



Kinetics of cure for a coating system including DGEBA ($n = 0$)/1,8-NDA and barium carbonate

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ABSTRACT

The increasing demand for low-cost and high performance coatings has promoted the development of chip epoxy-based coatings using inert fillers. Attention has been paid here on employing mixtures of DGEBA with barium carbonate as novel ceramic-based filler to produce a coating using 1,8-naphthalene diamine (1,8-NDA) as the crosslinking agent. A substantial increase in the T_g , from 85 to 100 °C, is observed for the optimum composition. The 1,8-NDA-cure of the epoxy composites showed an autocatalytic mechanism. At a specific conversion range the cure reaction of the composites will be controlled by a diffusion-control cure reaction rather than by Kamal autocatalytic model. Model-free isoconversional method is utilized to construct apparent activation energy dependence on conversion plot. The effect of diffusion control is described by an approach proposed by Chern and Poehlein. Greater diffusion control is observed as the cure temperature decreased.

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1. Introduction

Epoxy resins are the most important class of thermosetting resins that find application in surface coating, composite matrices, adhesive, encapsulation of electronic components, and aerospace industries [1]. However, the curing reactions of epoxy resins are normally complex due to many reactive processes that occur simultaneously. There are other parameters that increase the complexity of the curing reaction, such as vitrification and gelation phenomena, and the change from chemical kinetic control to diffuse control during the reaction progress [2–4]. The kinetics of the curing of epoxy resin has been widely studied with isothermal and dynamic differential scanning calorimetry (DSC). Differential scanning calorimetry (DSC) which measures the heat flow from the reacting system is broadly used to study curing reactions [5–8]. During curing epoxy resins exhibit extensive branching passing through the gel point before the formation of macromolecular structures. Gelation generally occurs before vitrification and is characterized by the incipient formation of a material having infinite molecular weight [9]. The two mentioned phenomena indicate the conditions of the materials processability. Moreover, in the early stages of cure, before gelation and vitrification, the reaction took place in the liquid phase and is controlled by the chemical reactivity of the functional groups. As the reaction progresses, the free volume of the material decreases, and when conversion

reaches a critical value, α_c , the mobility of the reacting components is reduced promoting the system to be influenced by diffusion affects. Hence, the α_c value would reflect the state of cure of the system rather than the temperature of the cure. The critical conversion for the onset of diffusion-controlled reactions is taken formally as the point at which a three-dimensional crosslink network is formed. This seems reasonable, because at this point the molecular weight of the reacting components increases dramatically. One of the major applications of epoxy-based thermosetting polymers is in the protective coating industry. Today, epoxy powder coatings are most widely used owing to their distinguished corrosion, dielectric, and mechanical properties. However, the main drawback of these materials is weak toughness. So, toughness improvement of the epoxy coating is crucial. Many materials like rubber elastomer, thermoplastics, liquid crystalline epoxy, micro- and nano-particles are used to improve its toughness [10–15]. Thermoset polymers also have low tensile and storage modulus. In many cases, it is necessary to add other materials to the resin matrix in order to enhance its properties and/or to decrease the prices of the produced polymers. One of these classes of components is inert filler. Much research has been reported on the preparation of epoxy coatings using micron and nanosized calcium carbonate as filler [16–20].

In the first part of the present study, the cure behavior of epoxy/1,8-naphthalene diamine/barium carbonate system is investigated with the aim of bearing in mind its potential use as a coating. Since the physical, mechanical, and electrical properties of a thermosetting polymer depend on the cure degree, rate and value of polymerization, so, kinetic characterization of the

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reactive components is important for better understanding of the structure–property relationships and optimization process.

2. Experimental

2.1. Materials

The epoxy system used in this work was Epon 828, from Shell Chemical Company. Epon 828 is, basically, DGEBA having an epoxy equivalent weight (eew) of 185 equiv./g. 1,8-Naphthalene diamine is a solid difunctional aromatic amine with a molecular weight of 158.2 g mol⁻¹. The diamine was purchased from Merck and purified twice prior to use. Barium carbonate was also supplied by Fluka and used without further purification.

