polymer

Experimental modeling of the cure kinetics of an epoxy-hexaanhydro-4-methylphthalicanhydride (MHHPA) system

F.Y.C. Boey[*], W. Qiang

Nanyang Technological University, School of Mechanical and Production Engineering, North Spine (N3), Level 2, Nanyang Avenue, Singapore 639798

Abstract

The DEBGA–MHHPA epoxy system has found increasing applications in microelectronics packaging for which the ability to understand and model the cure kinetics mechanism accurately is crucial. The present paper reports on the work carried out to elucidate an accurate cure kinetics model for the DEBGA–MHHPA epoxy system, using both the isothermal and non-isothermal DSC methods. The results indicates that both the Kissinger and Ozawa's methods for calculating the activation energy value gave fairly close results of 71.6 and 74.7 kJ/mol, respectively. A autocatalytic model with a total order of reaction of about 2.5 was successfully used to model the process. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: DEBGA–MHHPA epoxy system; Cure kinetics; Autocatalytic model

1. Introduction

Interest in the low viscosity, highly transparent and excellent electrical insulation epoxy DEBGA–MHHPA system has received increasing attention due to its application in high grade LEDs, IC die encapsulation, conductive ink paste, adhesives etc. in the microelectronics industries as well as in structural component using resin transfer molding techniques. Specific to these applications, the ability to maximize the glass transition temperature in the shortest possible time is crucial, as the transition temperature directly correlates to a highest possible service temperature without adverse effects. Basic to such an optimal curing process is the need to firstly understand the physical curing mechanism and cure kinetics underlying the process, and then to be able to model the cure process accurately. This includes the determination of the mechanism or appropriate kinetic equation for the system being analyzed, and measurement of the reaction orders, activation energies and frequency factors of the reaction. An accurate model not only helps to predict cure behavior for process design and control, but also can be used to predict aging, or degradation of thermosetting polymer systems, and also to compare the cure behavior of different systems or formulations using different matrices, catalysts, or fillers and additives.

The current extent of understanding of the mechanism and kinetics of cure has not match up with the rapidly increasing formulations and application of epoxy based resin and composite systems industrially. A comprehensive understanding of the mechanism and kinetics of cure leading to an accurate model for an optimal curing process has yet to be clearly established. This is particularly true for catalyzed curing reactions of epoxy resins and cyclic anhydrides, particularly for the MHHPA system, as is evident from the number of conflicting reaction mechanisms have been proposed to date. To date, no studies have been reported on the cure kinetics modeling of DEBGA–MHHPA system. As such, the objective of this project is to develop a method based on thermal analysis to elucidate the mechanism of the cure kinetics and which can be used to develop a generalized curing model for optimal curing of DEBGA– MHHPA system.

Firstly, an appropriate method must be used to accurately measure the cure kinetics parameters, namely the degree of conversion (α), defined as the fraction or extent to which the maximum possible cross links has been produced in a reaction, the conversion rate, $d\alpha/dt$, and the activation energy, E. An appropriate constitutive equation can then be used to accurately model the relationship of these parameters during cure.

The differential scanning calorimeter (DSC) has been widely utilized to elucidate key cure process parameters such as the extent and rate of chemical conversion, glass

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* Corresponding author. Tel.: +65-7995609; fax: +65-7924062.

transition temperature (T_g) etc. [1,2]. The method assumes that for a cure process the measured heat flow (dH/dt) is proportional to the conversion rate, $d\alpha/dt$. This assumption is valid for materials with a single reaction and no other enthalpic events, such as the evaporation of solvent or volatile components, enthalpy relaxation, or significant changes in heat capacity with conversion. Where the reaction occurs with simultaneous evaporation of solvents etc., the analysis would necessarily take a more complicated process to differentiate the two enthalpic events. In practice, however, it has proven to be a reasonably good assumption. The rate of change in the conversion can also therefore be defined as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{Rxn}} \tag{1}$$

Techniques using DSC can use two basic approaches: an isothermal approach where a single cure temperature is used at a given cure cycle, and a dynamic approach where the rate of heating is kept constant for a given cure cycle.

The isothermal cure method monitors the conversion and the rate of conversion continuously, as the uncured resin is curing isothermally, over the entire course of the reaction. The conversion is measured using the DSC as:

$$\alpha_t = \frac{\Delta H_t}{\Delta H_{Rxn}} \tag{2}$$

where the subscript t indicates the value at time t. An alternative method is to measure the heat evolved during the completion of cross-linking of partially cured samples. This latter method becomes necessary when the exotherm is too small for detection in the former method, for example, when measuring the cure at low temperatures, or when the inherent rate of reaction is very small. A distinct advantage of the latter method is the simultaneous measurement of T_g and conversion [5,6]. The percentage of conversion for this method is calculated from:

$$\alpha_t = \frac{\Delta H_{Rxn} - \Delta H_r}{\Delta H_{Rxn}} \tag{3}$$

Correspondingly, this method becomes less sensitive as the residual exotherm diminishes. Quantitative measurement of the residual exotherm for a material exceeding 95% conversion is made difficult by the small exotherm, when the measurement of the T_g is in fact a more sensitive measure of the conversion.

Constitutive modeling equations for the cure kinetics of thermosetting materials generally fall under two general categories: nth-order and autocatalytic. As there may be more than one chemical reaction occurring during cure, the kinetics modeled may represent an overall process if these chemical reactions occur simultaneously [10]. For thermoset materials that follow nth-order kinetics, the rate of conversion is proportional to the concentration of

unreacted material, such that

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{4}$$

where n is the reaction order, and $k(T)$ the temperature dependent rate constant given by Arrhenius relationship:

$$k = A \exp(-E/RT) \tag{5}$$

where E is the activation energy, R the gas constant, T the absolute temperature, and A the pre-exponential or frequency factor. Eq. (4) indicates that the maximum conversion rate occurs at $t = 0$. Also, the rate of reaction $d\alpha/dt$ is dependent only on the amount of unreacted material remaining and assumes that the reaction products does not become involved in the reaction. As such, a logarithmic plot of Eq. (4) would result in a linear relationship.

Autocatalyzed cure reactions on the contrary assumes that at least one of the reaction products is also involved in the propagating reaction, and thus are characterized by an accelerating isothermal conversion rate, which typically reaches its maximum between 20 and 40% conversion. The kinetics of autocatalyzed reactions are described by the following equation [11]:

$$\frac{d\alpha}{dt} = k'\alpha^m(1 - \alpha)^n \tag{6}$$

where m and n are the reaction orders and $k'(T)$ is the specific rate constant also given similarly by Eq. (5). According to the autocatalytic model, the rate is zero or very small initially and attains a maximum value at some intermediate conversion, typically between 20–40% conversion. The initial rate of autocatalytic reactions may not be necessarily zero, as there is a possibility that reactants can be converted into products via alternative paths. To take into account these autocatalytic characteristics, a generalized expression as follows can be used:

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

Such a model has also been successfully applied to autocatalytic polymerization reactions [12,13]. In this case, the influence of the reaction products on the conversion rate is given by the term $k_2\alpha^m$. Further, other non-autocatalytic complex processes can also be represented by the same model [17,18].

For complex reactions [19] the phenomenological model be separated into two elemental parts with one represented by an nth order type reaction and the other by an autocatalytic type reaction to obtain:

$$\frac{d\alpha}{dt} = k_a(1 - \alpha)^l + k_b\alpha^m(1 - \alpha)^n \tag{8}$$

where k_a and k_b are the non-catalytic and autocatalytic rate constant, respectively, and l, n and m are the respective reaction orders. Both k_a and k_b can also be combined as a weighted component [20].

The determination of which of the types of models would appropriately represent a curing system is carried out by plotting the experimentally obtained cure parameters for an isothermal cure. For *n*th-order reactions, based on Eq. (4), a plot of $\ln(d\alpha/dt)$ against $\ln(1 - \alpha)$ should yield linear relationship:

$$\ln(d\alpha/dt) = \ln k + n \ln(1 - \alpha) \tag{9}$$

For an *n*th-order reaction where $n \neq 1$

$$-\ln(1 - \alpha) = \frac{1}{n - 1} \ln[1 + (n - 1)kt] \tag{10}$$

Using this methodology, the cure kinetics of a DGEBA–anhydride system [21], a DGEBA–DDS system [22] and a DGEBA–trimellitic anhydride (TMA) [23] and commercial epoxy system [24] were found to be described well by the *n*th-order kinetic model over the whole range of conversion of the primary amine, whereas the secondary amine–epoxy reaction was described by both the *n*th-order kinetic and first-order autocatalytic models.

