatalytic model

$$\frac{d\alpha}{dt} = [k_1(T) + k_2(T)\alpha^m](1-\alpha)^n \tag{7}$$

was proposed by Kamal [18]. Model fitting is facilitated by setting constraints on the values of m and n. It is usually assumed that $m+n$ equals 2 [18,19].

Eq. (7) can be transformed into Eq. (8)

$$\frac{(d\alpha/dt)}{(1-\alpha)^n} = k_1(T) + k_2(T)\alpha^m \tag{8}$$

the left hand side of which should be linear with respect to α^m. Nevertheless, the use of this equation leads to kinetic exponents m and n that will vary with the isothermal temperature or heating rate used [20] as a consequence of the change in mechanism during curing.

2.7. Non-isothermal model-fitting method

2.7.1. n^{th} order model

Linearization of Eq. (2) gives:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A - \frac{E}{RT} + n\ln(1-\alpha) \tag{9}$$

The method of kinetic regression has been used to derive kinetic parameters by means of Eq. (9) from nonisothermal data.

2.8. Isoconversional methods and model-free kinetics

If changes in the mechanism are associated with changes in the activation energy, they can be detected by using the model-free isoconversional methods [2,13,20–23]. These methods are based on the isoconversional principle that states that the reaction rate at constant extent of conversion is only a function of the temperature

$$\left[\frac{d\ln(d\alpha/dt)}{dt}\right]_\alpha = -\frac{E_\alpha}{R} \tag{10}$$

(henceforth the subscript α indicates the values related to a given extent of conversion). E_α is computed for various α values ranging between 0 and 1. For single step reactions E_α is constant over the whole temperature (or conversion) interval. For multi-step kinetics, E_α will vary with α and this reflects the variation in relative contributions of single steps to the overall reaction rate. The goal of the model-free kinetics (MFK) and of the isoconversional analysis is to use this variation, as additional information on the reaction mechanism [15,20–23].

Common integral methods make use of various approximations to evaluate the so-called “temperature integral” [13,23]. The use of differential methods, i.e. Friedman method in the case of isoconversional methods, avoids this limitation inherent of integral methods, but differential methods are known to be noise sensitive if no modification is used [23]. For these reasons, Sbirrazzuoli et al. [23] and Vyazovkin [24,25] have developed integral methods based on numerical integration. The method proposed by Sbirrazzuoli et al. [23] was called “Ozawa corrected method” while that of Vyazovkin [24,25] is the “advanced isoconversional method”. An additional advantage of the advanced isoconversional method is that it is not limited to linear temperature programs, and it takes into account possible variations in the activation energy.

To estimate the E_α-dependencies for epoxy cures, we used the advanced isoconversional method developed by Vyazovkin [24,25]. According to this method, for a set of n experiments carried out at different arbitrary heating programs $T_i(t)$, the activation energy is determined at any particular value of α by finding the value of E_α that minimizes the function

$$\Phi(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{11}$$

In Eq. (11), the integral

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \tag{12}$$

is evaluated numerically for a set of experimental heating programs. Integration is performed over small time segments (Eq. (12)) that allows for eliminating a systematic error occurring in the usual integral methods when E_α varies significantly with α. In Eq. (12), α is varied from $\Delta\alpha$ to $1-\Delta\alpha$ with a step $\Delta\alpha = m^{-1}$, where m is the number of intervals chosen for analysis. The integral, J in Eq. (12) is evaluated numerically by using the trapezoid rule. The minimization procedure is repeated for each value of α to determine the E_α-dependence. Isoconversional methods determine the E_α values independent of the preexponential factors, which are not directly produced by these methods. This allows the elimination of the bias from the value of the activation energy which could be caused by its strong correlation with the preexponential factor that is generally found when both parameters are fitted simultaneously [26].

By contrast with usual isoconversional methods, sample (non-linear) temperature variations and non-linear interpolation algorithm were used to compute the E_α-dependence, for both isothermal and non-isothermal data. All the kinetic methods (model-fitting, isoconversional, advanced) were programmed in a homemade software already described and regularly upgraded [23,27].

2.9. *Estimation of the activation energy at the gel point*

Eq. (2) can be transformed into Eq. (13)

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^1 k(T)dt \tag{13}$$

according to the conditions $\alpha = 0$ at $t = 0$ and $\alpha = \alpha_{gel}$ at $t = t_{gel}$

$$\ln(t_{gel}) = \ln g(\alpha) - \ln A + \left(\frac{E_g}{RT}\right) \tag{14}$$

E_g being the activation energy at the gel point.

Gelation occurs at a constant degree of cure independent of the cure temperature [28]. According to the isoconversional principle (Eq. (10)), E, A and $g(\alpha)$ should be constant for the constant value of the conversion degree $\alpha = \alpha_{gel}$

$$\ln(t_{gel}) = C + \frac{E_g}{RT} \tag{15}$$

where C is a constant. The plot of $\ln(t_{gel})$ versus $1/T$, will give E_g/R [29,30].

3. Results and discussion

3.1. *Isothermal model-fitting methods*

3.1.1. *n^{th} order model*

3.1.1.1. DGEBA/m-PDA 1:1 system. Thermoanalytical curves obtained for the isothermal curing of the stoichiometric epoxy-amine system were already presented [15]. The DSC peaks have been integrated in order to estimate the total heat release of the isothermal cure. For the isothermal cure at 180 °C an anomalous lower value is obtained due to the fact that the reaction already starts during the period of temperature stabilization in the DSC apparatus. So, the experiment at 180 °C will not be considered in the calculation.