2.2. Sample preparation

For the system without barium salt, epoxy resin and 1,8-NDA at stoichiometric ratio (21.4 Phr) were carefully and homogeneously mixed by stirring the mixture under a nitrogen atmosphere. For the composites, a specific level of the barium salt is added into epoxy matrix before being added the curing agent at a stoichiometric ratio. In a series of various experiments the amount of barium salt was 2, 5, 10, 15 Phr of the total weight of the compositions (epoxy/1,8-NDA/Barium carbonate). It should be noted that the amount of the filler is selected respect to the value of resin/hardener system. Bulk samples of 1000 mg are prepared and then about 10 mg in size samples are used for DSC measurements. The samples are sealed with an aluminum pan and kept in a refrigerator before introducing them toward thermal treatment.

2.3. Differential scanning calorimetry (DSC) measurements

A Perkin-Elmer DSC-7 unit, under control of a 1020 system controller is employed for calorimetry measurements. Due to the use for this study, the calorimeter was calibrated using indium standard before each measurement. To measure the reaction heat, the glass transition temperature (T_g) of the fully cured samples and to find the desired temperatures for isothermal measurements, non-isothermal DSC experiments are conducted in the temperature range of 25–280 °C under nitrogen atmosphere. Runs at a constant heating rate of 10 °C/min are performed on each sample three times. Kinetic studies are also performed using DSC working isothermally in the temperature interval from 180 to 230 °C. To minimize the effects of diffusion on the curing reaction, we conducted our isothermal experiments at high temperatures. Noticeably, since the reaction rate is too fast at these high temperatures, the experimental $t=0$ is defined to be the time at which temperature equilibration is completed. For this work, the T_g is taken as the temperature at the midpoint between the initial and final heat capacity curves on the isothermally cured samples which were reheated at 5 °C/min. The data files were transformed into an Excel program and then by means of suitable equations the kinetic parameters are calculated.

3. Results and discussion

3.1. Kinetic analysis

The curing of a thermoset and particularly epoxy resins involves the formation of a rigid three-dimensional network by a reaction between the oxirane rings of the epoxy oligomer with hardeners that have more than two reactive functional groups. The formation and linear growth of the chain, which soon begins to branch and then crosslink is a general scheme in the mechanism of epoxy

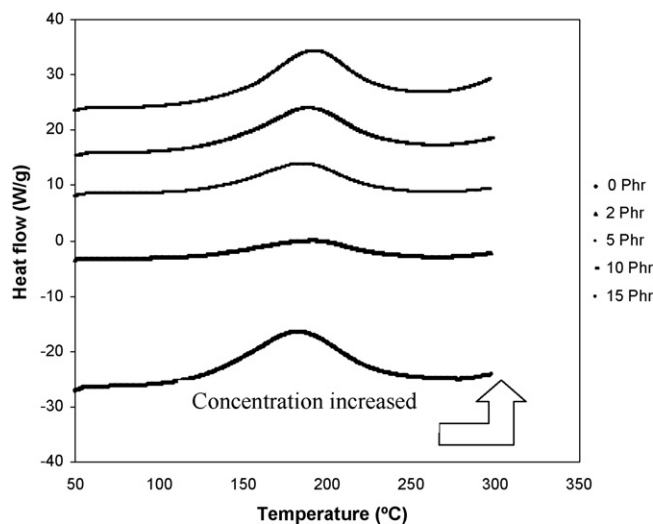


Fig. 1. DSC curves of DGEBA/1,8-NDA/BaCO₃ for different percentages of inert filler (curves have been stacked horizontally for better clarity).

polymerization with diamines. As the cure proceeds, the molecular weight increases rapidly. Fig. 1 shows DSC curves recorded for epoxy cured with hardener at different concentrations.