For autocatalytic reactions, at least two reaction orders (m, n) are to be determined. Numerical methods have been proposed [25] for estimating the parameters that depends on the extent of reaction at the exotherm peak α_p as well as the rate of reaction at the peak, $r_p = (d\alpha/dt)$ where $t = t_p$, the location of the peak in time t_p). This method has been successfully applied to model the cure behavior of epoxy systems, though in most cases, to simplify the analysis, it was necessary to assume that the total reaction order was two $(m + n = 2)$, even for non-linear regression analysis [26,27]. Whichever the kinetic model, the ability to calculate the activation energy for the cure process would help to increase the accuracy of the model, as the rate constant would be more precisely known. This can be carried out using a isothermal cure approach, where the activation energy can be estimated from the temperature dependence of the time to reach a constant extent of conversion [3]. The activation energy may be estimated from an Arrhenius plot of $\ln(d\alpha(dt)_{\alpha i}$ versus T^{-1}, where the $(d\alpha(dt)_{\alpha i}$ is the conversion rate associated with a fixed conversion α_i [30].

1.1. Non-isothermal heating methods

Non-isothermal methods that can be used includes single-heating rate method, which and the multi-heating rate method. The single-heating method measures the curing process based on only a single constant heating rate cycle, from which parameters of cure are then determined. Single-heating-rate data are most frequently analyzed according to Eq. (4) with $f(\alpha) = (1 - \alpha)^n$, assuming *n*th-order kinetic. This probably limits the reliability of the system as many systems are in fact not of the *n*th-order type, though the advantage is it can provide extensive information from only a single dynamic scan. The kinetic parameters n, $\ln A$, and E are thus experimentally determined from a single-heating-rate DSC experiment, with a plot of $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ versus T^{-1}, from which, if the linearity assumption is correct, will yield values for n, $\ln A$ and E from the intercept and slope, respectively.

Multiple-heating-rate methods are iso-conversion methods, that is, it assumes that the conversion value is constant at the peak exotherm temperature, α_p in a DSC analysis, and is independent of the heating rate [31,32]. This makes it equally effective for both the *n*th order and the autocatalytic reactions. Two such multiple heating rate methods that have been shown to be effective are that proposed by Ozawa [33] and Flynn and Wall [34], and that proposed earlier by Kissinger [35,36].

The Kissinger method utilizes the relationship that, for thermoset curing, the extent of reaction at the peak exotherm, α_p, is constant and independent of the heating rate. The activation energy E can be obtained by:

$$\frac{d[\ln(\phi/T_p^2)]}{d(1/T_p)} = -\frac{E}{R} \tag{11}$$

where ϕ is the heating rate, T_p the peak exotherm temperature, and R the universal gas constant (8.3 J/mol/K). It is simplistic to assume a single reaction occurring during the curing process given the complexity of the reaction. Thus the value of E obtained in Eq. (11) is an overall value representing all complex reactions that occur during curing.

The Kissinger method assumes that the DSC peak exotherm is iso-conversional and so its value is not dependent on the heating rate. This assumption may not be valid for all systems, and has to be verified [10]. It also measures changes in the reaction mechanism via changes in the activation energy with conversion [3]. For both *n*th-order and autocatalytic reactions, the values of E, $\ln(A)$ and conversion rates obtained are comparable to isothermal methods [39,40]. Applications of the multiple-heating-rate method include the following: determination of epoxy cure schedules [42]; characterization of the cure kinetics of high-performance epoxy resin systems [43]; study of the effects of stoichiometry on the cure of a bismaleimide–triazine system [44]; determination of the effects of curing agent concentration and alumina trihydrate filler on the cure of allyl ester resins [45]; characterization of the initial degree of cure on the cure kinetics of an epoxy–anhydride system [46,47]; and study of the kinetics of an epoxy–amine whose cure includes vitrification [48].

The Ozawa method yields a simple relationship between the activation energy, the heating rate, and iso-conversion temperature, giving the activation energy as:

$$E = \frac{-R}{1.052} \frac{\Delta \ln \phi}{\Delta(1/T_i)} \tag{12}$$

where ϕ is the heating rate, T_i the iso-conversion temperature and R the universal gas constant. The advantage here is that the activation energy can be measured over the entire course of the reaction.
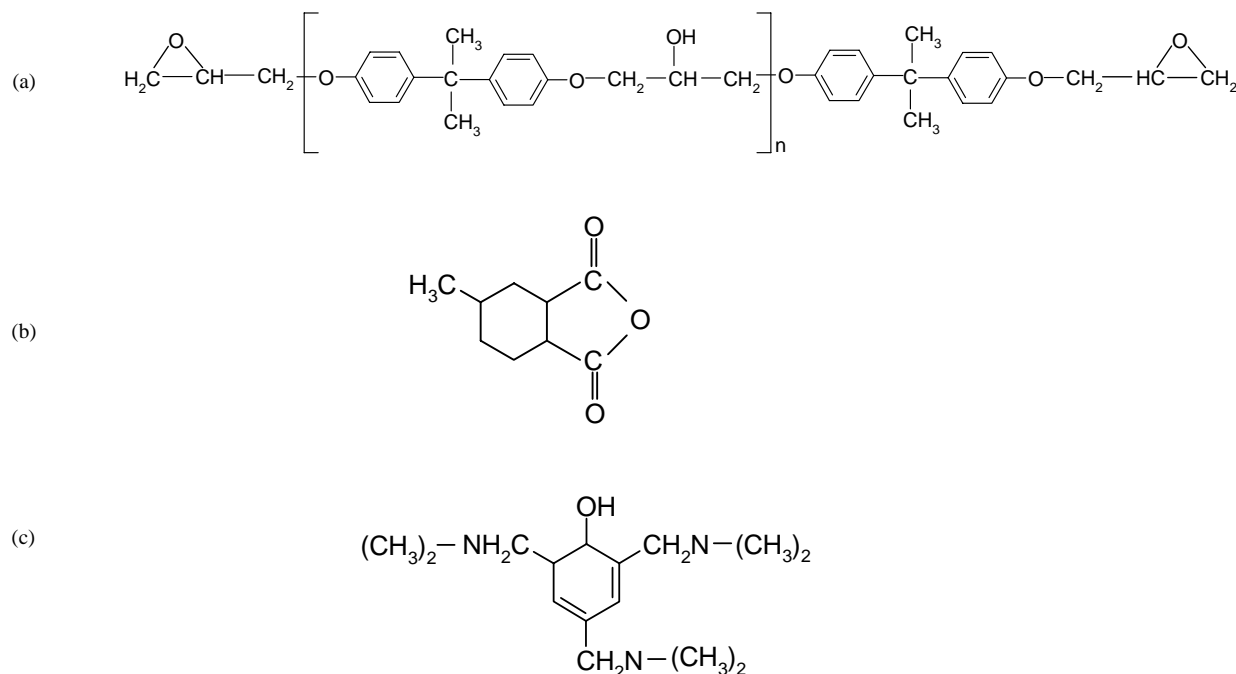
Fig. 1. (a) Structure of DGEBA epoxy; (b) structure of Hexahydro-4-methylphthalic anhydride; and (c) structure of 2,4,6-Tris (dimethylaminomethyl) phenol.

2. Experimental procedure

The epoxy resin used in this study was the diglycidyl ether of bisphenol A (DGEBA; Epikote 828, Shell Chemicals, $n = 0.2$, $M_w = 383$). The hardener used was a Hexahydro-4-methylphthalic anhydride(MHHPA) from Aldrich. The tertiary amine used was the 2,4,6-Tris (dimethylaminomethyl)phenol (DMP-30). The structures for the three systems are shown in Fig. 1.