The use of Eq. (4) requires a plot of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$. This plot is presented in Fig. 1, and was used to select the more suitable conversion interval for the computation of $\ln k(T)$ and n ($\sim 0.5 < \alpha < 0.7$). Results obtained with multiple linear regression of Eq. (4), for each appropriate conversion interval (computed using $Q_{thr} = 560\ \mathrm{J\,g^{-1}}$), are presented in Table 1. The values of the apparent reaction order n decreases when the temperature decreases. This may be an indication of a change in the reaction mechanism during cure.

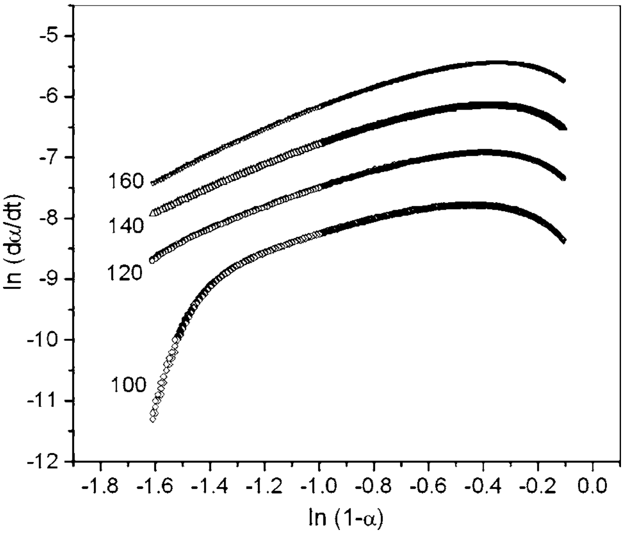


Fig. 1. Plot of $\ln(d\alpha/dt)$ vs. $\ln(1-\alpha)$ according to Eq. (4) for the stoichiometric mixtures. The temperature of each experiment (in °C) is indicated by each curve.

Presuming that the reaction obeys the same mechanism on the whole interval of conversion and temperature (hypothesis of Eq. (4)), we can calculate the activation energy (E) and the preexponential factor ($\ln A$) by plotting $\ln k(T)$ versus $1/T$ in the linear region. The obtained values are $E = 61.5\ \mathrm{kJ\,mol^{-1}}$ and $\ln A = 12.89$, with a correlation coefficient $r = 0.99907$. The shape of the plot of $\ln(d\alpha/dt)$ versus $\ln(1-\alpha)$ clearly indicates that this model is not suitable to describe the whole reaction mechanism of the process.

3.1.1.2. DGEBA/m-PDA 1:5 system. In spite of a great number of works regarding the study of epoxy/amine curing, the kinetics and the mechanism of reaction still present non-elucidated aspects. Recently, Sbirrazzuoli et al. [31] have proposed to vary the proportions of the reactants in order to elucidate the reaction mechanisms with the use of isoconversional methods. Based on this idea, curing of the mixtures containing a five-fold excess of amine is proposed to investigation. So, the reactions will occur dominantly between primary amine groups, in large excess, and epoxy. The obtained DSC thermograms for isothermal curing of this mixture are shown in Fig. 2. Integration of the DSC peaks gives a constant value of $Q_{thr} = 360 \pm 10\ \mathrm{J\,g^{-1}}$ for the isothermal temperatures 70, 90, 100 and 120 °C (140 and 160 °C were

Table 1
Kinetic parameters of isothermal curing of stoichiometric DGEBA/*m*-PDA system

T (°C)[a]	$1/T$ (K)	$\ln k(T)$ ($\mathrm{s^{-1}}$)	n
100	0.00268	−6.98694	1.29
120	0.00254	−5.86405	1.64
140	0.00242	−5.05278	1.74
160	0.00231	−4.20881	1.95

[a] The experiment at 100 °C was not considered for calculations.

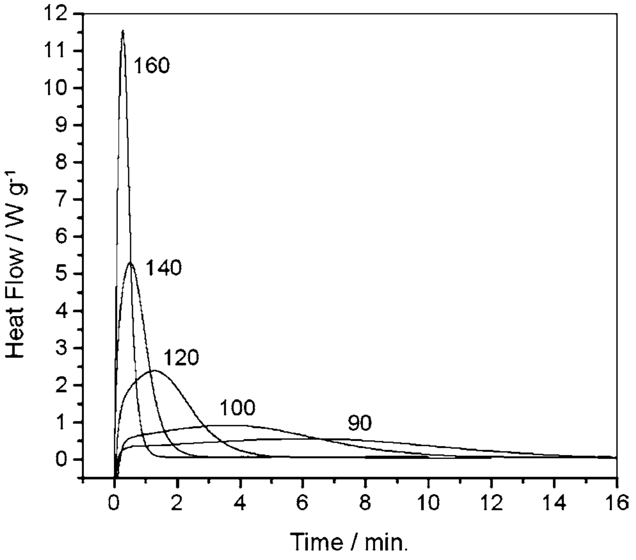


Fig. 2. DSC data showing the heat release during isothermal cures of the mixtures containing a five-fold excess of amine. The temperature of each experiment (in °C) is indicated by each curve.

not used in the calculations for similar reasons as previously mentioned).