In some cases, determination of activation energy and polymerization kinetics from temperature scanning DSC experiments, either multiple or single scans, is fraught with difficulties. The problems could be related to the limitations of the used kinetic model, in the cases of single heating and model-fitting approaches, and the presence of some uncontrollable thermal events such as thermal degradation and side reactions at higher temperatures. However, to gain idea about the cure behavior of the system under study, the detailed kinetics studies are carried out using isothermal DSC. As a first stage, this study needs to determine the optimum barium salt concentration which should be added into the epoxy matrix, as the isothermal kinetics parameters will be determined for the optimum composition of the tertiary system examined here. Having this aim in the mind, dynamic experiments on the compositions involving different amounts of the barium salt (2, 5, 10 and 15 Phr) are introduced. Three experiments are performed for each concentration and the change in reaction enthalpy in terms of the filler concentration is depicted in Fig. 2. Clearly, the only reproducible results are those corresponding to the composition involving 2 Phr barium carbonate. This may be attributed to the fact that at higher filler concentrations, its distribution is a rather heterogeneous producing local aggregation in the matrix bulk which acts as a barrier in the crosslinking process.

Table 1 summarizes the thermal data obtained from dynamic DSC scans. As it is seen in the table, the reaction heat of the

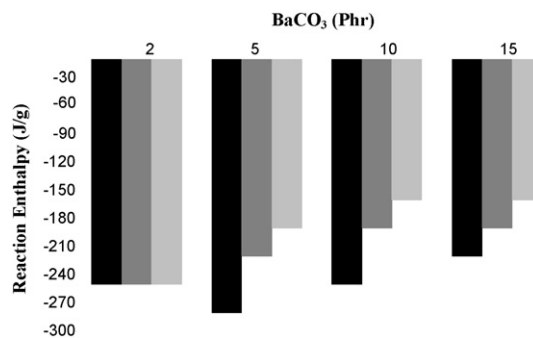


Fig. 2. Plots of reaction enthalpy versus the filler concentration (Phr) for the three experiments done on the samples.

Table 1Data from dynamic DSC measurements on neat epoxy and its composites having different amounts of BaCO₃ at heating rate of 10 °C/min.

BaCO ₃ concentration (Phr)	ΔH_T^a (J/g)	Peak cure onset (°C)	T_g (°C)	Peak cure max (°C)
0	-282 ± 1	84	85	181
2	-239.7 ± 1	85	100	182
5	-219.7 ± 4.3	86	97	184
10	-190 ± 2.8	87	95	187
15	-180 ± 2.2	89	92	191

^a The heat of reaction reported here is an average value of the three DSC scans on each sample.

sample having 2 Phr barium salt is higher than that of the others. Also, the T_g of the composites is higher than that of the neat epoxy system and its value decreases at the high level of 15 Phr. It may be implied that at high level of the filler loading the crosslink density will decrease owing to topological restrictions resulting in lower values of reaction heat as shown in Table 1. The increase in T_g of the filled systems respect to the neat epoxy could be attributed to the decreased mobility of chain segments of epoxy resins owing to the filler/resin matrix interactions.

From the thermal analysis data shown in Fig. 2 and Table 1, it is concluded that the best formulation for compounding three reactants is when 2 Phr barium carbonate is incorporated into the resin matrix. Upon finding out the optimum composition four isothermal experiments are carried out and the curves are shown in Fig. 3.

The conversions (α) of the epoxy, at cure time t , are determined from the heat evolved up to that time (ΔH_t), by the expression:

$$\alpha = \frac{\Delta H_t}{\Delta H_T} \quad (1)$$

where ΔH_t is the heat evolved up to a specific time and ΔH_T is the total enthalpy of the cure reaction. Since the cure rate is proportional to the rate of heat flow, the rate of conversion is given as

$$\frac{d\alpha}{dt} = \frac{d(\Delta H_t)}{dt} \times \frac{1}{\Delta H_T} \quad (2)$$

Curves of conversion rate versus conversion and conversion versus time are obtained from the isothermal DSC data by numerically integrating the heat flow against time curves and scaling by total reaction enthalpy. The curve of α versus time is exhibited in Fig. 4. As it is clear, the time for being fully crosslinked, apparently, is decreased with curing temperature. Fig. 5 shows the reaction rate versus conversion. As expected, the reaction rate is promoted by

selecting higher values of cure temperature. Otherwise, at a given conversion a higher isothermal curing temperature gains a higher reaction rate. This increase in rate is more considerable prior to the curve maximum where the α value is still low.