The epoxy, hardener and the catalyst were mixed according to different ratios. Three molar ratios (1.2:1, 1:1, and 0.8:1) of anhydride to epoxy were used. To characterize the cure kinetics of our resin system, two series of isotherm al tests were performed. The first series, labeled as Isothermal Method 1, were isothermal curing tests carried out in the DSC on previously uncured resins, at 100, 120, 140 and 160°C, respectively. All samples were initially placed in the DSC cell and equilibrated at 50°C. After the system equilibrium, the temperature is then raised immediately to the isothermal curing temperature at 200°C/min. This is to avoid significant unrecorded heat due to the instrument equilibrium. A series of isothermal tests, labeled as Isothermal Method 2, were performed. For this series, the samples were first cured isothermally for varying periods and at different isothermal temperatures within the DSC. The samples were then subsequently scanned from 50°C at 5°C/min to determine the residual heat, with the degree of conversion calculated using Eqs. (2) and (3) mentioned above.

The dynamic DSC tests were run at 2, 5, 10°C/min and 20°C/min, respectively. The kinetic parameters from the single-heating-rate method were then calculated with the Perkin–Elmer DSC Kinetics analysis software version 3.0. The heating rates tested were at 2, 5, 10 and 20°C/min, in the DSC dynamic scan.

3. Results and discussion

Fig. 2 shows the results obtained for the conversion, α, by means of both isothermal Methods 1 and 2. The results have been plotted against the curing time (t) for isothermal curing at 100, 120 and 140°C, clearly showing that both methods gave a good agreement, suggesting that they were equally effective in the characterization of the time–conversion relationship of the DGEBA–MHHPA system. Isothermal Method 2 was less sensitive as the exotherm diminished in the later stage of cure, simply because of the diminishing size of the increasingly smaller exotherm; this problem was particularly acute when the glass transition immediately preceded the small residual exotherm. As such, Isothermal Method 1 appeared to be more suitable for monitoring the evolution of the extent of cure over the entire course of cure. The time–conversion relationship of the DGEBA–MHHPA system at 100, 120, 140 and 160°C have been plotted in Fig. 3, where the conversion was calculated using Isothermal Method 1. This would be later compared to the data calculated from the model to be proposed to represent the cure process.

Table 1 tabulates the kinetic parameters obtained by multi-linear regression for different constant heating rates, using the single heating rate method. It can been seen that the observed total reaction heat, ΔH, was not constant, with its value decreasing particularly for the higher heating rates
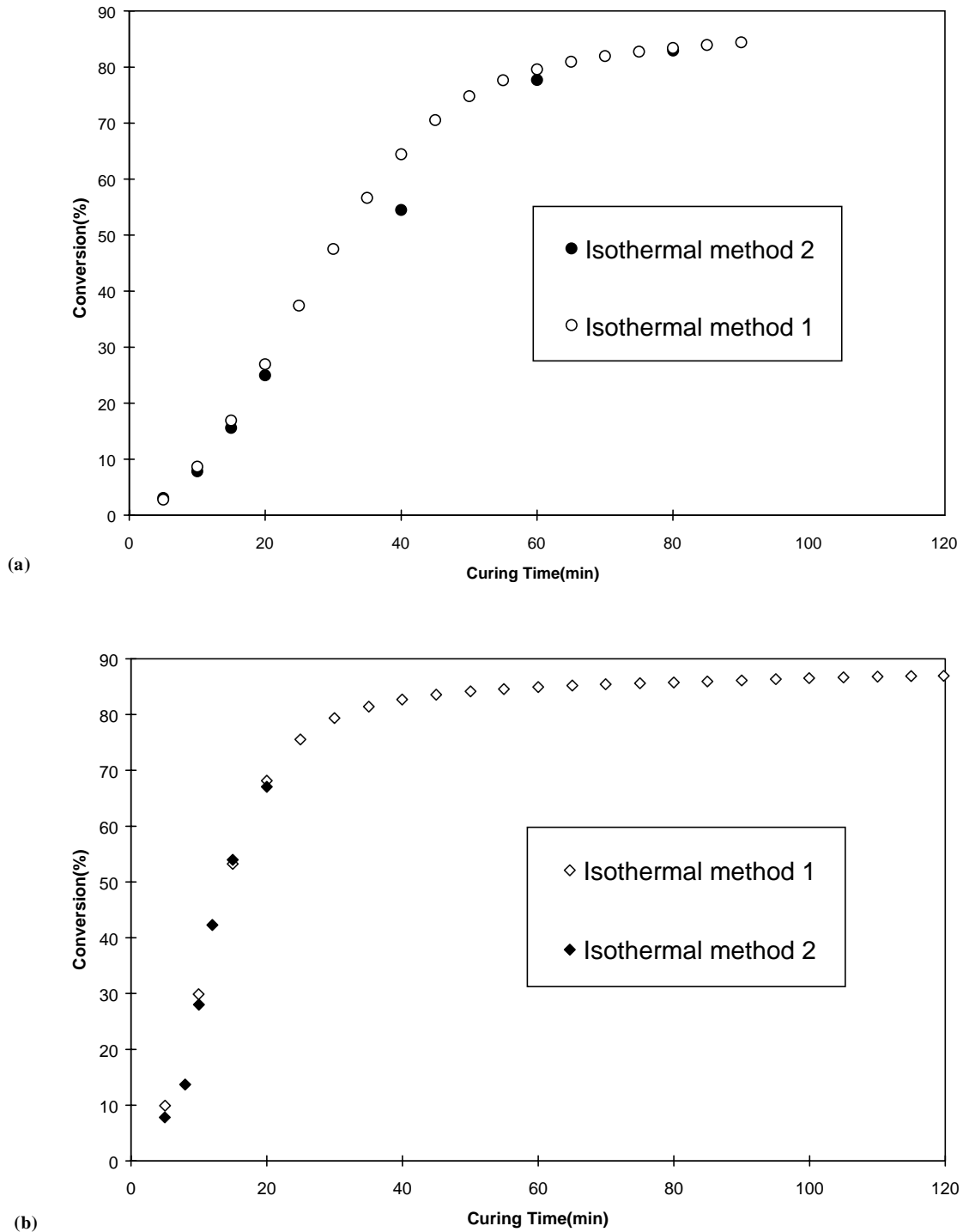
(a)

(b)

Fig. 2. Time–conversion relationship at three curing temperature by Isothermal Methods 1 and 2: (a) 100°C; (b)120°C; (c)140°C.

of 10 and 20°C/min. This is probably because the higher heating rate increased the thermal degradation of the curing resin to occur [6,44]. As the degraded portion of the resin did not eventually contribute to the cure exothermic heat output, ΔH appears to diminish progressively with the increasing heating rate.

The overall activation energy obtained by this method was in the range of 144–152 kJ/mol. The value is significantly higher than the results obtained by using a multiple heating rate method as shown later, and when compared to isothermal methods as noted in [49,50]. Fig. 4 plots the obtained $\ln(k)$ against $1/T$ to determine the rate constant. The results clearly show that for a given temperature, the rate constant decreased with increasing heating rate.