The plots obtained by using Eq. (4) are shown in Fig. 3. In contradiction with the stoichiometric epoxy/amine cure, a quasi constant value of the reaction order n ($0.96 < n < 1.01$) is obtained for a n-order kinetic model $f(\alpha)=(1-\alpha)^n$ (Table 2). This quasi-constant value, very close to one, is not common for usual curing reactions that are known to involve several steps [19–22]. This confirms our hypothesis that the reactions will occur dominantly between primary amine groups and epoxide. The corresponding activation energy and logarithm of the preexponential factor were estimated to be 50.21 kJ mol^{-1} and respectively 11.44 using this method.

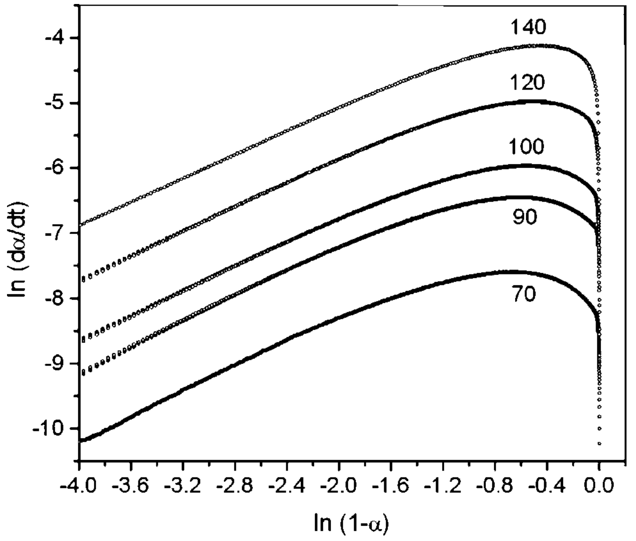


Fig. 3. Plot of $\ln(d\alpha/dt)$ vs. $\ln(1-\alpha)$ according to Eq. (4) for the mixtures containing a five-fold excess of amine. The temperature of each experiment (in °C) is indicated by each curve.

Table 2
Kinetic parameters of isothermal curing of DGEBA/*m*-PDA 1:5 system

T (°C[a])	$1/T$ (K)	$\ln k(T)$ (s^{-1})	n
70	0.00291	−6.18490	1.01
90	0.00275	−5.11204	1.01
100	0.00268	−4.80801	0.96
120	0.00254	−3.91957	0.96

[a] The experiments at 140 and 160 °C were not considered for calculations.

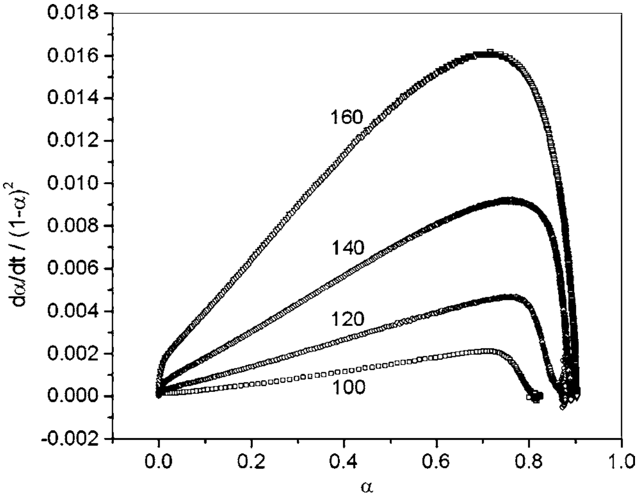


Fig. 4. Plot of the reduced reaction rate vs. α according to Eq. (6) for the stoichiometric mixtures. The temperature of each experiment (in °C) is indicated by each curve.

3.1.2. Two-step autocatalytic models

3.1.2.1. DGEBA/m-PDA 1:1 system. The left side of Eq. (6), called the reduced reaction rate, was plotted against α (Fig. 4), for each isothermal temperature. Linearity is observed for the interval $0.1 < \alpha < 0.5$ which was used to estimate $k_1(T)$ and $k_2(T)$. The resulting values are presented in Table 3 (100 °C was not used in the calculations because the reaction rate is too low at this temperature).

The plot of $\ln k_1(T)$ and $\ln k_2(T)$ versus $1/T$ allows the determination of $E_1 = 89.80$ and $E_2 = 47.75$ kJ mol^{-1}, $\ln A_1 = 18.47$ and $\ln A_2 = 9.55$. These values are in agreement with Sourour and Kamal (81 and respectively 45.6 kJ mol^{-1}, $0.1 < \alpha < 0.3$) [17]. According to the curvature of the plots in Fig. 4 and to previous work [15,21], it is obvious that this reaction is not chemically controlled for the entire range of conversion, as previously assumed by the Kamal and Sourour model [16–18]. This reveals that the model is not applicable in the whole range of conversion

Table 3
Kinetic parameters of isothermal curing of stoichiometric DGEBA/*m*-PDA system

T (°C[a])	$1/T$ (K)	$k_1(T)$ (s^{-1})	$k_2(T)$ (s^{-1})
120	0.00254	0.00012	0.00631
140	0.00242	0.00047	0.01297
160	0.00231	0.00156	0.02431

[a] The experiment at 100 °C was not considered for calculations.