3.2. Cure kinetics of DGEBA/1,8-NDA/barium carbonate system under isothermal conditions

As it is shown (see Figs. 4 and 5) the reaction rate is affected by the selected isothermal temperature and the conversion. Based on the above experimental phenomenon and not considering individual reactions in the curing process, the phenomenological approach is used to describe isothermal curing reaction. Two different

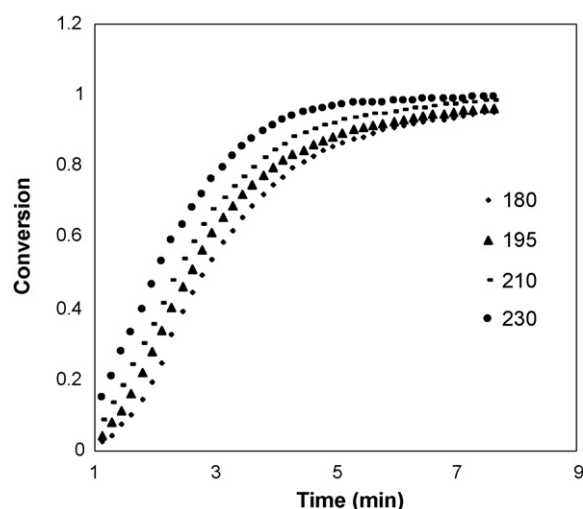


Fig. 4. Degree of conversion versus time plots at various temperatures.

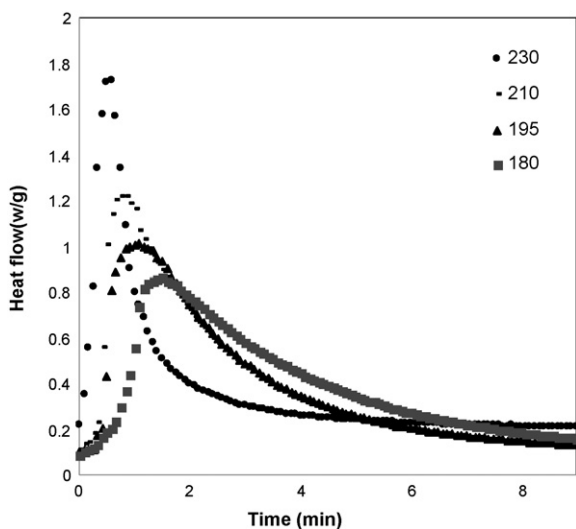


Fig. 3. DSC curves of the composite having 2 Phr Barium carbonate DGEBA/NDA at various isothermal temperatures.

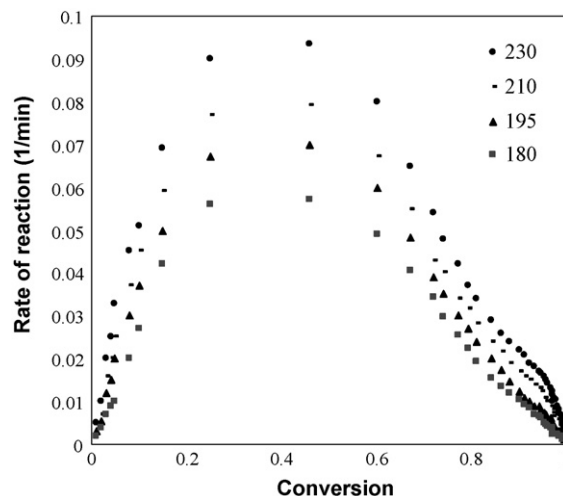


Fig. 5. Reaction rate versus conversion plots at various temperatures.

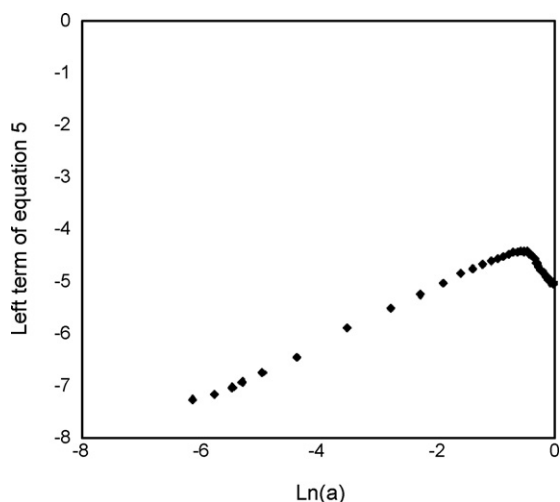


Fig. 6. Graphical representation of Eq. (5) to calculate m and k_2 at 180 °C.