The kinetic parameters obtained above is used to compute the curing time–conversion curves shown in Fig. 5 and

(c)
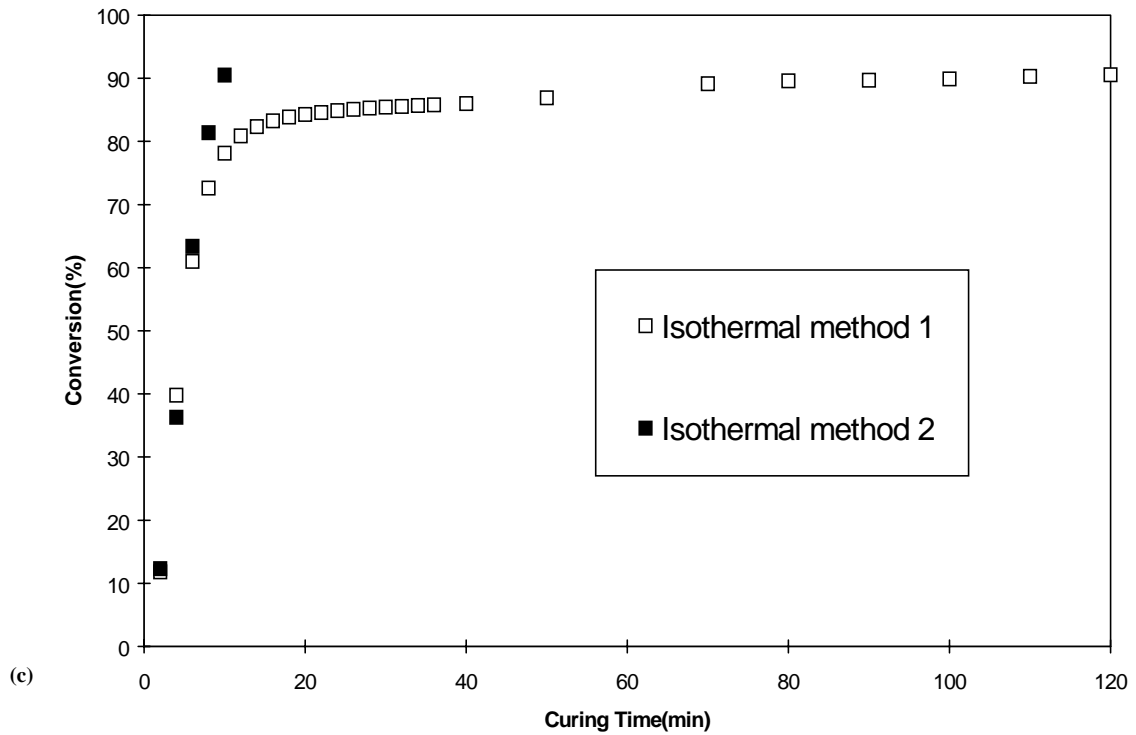
Fig. 2. (*continued*)

compared to the experimentally obtained results, for curing at (a) 160°C, (b)140°C, (c) 120°C and (d) 100°C. From the graphs it can be seen that while the calculated time–conversion relationships were reasonably constant for the various

heating rates tested at 160°C, this was not the case at the lower temperatures of 140, 120 and 100°C. The disparity was greater the lower the temperature, with the calculated conversion being lower the higher the heat rate. Evidently,
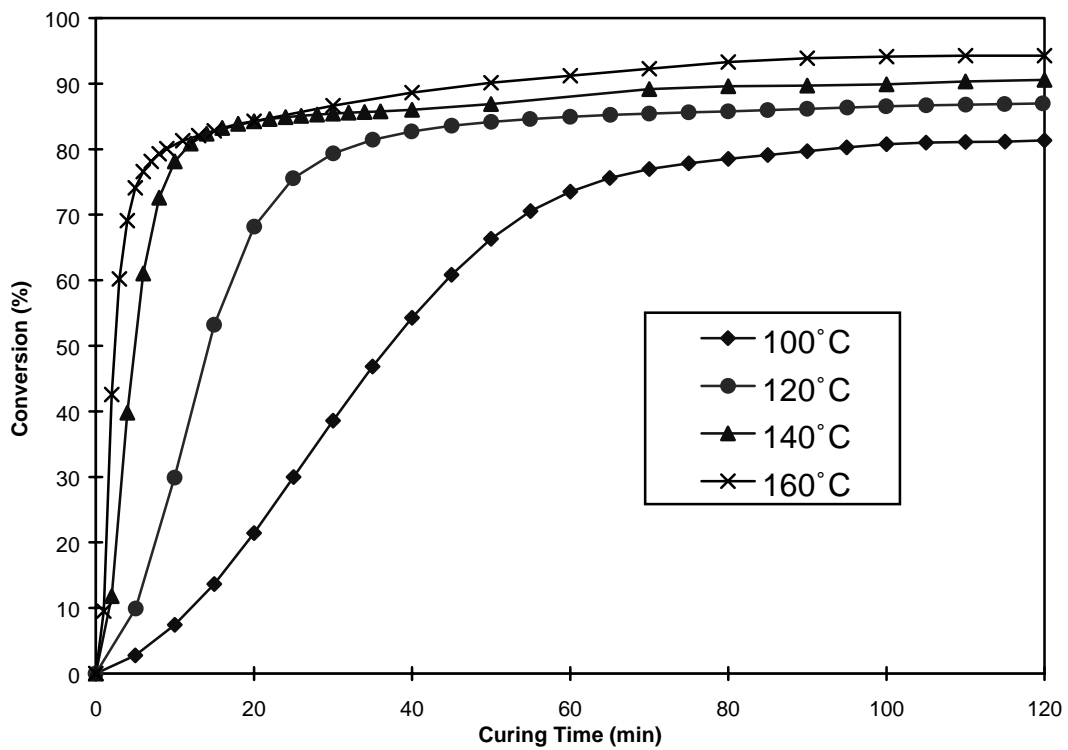

Fig. 3. Curing Time–conversion relationship at four isothermal curing temperature.

Table 1
Kinetic parameters of DGEBA–MHHPA by single-heating-rate method

Heating rate (°C/min)	ΔH (J/g)	E_a (kJ/mol)	ln A (l/s)	n
2	− 314.9	151.8	40.07	1.46
5	− 316.7	144.3	36.8	1.51
10	− 279.6	144.4	36.2	1.36
20	− 257.95	147.3	36.4	1.34

Table 2
The DSC exotherm peak conversion at different heating rates

Heating rate (°C/min)	α_p (%)
2	55.51
5	55.37
10	55.08
20	55.62

the single heating rate method, which assumes an nth-order reaction, has not been able to accurately describe the curing process of the DGEBA–MHHPA system, particularly at a low curing temperature.

Fig. 6 shows the results for the DSC exotherm curves tested at 2, 5, 10 and 20°C/min, respectively. These exotherms were then analysed using the multiple heating rate method to obtain the activation energy value. Fig. 5 shows that the peak of the exotherms occurred at increasingly higher temperature as the heating rate increased. Table 2 tabulates the result obtained for the conversion at the peak exotherm, for different heating rates. It is evident that the conversion values obtained were very close in value, confirming that for the system tested, the assumption that the conversion was independent of heating rate was valid.

Based on Eq. (11), the activation energy E was then obtained by plotting $\ln[\phi/T_p^2]$ versus $1/T_p$. This has been carried out in Fig. 7, showing the experimental data obtained for the epoxy–anhydride system tested. A linear relationship was obtained, thus confirming the validity of

the proposed model given in the equation. The activation energy E was calculated from the slope, yielding a value of 71.6 kJ/mol. This value agreed reasonably well with the activation energy of similar epoxy–anhydride systems obtained by other researchers. For example Fava [6] obtained a value of 74.6 kJ/mol; Montserrat et al. obtained values of 69 ± (and 73 kJ/mol [46,47,51]; Zukas obtained a value of 75.6 kJ/mol [33].

Fig. 8 plots the conversion percent against the dynamic cure temperature, for various heating rates as shown, based on the results obtained in the DSC curves shown in Fig. 6. From Fig. 8, it is seen that at the same conversion value, the iso-conversion temperature, T_i was higher when the test heating rate was increased. From Eq. (12), it is seen that the plot of $\ln \phi$ against $1/T_i$ enables the calculation of the activation energy at any conversion by the Ozawa method, as has been carried out in Fig. 9, for the conversion from 5 to 95%.