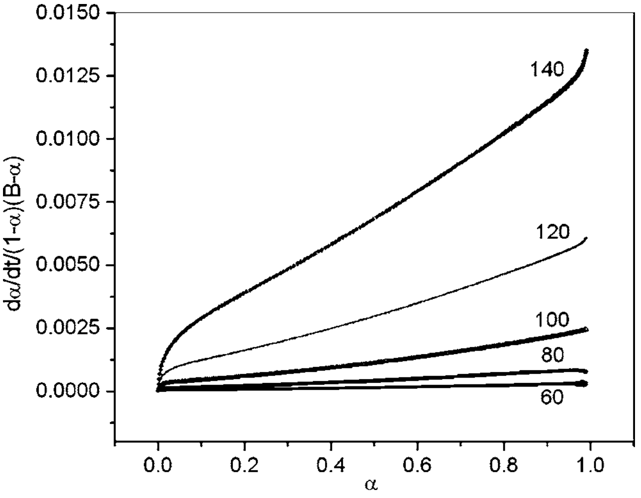


Fig. 5. Plot of the reduced reaction rate vs. α according to Eq. (6) for the mixtures containing a five-fold excess of amine. The temperature of each experiment (in °C) is indicated by each curve.

of the reaction. This model is only applicable in the chemically controlled part of the reaction.

3.1.2.2. DGEBA/m-PDA 1:5 system. For the non-stoichiometric mixtures containing a five-fold excess of amine the characteristic decrease of the reduced reaction rate at the end of the reaction is not observed (Fig. 5). Nevertheless, the plots show a certain curvature and the linearity region was estimated to be $0.1 < \alpha < 0.3$. The kinetic constants obtained using Eq. (6) are presented in Table 4.

The plot of $\ln k_1(T)$ and $\ln k_2(T)$ versus $1/T$ allows the determination of $E_1 = 59.66$ and $E_2 = 57.06\,\mathrm{kJ\,mol^{-1}}$, $\ln A_1 = 11.12$ and $\ln A_2 = 11.94$. A quasi-unique value of the activation energy is obtained, in agreement with our assumption that, in the presence of excess amine, the processes predominately occur via reaction with primary amine [15].

3.2. Non-Isothermal model-fitting method

3.2.1. n^{th} order model

3.2.1.1. DGEBA/m-PDA 1:1 system. Thermoanalytical curves obtained for the non-isothermal curing of stoichiometric epoxy-amine system are shown in Fig. 6. The method of multiple linear regression has been used to derive kinetic parameters by means of Eq. (9) for degrees of cure in the interval $0.3 < \alpha < 0.7$. Results are presented in Table 5.

The values of the apparent parameters E, $\ln A$ and n show great variations when the heating rate increases. This may be an indication of a change in the reaction mechanism during cure and suggest that this model is not suitable to describe the cure kinetics of this system.

Table 4
Kinetic parameters of isothermal curing of DGEBA/*m*-PDA 1:5 system

T (°C)	$1/T$ (K)	$k_1(T)$ ($\mathrm{s^{-1}}$)	$k_2(T)$ ($\mathrm{s^{-1}}$)
60	0.00300	0.00003	0.00018
80	0.00283	0.00010	0.00054
100	0.00268	0.00028	0.00153
120	0.00254	0.00082	0.00408
140	0.00242	0.00199	0.00955

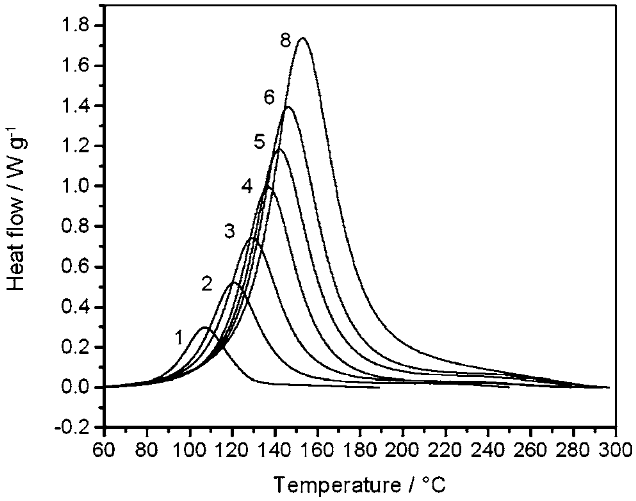


Fig. 6. DSC data showing the heat release during nonisothermal curves of the stoichiometric mixtures. The heating rate of each experiment (in $\mathrm{°C\,min^{-1}}$) is indicated by each curve.

Table 5
Kinetic parameters of nonisothermal curing of stoichiometric DGEBA/*m*-PDA system

β ($\mathrm{°C\,min^{-1}}$)	E ($\mathrm{kJ\,mol^{-1}}$)	$\ln A$ ($\mathrm{s^{-1}}$)	n
1	125.60	34.06	0.68
2	115.24	30.24	0.59
4	223.46	61.48	3.62
8	242.56	65.09	4.28

3.2.1.2. DGEBA/m-PDA 1:5 system. The DSC thermograms for non-isothermal curing of this mixture were already presented [15]. Integration of the DSC peaks gives a constant value of $Q_{\mathrm{thr}} = 380 \pm 5\,\mathrm{J\,g^{-1}}$ for the respective heating rates 1, 2, 4, 8 and $12\,\mathrm{°C\,min^{-1}}$. The same conversion degree is reached at a lower temperature for the reaction performed with an excess of amine. The application of Eq. (9) gives the kinetic parameters for the non-isothermal curing process with an excess of amine. The resulting values, computed for $0.25 < \alpha < 0.75$ are shown in Table 6.