models, namely n -order and autocatalytic, have been used in the literature to explain thermosetting polymers reaction kinetics. In order to determine the suitable model a common simple approach is employed. Firstly, the experimental phenomenon is compared to the features of the two models, and then an appropriate model is selected to test the experimental data and finally, the parameters of the model will be found. Correspondingly, the characters of the curing reaction are first examined in this study. From Fig. 5, it is obvious to see that the reaction rate of the composite system reaches a maximum at non-zero time, typically between $\alpha = 0.2$ and 0.6, which is characteristic of an autocatalytic reaction. Therefore, we used the Kamal autocatalytic model [21,22] to describe kinetics of cure for epoxy resin in the presence of barium carbonate. The model can be illustrated by the following equation:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (3)$$

where α is the conversion, k_1 and k_2 are the apparent rate constants, and m and n are the kinetic exponents of the reactions. There are various methods to determine the four parameters of the Kamal equation but the most utilized one is a graphical method. According to this method, the constant k_1 in Eq. (3) can be calculated from the initial reaction rate at $\alpha = 0$. With rewriting Eq. (3) in the following form:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(k_1 + k_2\alpha^m) + n \ln(1 - \alpha) \quad (4)$$

Except in the initial region ($\alpha < 0.1$), a plot of $\ln(d\alpha/dt)$ versus $\ln(1 - \alpha)$ is expected to be linear with a slope n . This last equation is then organized to give the following equation:

$$\ln\left\{\left[\frac{d\alpha/dt}{(1-\alpha)^n}\right] - k_1\right\} = \ln k_2 + m \ln \alpha \quad (5)$$

This recent equation is employed to evaluate m and k_2 from the slope and intercept, respectively. The corresponding plot at 180 °C is addressed in Fig. 6. Preliminary kinetic parameters can be obtained on the first test. The kinetic parameters of k_2 , m and n can be finally estimated from the stated procedure according to an iterative formalism.

Furthermore, Eq. (5) can be rearranged to present the following form:

$$\ln\left(\frac{d\alpha}{dt}\right) - \ln(k_1 + k_2\alpha^m) = n \ln(1 - \alpha) \quad (6)$$

The left terms of Eq. (6) can be plotted against $\ln(1 - \alpha)$. A new value of the reaction order n can be obtained from the slope. The

Table 2
Kinetic parameters of k_1 , k_2 (min^{-1}) and reaction orders obtained using the Kamal autocatalytic model.

Temperature (°C)	k_1	k_2	m	n	$m + n$
180	0.007	0.011	0.41	0.67	1.08
195	0.018	0.026	0.44	0.68	1.12
210	0.045	0.052	0.63	0.70	1.33
230	0.067	0.070	0.75	0.76	1.51

same iterative procedure is repeated until apparent convergence of m and n values. The results of applying the above mentioned graphical method is shown in Table 2.

As the cure of epoxy-based composites involves a multi-step process model fitting methods can not describe the events occurring during the polymerization successfully. Model-free approaches are the suitable tools that are extensively employed by the researches to better interpret the epoxy cure. Therefore, we attempt to apply model-free iso-conversional analysis to the conversion versus time data according to the following equation [23]:

$$-\ln t_{\alpha,i} = \ln\left[\frac{A(\alpha)}{G(\alpha)}\right] - \frac{E_a}{RT_i} \quad (7)$$

The corresponding plot of activation energy against conversion is shown in Fig. 7. The average value of activation energy in the 0.05–0.6 conversion interval is found to be 94.2 kJ/mol. However, the value of E_a is moved downwards as the conversion is going to be higher than that its values at $\alpha > 0.7$.