Fig. 10 plots the values of the activation energy calculated by the Ozawa method for different values of the
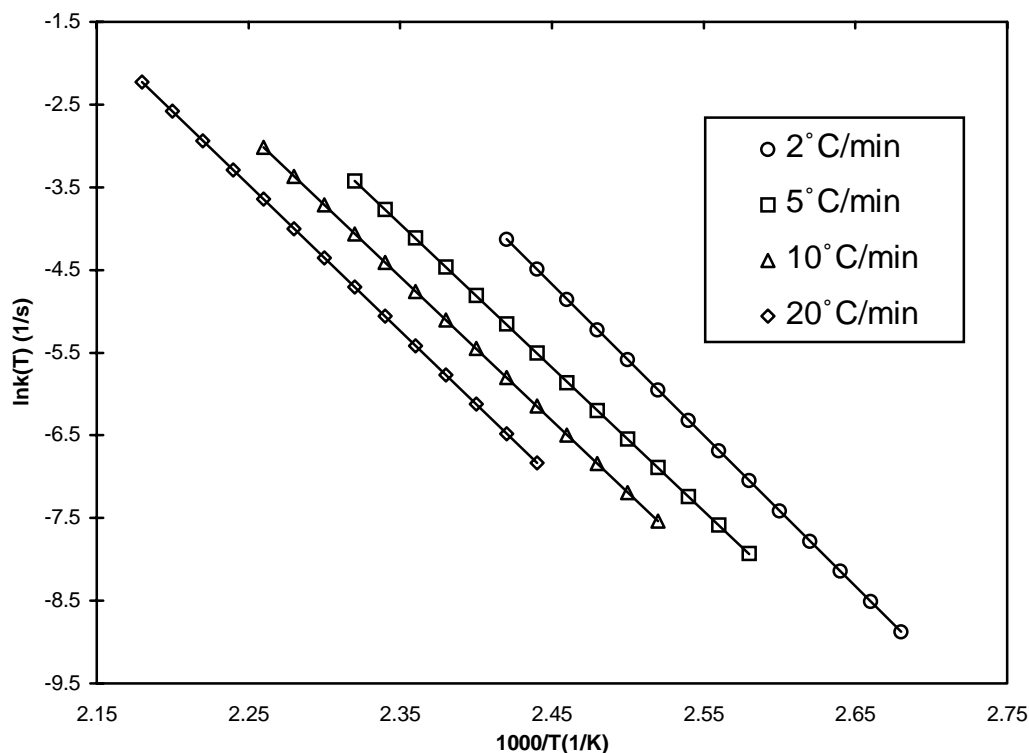

Fig. 4. Plot of the ln k against $1/T$ by the single-heating-rate method.

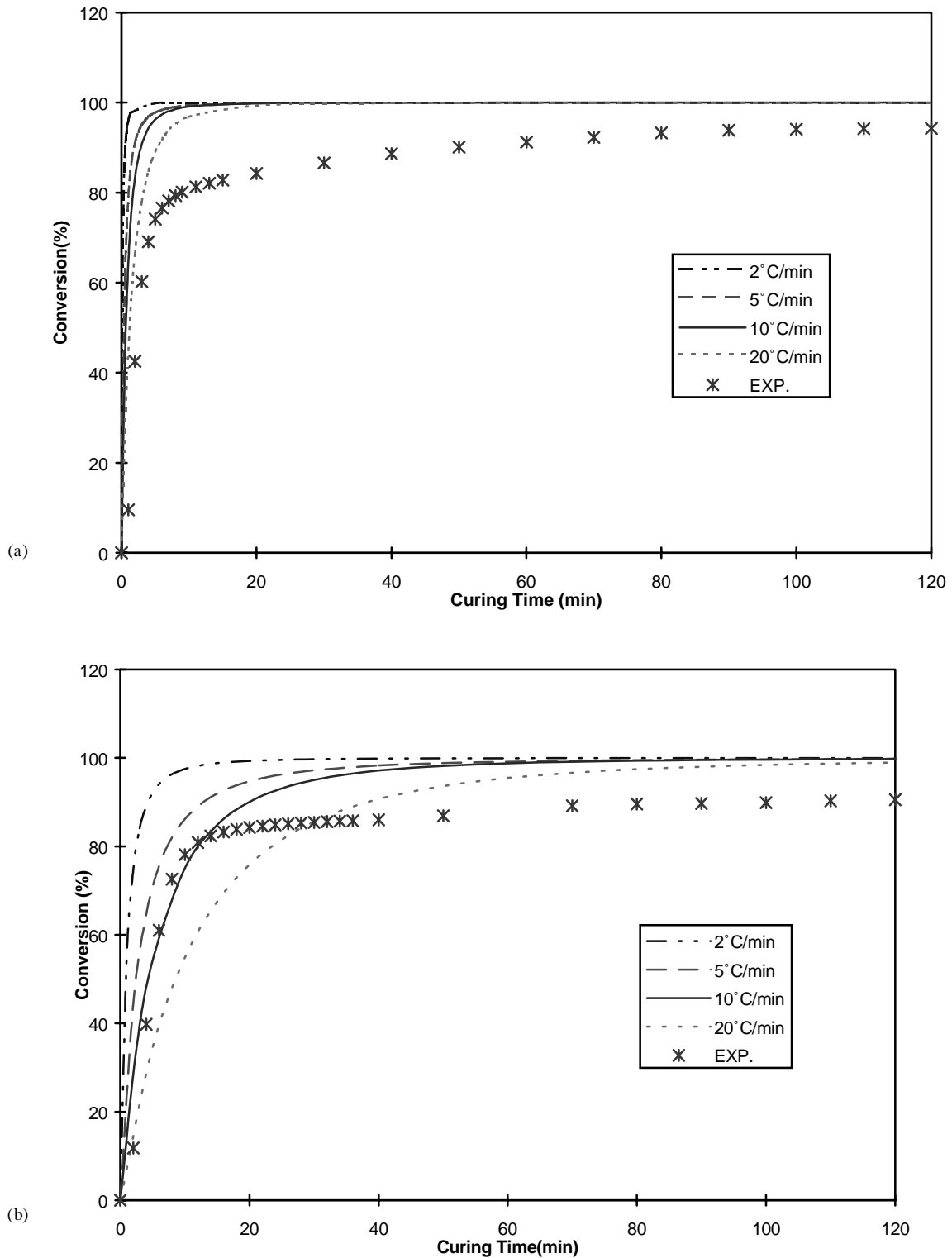F.Y.C. Boey, W. Qiang / Polymer 41 (2000) 2081–2094

(a)

(b)

Fig. 5. Computed isothermal conversion–time relationship at different temperature by single-heating rate method: (a) 160°C; (b)140°C; (c) 120°C; (d) 100°C.

conversion, showing E to gradually increase with the extent of cure. This may be due to the decrease of the mobility of the reactive groups of the partially cured epoxy. The value of the activation energy is about constant in the interval $20\% < \alpha < 80\%$. The activation energy so obtained is

74.7 kJ/mol, which is slightly higher than by the Kissinger method.

Fig. 11 shows the isothermal DSC result of the system at 140°C. Fig. 12 is the plot of the conversion rate against the conversion itself, for the DGEBA–MHHPA system, showing

(c)