As with isothermal data (Table 2), we observe a quasi-constant value of the parameter n which is near to one. This may indicate that, in the presence of the excess of amine, the rate of curing is controlled by a single step, in agreement with

Table 6
Kinetic parameters of nonisothermal curing of DGEBA/*m*-PDA 1:5 system

β ($\mathrm{°C\,min^{-1}}$)	E ($\mathrm{kJ\,mol^{-1}}$)	$\ln A$ ($\mathrm{s^{-1}}$)	n
1	123.27	35.92	0.93
2	122.73	35.05	0.97
4	114.81	31.61	0.91
8	110.42	29.60	0.92

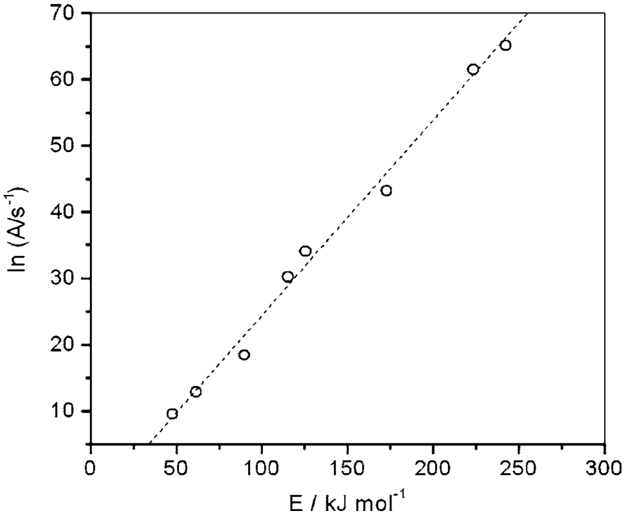


Fig. 7. Plot of E vs. $\ln A$ obtained with iso and nonisothermal model-fitting methods for the stoichiomeric system.

our assumption that the excess amine processes predominately occur via reaction with primary amine [15].

In order to confirm this hypothesis, the values of E previously computed for the stoichiometric system with model-fitting methods were plotted versus $\ln A$ as presented in Fig. 7. It is noteworthy that the respective estimates of $E, E_1, E_2, \ln A, \ln A_1, \ln A_2$ are strongly correlated ($r = 0.99252$, Fig. 7). This confirms that the obtained values can be meaningless [20].

3.3. Isoconversional analysis applied to the epoxy/amine reactions

3.3.1. Isothermal and non-isothermal DSC measurements

The obtained DSC data were used for evaluating the E_α-dependencies in accord with Eqs. (11) and (12). The application of the isoconversional analysis to incomplete cures performed below $T_{g,\infty}$ has been discussed earlier [32]. The resulting dependencies were presented [15]. Very similar dependencies (not presented here) were obtained in this work despite slightly different experimental conditions ($\beta = 1$, 2, 4 and 8 °C min^{-1} in Ref. [15] and $\beta = 1$, 2, 3, 4, 5, 6 and 8 °C min^{-1}). In contradiction with the results obtained with n^{th} order methods, it was shown that for the stoichiometric system, the E_α-dependencies derived from isothermal and nonisothermal data are in good agreement with each other. Both dependencies are decreasing and reveal practically the same value of the activation energy at the beginning of curing (i.e. at $\alpha \to 0$). The respective value of E_α is around 55–60 kJ mol^{-1} that is quite typical for epoxy-amine copolymerizations. It was shown that this value obtained for the stoichiometric system is consistent with the values obtained for the systems with an excess of amine for both isothermal and nonisothermal conditions. For the systems with an excess of amine the E_α values are around 55–60 kJ mol^{-1} and independent of the extent of conversion, indicating that the rate of curing is controlled by a single step. This demonstrate that the processes in the presence of excess of amine predominately occur via reaction with primary amine and confirm the physical meaning of the kinetic parameters obtained using model-free kinetics.

As the degree of conversion increases, for the stoichiometric system, the effective activation energy of curing decreases to as low as ∼20 kJ mol^{-1}. This is an indication that the rate-determining step of curing changes to a chemically controlled process to a diffusion control [21].

Table 7
Isothermal time to gelation for curing of stoichiometric DGEBA/*m*-PDA system

Temperature (°C)	Time to gelation (s)
100	1984
110	1322
120	972

3.3.2. Isothermal rheological measurements

The isoconversional analysis has been applied to the rheological studies of curing in isothermal conditions of DGEBA/*m*-PDA 1:1 system. Theoretically [28], gelation should occur at a certain degree of cure that depends only on the functionality of the amine and epoxide. In DGEBA/*m*-PDA system, the amine is tetrafunctional and the epoxide is bifunctional so that the theoretical value of the extent of cure at gelation, α_{gel} should be [28]

$$\alpha_{\text{gel}} = \left(\frac{1}{(f_A - 1)(f_E - 1)}\right)^{1/2} = \left(\frac{1}{(4-1)(2-1)}\right)^{1/2} = 0.577 \qquad (16)$$

where f_A and f_E are the respective functionalities of the amine and epoxide.

Isothermal time to gelation estimated from rheological measurements, is given in Table 7.