3.3. Study of diffusion effect

As stated before, Fig. 5 shows the curve of reaction rate versus conversion. As expected, as the cure temperature is raised, the rate of polymerization at each conversion level noticeably increases. At temperatures exceeding the highest selected isothermal temperature, typically >240 °C, the level of conversion was approximately constant. Moreover, the peak of the conversion rate becomes higher and shifts to a shorter time with an increase in isothermal temperature. It is worthy to note that in the epoxy system, the cure reactions based on DGEBA are typically characterized by an initial accelerated reaction due to autocatalysis in the early stages while in the later stages a decrease in the reaction rate is shown to be owing to the onset of gelation and cross-linking. Thus, the mobility of the reactive groups is hindered and the rate of conversion is controlled by diffusion. This is also verified by fitting the experimental reaction

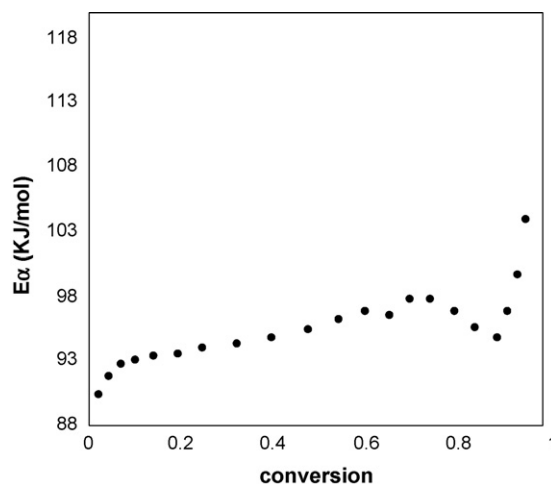


Fig. 7. Dependence of the apparent activation energy on the extent of conversion.

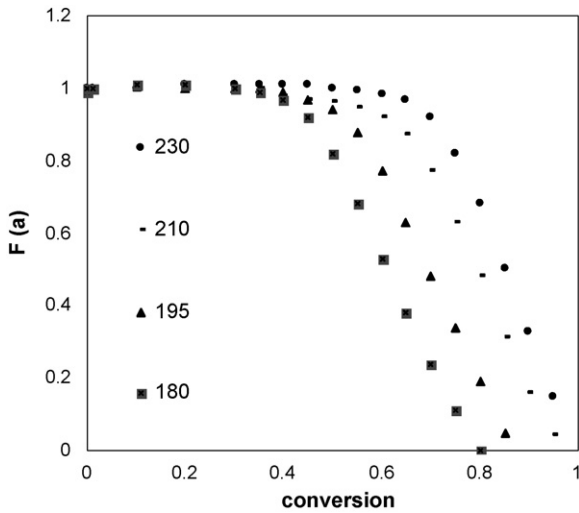


Fig. 8. $F_d(\alpha)$ versus α plots at various cure temperatures.

rate data to those values predicted by the four parameters of the Kamal model (see Table 2). In all cases, fitting was not satisfactory for the conversion level higher than 0.6 due to vitrification which makes the reaction mechanism controlled by diffusion. Taking into account the above points, to consider the effect of vitrification on the studied cure reaction, we have used a semi-empirical relationship proposed by other researchers [24,25]. When degree of cure reaches a critical value, α_c , diffusion becomes controlling and the rate constant k_d is given as

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \quad (8)$$

where k_c is the rate constant for chemical kinetics and C is a parameter the overall effective rate constant k_e can be defined in terms of the diffusion rate constant (k_d) and the reaction rate constant (k_c) in the following form:

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \quad (9)$$

By combining Eqs. (8) and (9) a diffusion factor is defined, $F_d(\alpha)$, with two empirical parameters as follows:

$$F_d(\alpha) = \frac{k_e}{k_d} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (10)$$

where C is a factor dependent on temperature and α_c is the critical conversion. When α is much smaller than its critical value, $\exp[C(\alpha - \alpha_c)] \approx 0$ and $F_d(\alpha)$ is approximately equal to 1. At this condition the effect of diffusion is negligible. As α reaches its critical value, $F_d(\alpha)$ begins to decrease reaching a value of 0.5 at $\alpha = \alpha_c$ and beyond this point approaches zero since the reaction becomes very slow and eventually stops. This exhibits that with increasing temperature the diffusion effect develops progressively. The effective conversion rate thus defined as the chemical conversion rate, equation (3), multiplied by $F_d(\alpha)$:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n F_d(\alpha) \quad (11)$$

Data for $F_d(\alpha)$ is determined as the ratio of experimental conversion rate to the conversion rate predicted by the Kamal model as follows:

$$F_d(\alpha) = \frac{(\frac{d\alpha}{dt})_{\text{experimental}}}{(\frac{d\alpha}{dt})_{\text{Kamal model}}} \quad (12)$$

Fig. 8 exhibits the values for $F_d(\alpha)$, which are obtained using Eq. (12), plotted against conversion at various temperatures. It is seen that the values of $F_d(\alpha)$ are approximately in unity in the early stages of the cure reaction which is indicative of an autocatalytic reaction.