(d)
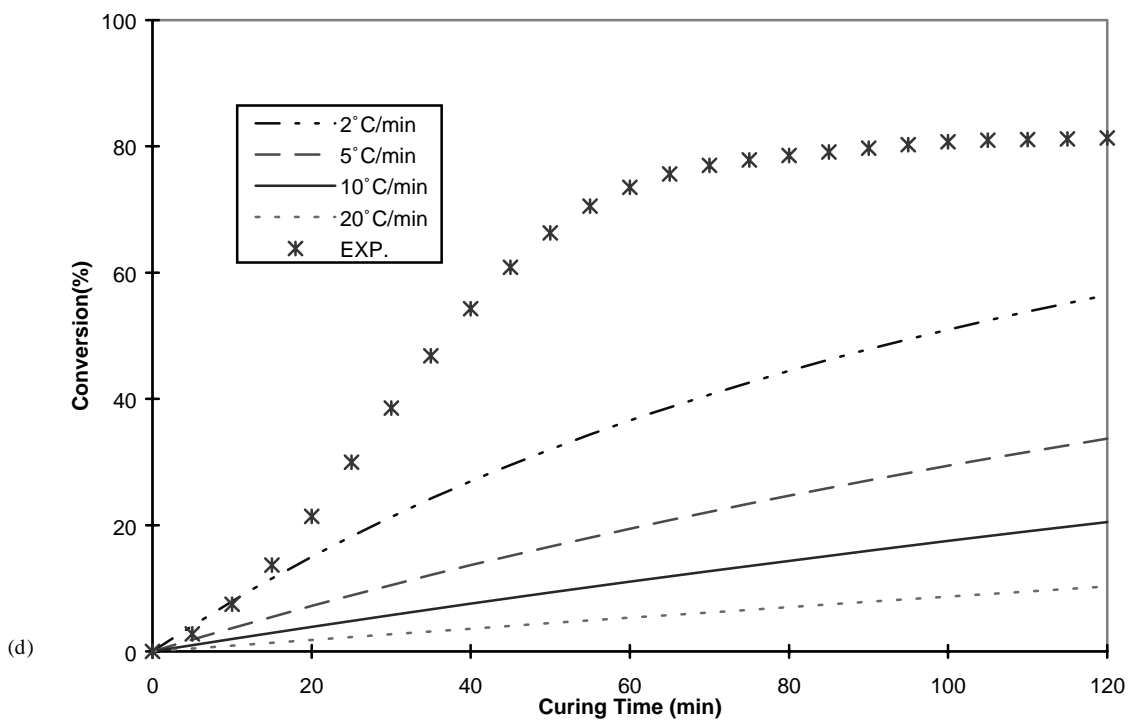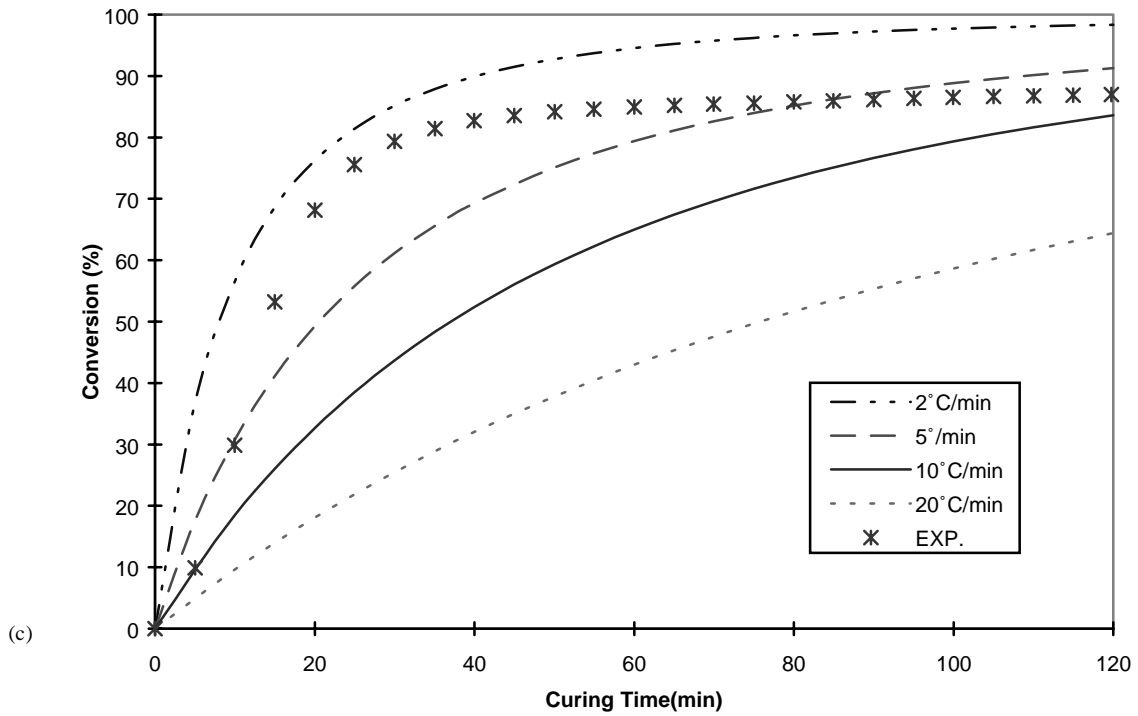
Fig. 5. (*continued*)

the maximum conversion rate at 20%, thus confirming that the curing process follows an autocatalytic model. Thus Eq. (12) is applied to the system, with the parameters determined using a least square regression method to fit our experimental data to the model, with the regression results for the kinetic parameters k, m and n tabulated in Table 3.

Table 3
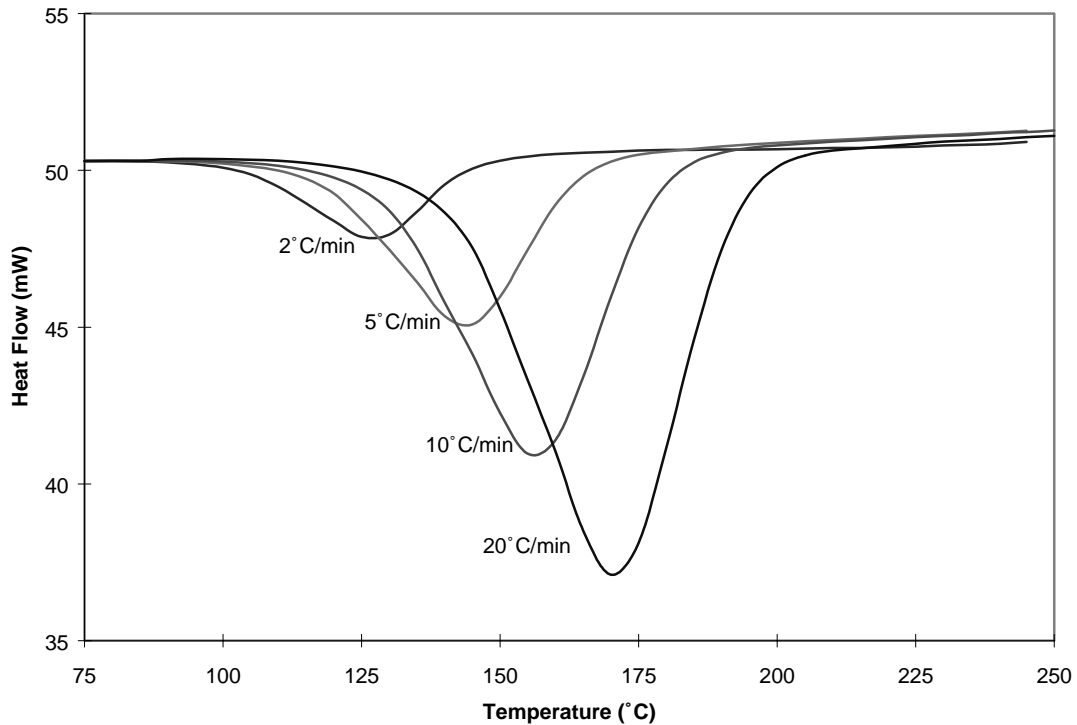The best fit kinetic parameters of the DGEBA–MHHPA system

k	0.010
m	0.635
n	1.833

Fig. 6. DSC cure exotherms at different scan rates.

Fig. 12 presents the comparison between the experimentally obtained data with the graph plotted using the autocatalytic model, with values of model parameters determined above. Excellent agreement is observed up to 70% conversion, with the degree of fit $R^2 = 0.978$. Beyond this, deviations were observed, possibly due to the onset of vitrification. As the cure progress and the resin cross-links, T_g of the system rises. At this stage, the
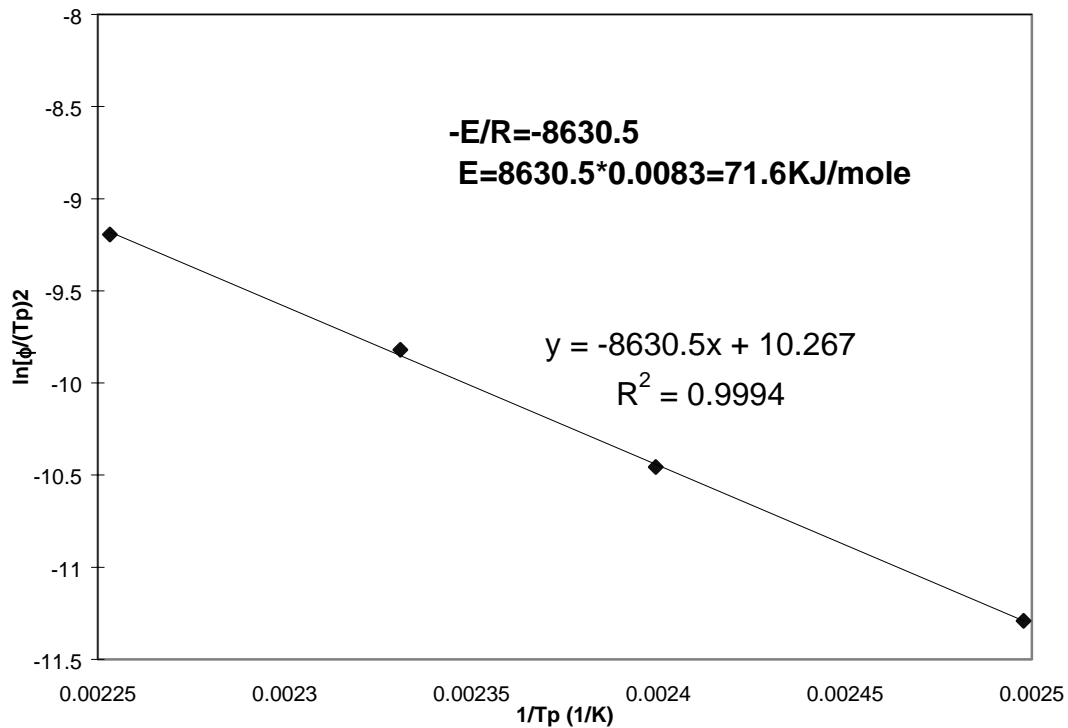