Experimental estimations of the activation energy at the gel point, E_g, using Eq. (15), give a value of about 44 kJ mol^{-1} (Fig. 8, $r = 0.99793$). This value is in good agreement with

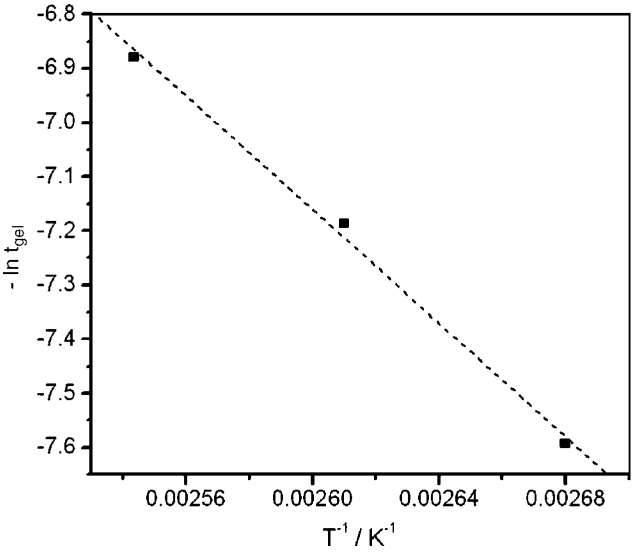


Fig. 8. Plot of $\ln(t_{\text{gel}})$ vs. $1/T$ according to Eq. (15).

the value of ~42 kJ mol^{-1} obtained from DSC data ($\alpha = 0.577$, [15]). These two so close results, experimentally obtained starting from independent different measurements, estimate very well the activation energy value. This confirms the validity of the application of the isoconversional analysis to describe complex cure kinetics.

3.4. Isoconversional analysis applied to the homopolymerization and/or etherification reactions

3.4.1. Homopolymerization of neat DGEBA

Despite the existence of several studies [6–9,33,34] on this subject, the influence of side reactions such etherification or homopolymerization is still the subject of numerous contradictory studies. It is known that side reactions, like etherification or homopolymerization, occur in crosslinking systems heated at elevated temperatures or in off-stoichiometric conditions. Heating epoxy resins to high temperature can promote homopolymerization reactions. Etherification is known to occur via the ring opening of epoxide group by hydroxyl group at high temperature (>150 °C [6]), with high activation energy value (97.2 [6], 101.4 [5] and 171.6 [7] kJ mol^{-1}), at late stages of reaction or in the presence of a large excess of the epoxide group [8]. On the other hand, several authors have concluded that side reactions are negligible for stoichiometric and off-stoichiometric systems [1,9,33]. Note that in both cases the reactions were investigated for a different temperature domain (up to 230 °C [1], up to 160 °C [9] and up to 270 °C [33]). Recently, Zhang and Vyazovkin [34], have attributed a small DSC peak near 240 °C (peak maximum temperature at 2 °C min^{-1}) to the self-curing of neat DGEBP (diglycidyl ether of 4,4′-bisphenol). For neat DGEBA heated from 25 to 300 °C, we observed a small thermal effect, between 180 and 300 °C (peak maximum temperature $T_p \sim 250$ °C at 5 °C min^{-1}), and presented in the insert of Fig. 9. Fig. 10 shows that the weight loss associated with thermal decomposition of neat DGEBA becomes significant above 300 °C ($\beta = 5$ °C min^{-1}). Accordingly, this very small exothermic peak can be attributed to the self-curing (homopolymerization) of neat DGEBA.

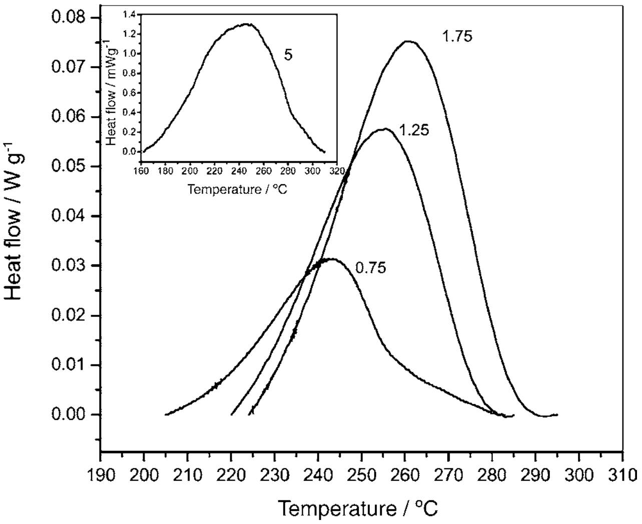


Fig. 9. DSC data showing the heat release during nonisothermal cures of the mixtures DGEBA/DMBA. The heating rate of each experiment (in °C min^{-1}) is indicated by each curve. Inset: homopolymerization of neat DGEBA ($\beta = 5$ °C min^{-1}) heated from 25 to 300 °C.