Fig. 7. Plots for determination the activation energy of the curing reaction by Kissinger method.
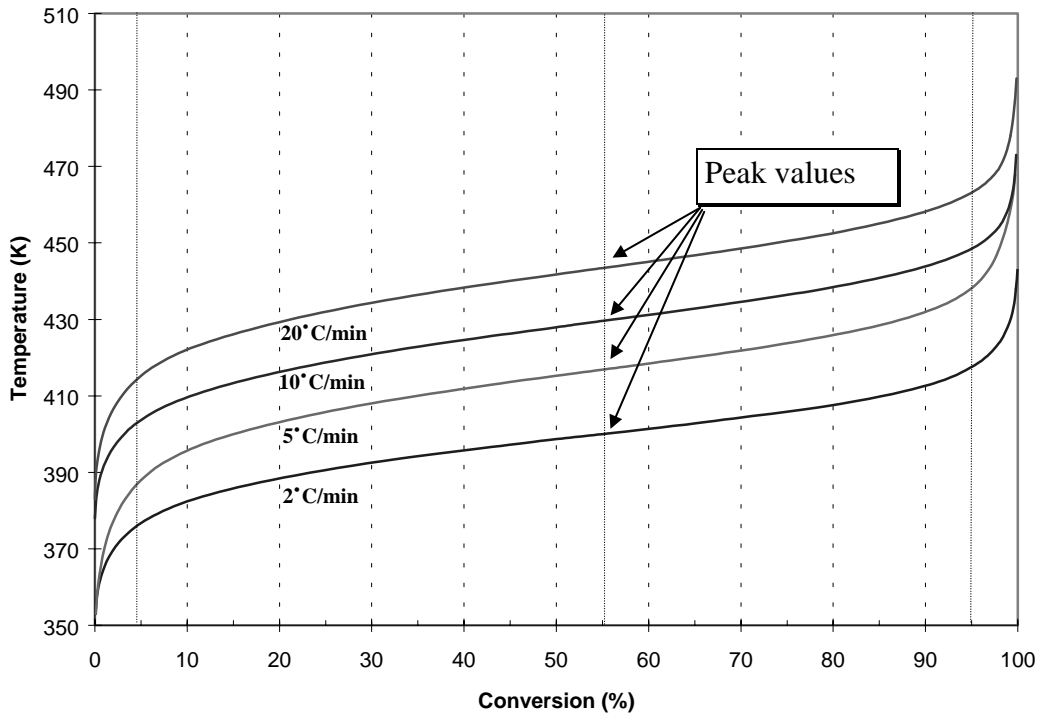
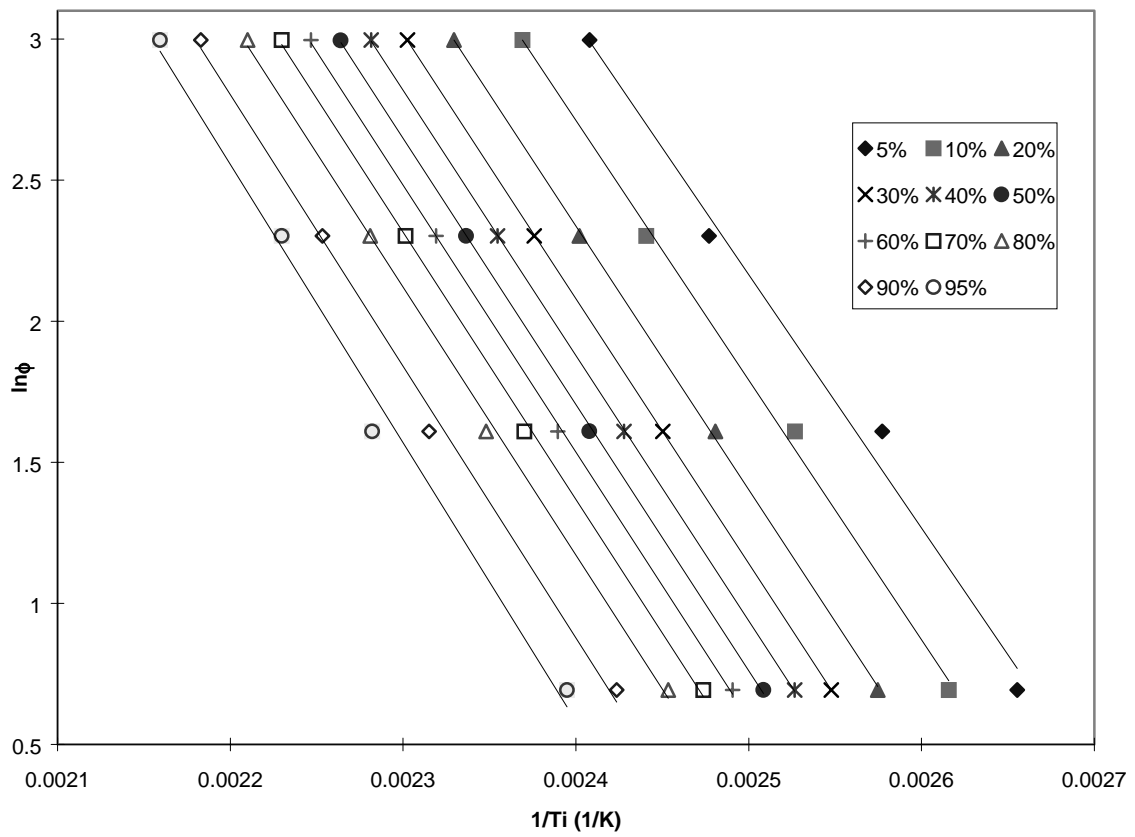Fig. 8. Plots of DSC isoconversion temperature at different heating rates.