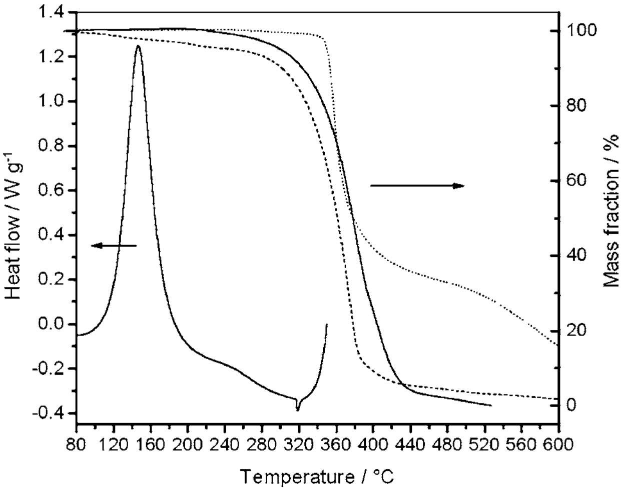


Fig. 10. TGA data of neat DGEBA (solid line), DGEBA/*m*-PDA (dot line) and DGEBA–DMBA (dash line) heated at $\beta = 5$ °C min^{-1}. DSC of nonisothermal cure of the DGEBA/*m*-PDA mixture at 6 °C min^{-1}, showing the heat release above 200 °C (solid line).

3.5. Etherification and homopolymerization of DGEBA/DMBA

Because tertiary amines are known to promote etherification or homopolymerization reactions [1,5,35], DSC measurements were performed on an epoxy-tertiary amine (DGEBA/DMBA) system, to confirm this hypothesis. The thermal effects were registered at temperatures ranging between 200 and 300 °C (Fig. 9). The peak maximum temperature at 1.75 °C min^{-1} is around 260 °C. This temperature range is in good agreement with the previously reported value for self-curing of neat DGEBA ($T_p \sim 250$ °C). Fig. 10 shows that the weight loss associated with thermal decomposition of DGEBA/DMBA becomes significant above 300 °C ($\beta = 5$ °C min^{-1}, open pans). The shape of the DSC peaks seems to indicate that decompositions reactions did not occur in glass pans in the temperature range of 200–300 °C, and the corresponding thermal effects can be attributed to etherification and/or homopolymerization reactions.

The resulting E_α-dependency obtained from DSC measurements performed on the DGEBA/DMBA system, taking into account the thermal effects occurring in the temperature range of 200–300 °C, is presented in Fig. 11. A quasi-constant value of the effective activation energy $E_\alpha \sim 104$ kJ mol^{-1} is obtained for $0 < \alpha < 0.7$. The mean temperature over the heating rates, $T_{m,}$ is ranging between 230 and 260 °C and falls with the temperature domain estimated for self-curing by Zhang and Vyazovkin [34].

Using the peak maximum evolution method of Kissinger [36] yields a value of $E \sim 101$ kJ mol^{-1} ($r = 0.98859$), in good agreement with the advanced isoconversional method. These values are also in perfect agreement with those reported for etherifica-

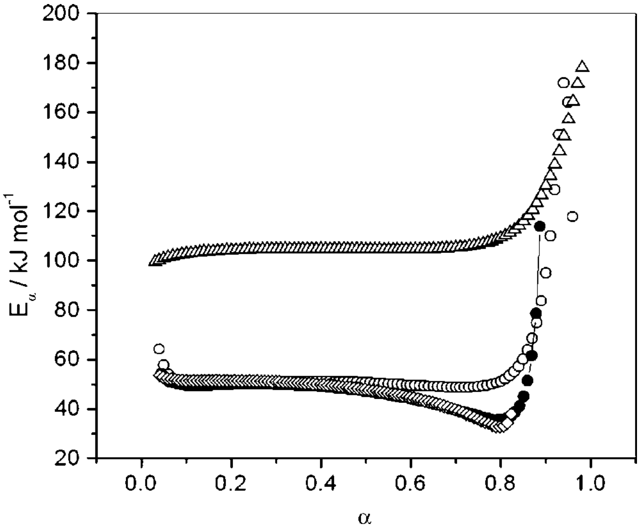


Fig. 11. Variation in the effective activation energy with conversion obtained for DGEBA/DMBA system (open triangles, nonisothermal conditions $\beta = 0.75$–$1.75\,^\circ\mathrm{C\,min^{-1}}$). Comparison with the stoichiometric system DGEBA/*m*-PDA for the heating rates 5, 6 and 8 °C min^{-1} to span in the temperature ranges of 55–220 °C (open diamonds), 55–260 °C (solid circles) and 55–300 °C (open circles). The conversion degree was rescaled in order to take into account the different values of the heat released (i.e. $\alpha = 1$ for Q_{thr} max = 600 J g^{-1} at 8 °C min^{-1}).

tion (including homopolymerization) by Chiao (97.2 kJ mol^{-1}) [6] and Cole et al. (101.4 kJ mol^{-1}) [5] for a different epoxy-amine system (TGDDM/DDS).

Fig. 11 shows a significant increase of E_α for $\alpha > 0.7$ ($T_m > 260\,^\circ\mathrm{C}$, $E_\alpha \to 180\,\mathrm{kJ\,mol^{-1}}$). Lee et al. [37] have estimated the activation energy of the decomposition of DGEBA/methylene dianiline system to 207 kJ mol^{-1}. Montserrat al. [38] calculate an energy of thermal degradation of about 225 kJ mol^{-1}. The resulting values of activation energy (~104 ± 10 and 180 ± 20 kJ mol^{-1}) and the temperature domain involved (260–300 °C) are too low to correspond to the decomposition. The increase of E_α from 104 to 180 kJ mol^{-1} could result to the transition of a control of the overall reaction rate from etherification to homopolymerization reactions.

3.6. *Etherification and homopolymerization of DGEBA/m-PDA*

The weight loss measured with TGA associated with thermal decomposition of DGEBA/*m*-PDA becomes significant above 350 °C ($\beta = 5\,^\circ\mathrm{C\,min^{-1}}$, Fig. 10). Fig. 10 clearly shows that decomposition is observed above 320 °C with DSC data. This indicates that the small exothermal effect observed in DSC between 200 and 300 °C for the stoichiometric DGEBA/*m*-PDA system in Fig. 10, cannot be attributed to decomposition.

For the stoichiometric DGEBA/*m*-PDA system, at the latter stage of the reaction, the higher temperature used in the computation of the E_α-dependency [15], is only 220 °C for $\alpha = 0.99$ for the higher heating rate (8 °C min^{-1}), while the increase of E_α (for $\alpha > 0.7$) attributed to the beginning of the homopolymerization of DGEBA/DMBA, correspond to a temperature above 260 °C.

It is known that the use of higher heating rates shift the reaction to higher temperature. Analysis of the DSC data showing the heat release during nonisothermal cures of the stoichiometric mixtures of Fig. 6, show that at 1 °C min^{-1} the thermal effect becomes negligible at $T > 150\,^\circ\mathrm{C}$, while this temperature is about 300 °C at 8 °C min^{-1}. This naturally suggests that side reactions will be more effective when using high heating rates or high cure temperature. As a consequence, if etherification and/or homopolymerization occur for the stoichiometric DGEBA/*m*-PDA system in the temperature range of 200–300 °C, the E_α-dependency computed for higher heating rates, will conduce to an increase of the E_α effective values. A comparison of the variation of the effective activation energy E_α with conversion for different temperature domains for the stoichiometric DGEBA/*m*-PDA system and computed using only the higher heating rates (5, 6 and 8 °C min^{-1}) is presented in Fig. 11.

Three sets of integration bounds were used to span in the following temperature domains of 55–220 °C ($Q_{\mathrm{thr}} \sim 500\,\mathrm{J\,g^{-1}}$), 55–260 °C ($Q_{\mathrm{thr}} \sim 550\,\mathrm{J\,g^{-1}}$) and 55–300 °C ($Q_{\mathrm{thr}} \sim 600\,\mathrm{J\,g^{-1}}$). The first domain corresponds to a temperature range below the beginning of side reactions. The second domain corresponds to a temperature range estimated for etherification reactions, while the last temperature domain corresponds to the region where homopolymerization starts to play an important role and may become the rate-limiting step of the overall reaction rate ($T > 260\,^\circ\mathrm{C}$). For the first temperature domain, we observe the characteristic E_α value for epoxy/amine reactions followed by a decrease attributed to the diffusion control. The computation of the E_α-dependency for the curves presented in Fig. 6 at 1, 2, 3, 4, 5, 6 and 8 K/min (not presented here) will also leads to a similar shape with the same decrease. For the second temperature domain, we still observe this decrease, followed by an increase to $E_\alpha \sim 114 \pm 20\,\mathrm{kJ\,mol^{-1}}$, which is near the previously estimated value ($E_\alpha \sim 104\,\mathrm{kJ\,mol^{-1}}$) for etherification of the DGEBA/DMBA system. For the third temperature domain, E_α increases to $E_\alpha \sim 170 \pm 20\,\mathrm{kJ\,mol^{-1}}$, that can be attributed to the transition from etherification to homopolymerization reactions.

The reported values of the activation energy found in the literature [5–7] span a broad region varying from 97.2 to 171.6 kJ mol^{-1}. This may be explained by the use of inadequate reaction models to compute the activation energy values over the whole temperature range. Each of these values may only correspond to a part of the whole reaction. On the opposite, the use of the E_α-dependencies explains why so different values have been obtained.

4. Conclusions

The kinetics of the epoxy/amine cure by classical model-fitting methods and by advanced isoconversional analysis has been proposed. For the stochiometric system, isothermal n^{th} order methods lead to values of the apparent reaction order that decreases when decreasing the temperature, while non-isothermal n^{th} order methods lead to increasing values of E and n when increasing the heating rate. The E_α values obtained for isothermal and non-isothermal heating program are very different. When applying the advanced isoconversional method, the

E_α-dependencies shapes are completely different when the stoichiometry is changed in agreement with our conclusion that the reaction mechanism is mainly controlled by a single-step in the case of an excess of amine. The E_α-dependencies derived from isothermal and nonisothermal data are in agreement with each other. The isoconversional method has also been applied to the rheological studies of curing in isothermal conditions. The activation energy at the gel point, E_g is in good agreement with DSC data. To quantify the energy of homopolymerization/etherification reactions, experiments were done using neat DGEBA and DGEBA/DMBA mixture. These studies confirm that side reactions, like etherification or homopolymerization, occur in systems heated at elevated temperatures, in the temperature region 200–300 °C. The corresponding energy for etherification is around $E_\alpha \sim 104 \pm 10\,\mathrm{kJ\,mol^{-1}}$. Etherification reactions start to play an important role for $T > 230\,^\circ\mathrm{C}$ and this temperature shift to $T > 260\,^\circ\mathrm{C}$ for homopolymerization. An activation energy of $170 \pm 20\,\mathrm{kJ\,mol^{-1}}$ could be associated to homopolymerization reactions.

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