Fig. 9. Plots of ln ϕ, against $1/T_i$ at different conversion to calculate the activation energy.
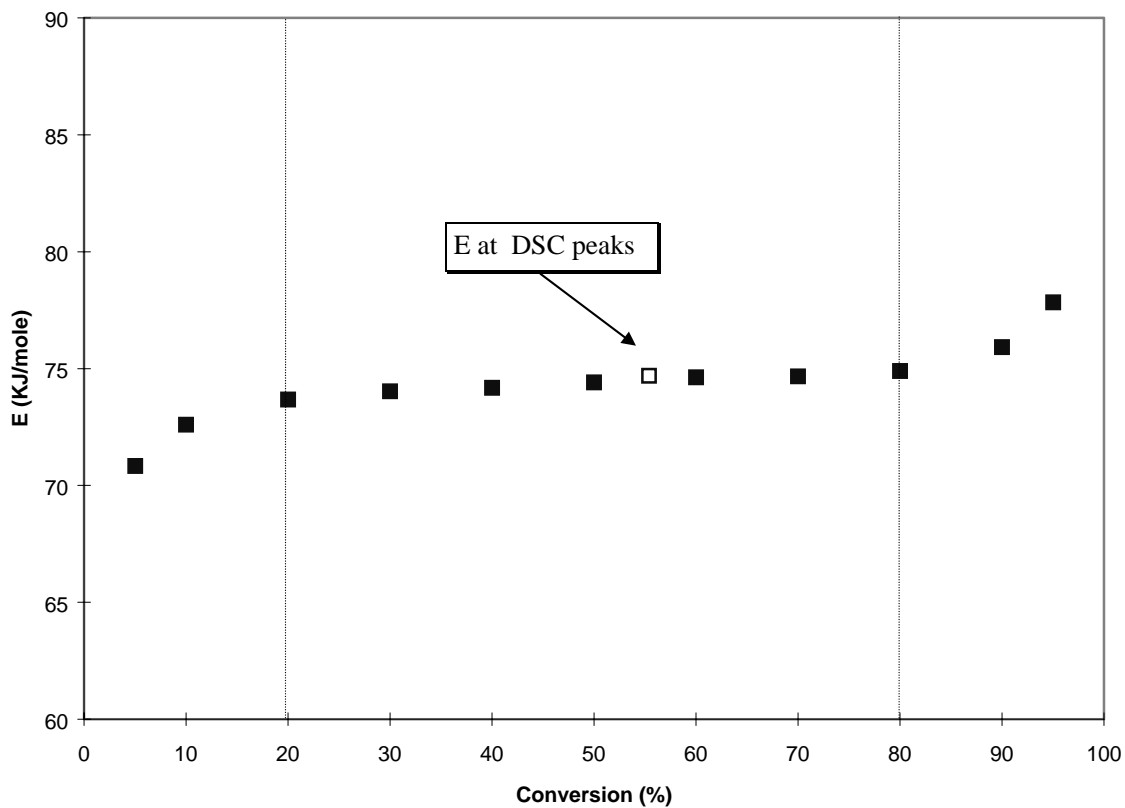
Fig. 10. The activation energy change calculated by the Ozawa method at various conversion.

mobility of the reaction groups could have been hindered, and the rate of the conversion was controlled by diffusion rather than chemical factors. This account for the fact that the experimental conversion and conversion rates are lower than those predicted by Eqs. (2) and (12). The total reaction order was about 2.6, which concurs with the values elucidated from most epoxy systems.
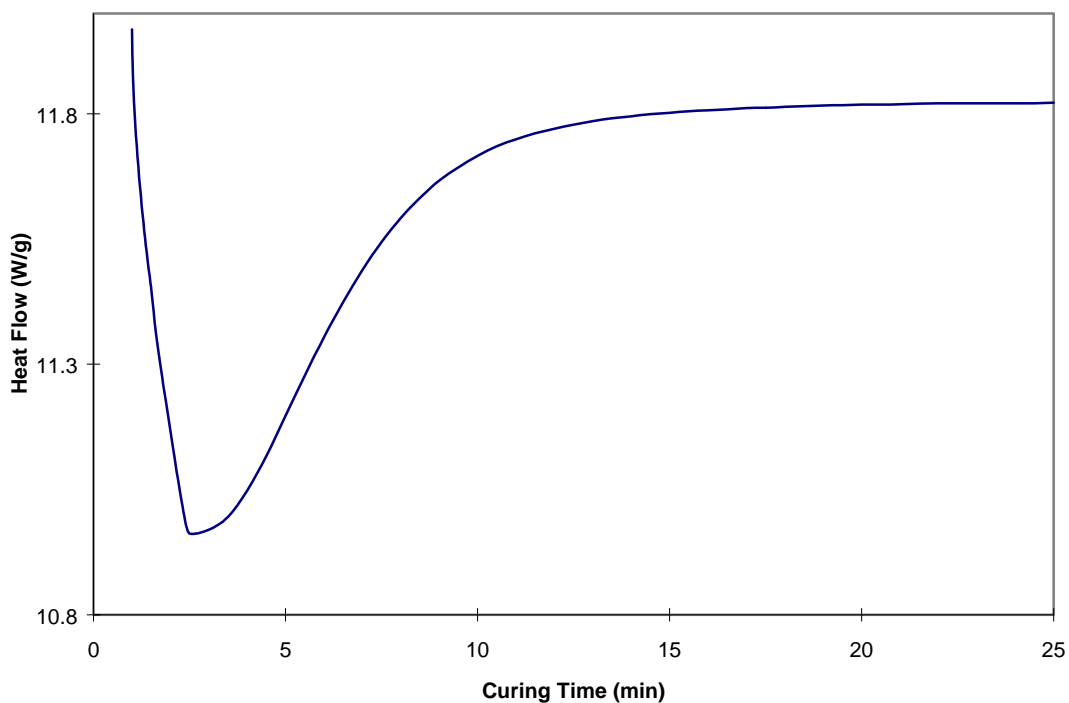

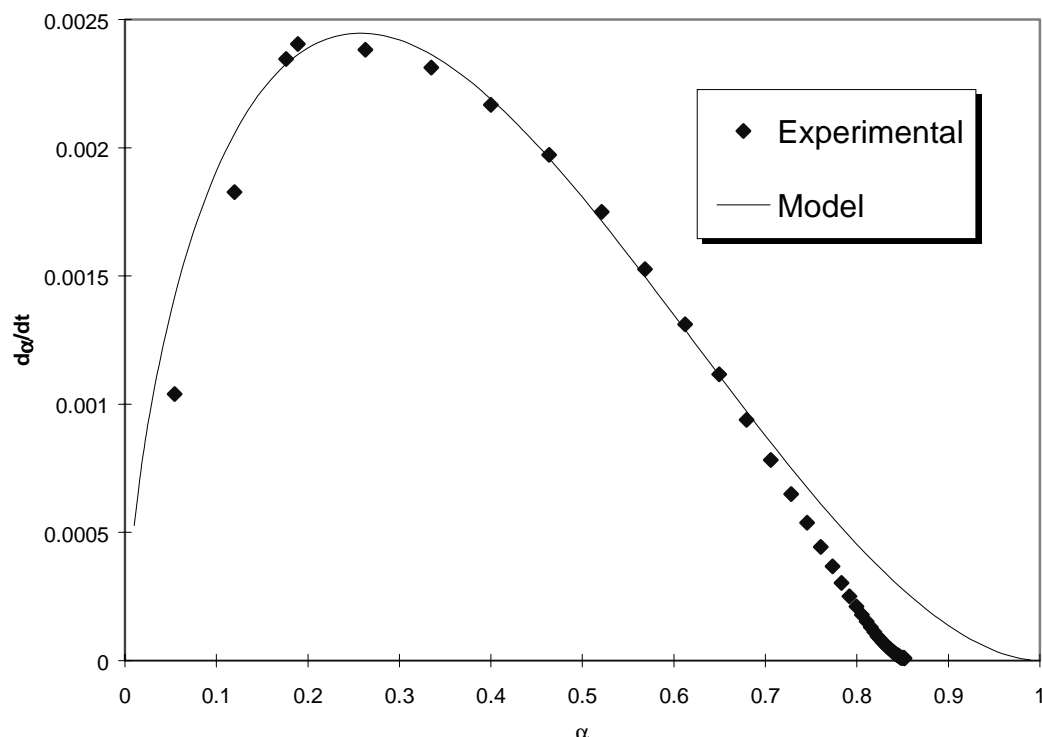Fig. 11. The isothermal DSC result of the DGEBA/MHHPA system at 140°C.

Fig. 12. Comparison of experimental data with the autocatalytic model at a curing temperature of 140°C: conversion rate, dα/dt, vs. conversion, α.

4. Conclusion

An accurate cure kinetics model for the DEBGA–MHHPA epoxy system has been elucidated using both the isothermal and non-isothermal DSC methods. The results indicates that both the Kissinger and Ozawa's methods for calculating the activation energy value gave fairly close results of 71.6 and 74.7 kJ/mol, respectively. An autocatalytic model with a total order of reaction of about 2.5 was successfully used to model the process.

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