Table 3
Values C and α_c at various isothermal cure temperatures.

Temperature ($^{\circ}\text{C}$)	C	α_c
180	8.01	0.72
195	8.37	0.75
210	10.47	0.80
230	10.67	0.83

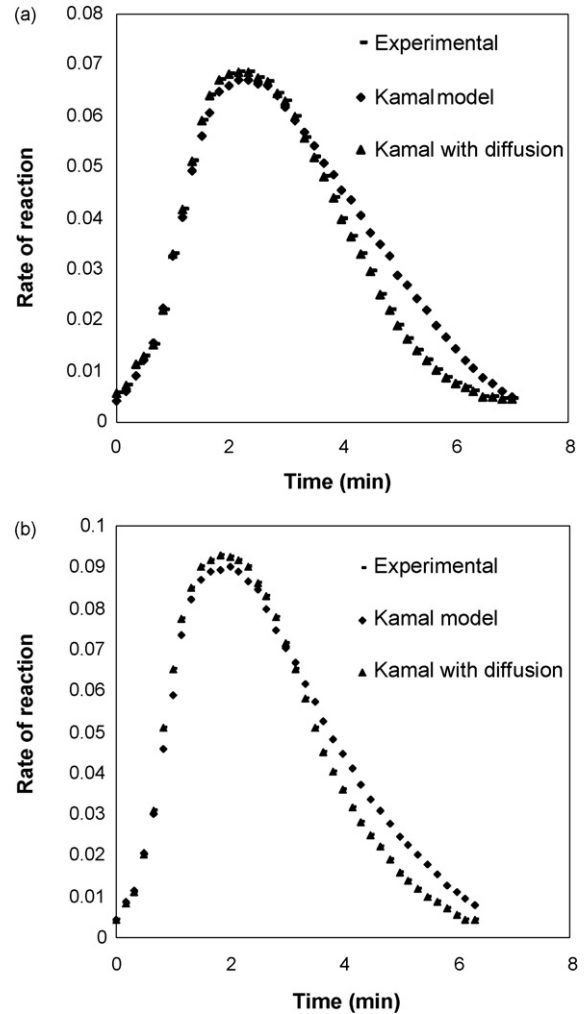


Fig. 9. Reaction rate against time for various cure temperature: (a) 195 $^{\circ}\text{C}$ and (b) 230 $^{\circ}\text{C}$.

As the cure progresses, the drop-off in the reaction rate, owing to the start of the diffusion control regime can obviously be observed.

The values of the parameters C and α_c are obtained by fitting the data shown in Fig. 8 using Eq. (10) and the results are summarized in Table 3. Obviously, the values of critical conversion increase with the curing temperature. However, the inclusion of the diffusion factor into the Kamal model leads to a good agreement of the model with experimental data at each examined temperature as shown in Fig. 9.

4. Conclusions

The effect of different amounts of barium carbonate on thermal curing of epoxy/1,8-naphthalene diamine system is investigated using DSC analysis. Because of reproducible and larger value of the reaction heat, it is recognized that the optimum behavior of the three-component system corresponds to a filler loading level 2 Phr.

The kinetic parameters (degree of conversion, reaction rate) of the curing reaction are obtained in the isothermal mode. It has been found that the curing reaction of the examined composite system proceeds through an autocatalytic kinetic mechanism. Therefore, the Kamal model is used to estimate the kinetic parameters. The kinetic constants k_1 and k_2 increase with increasing curing temperature and the overall reaction orders lies between 1 and 1.5. The model is also utilized to fit the experimental $d\alpha/dt$ versus time plot and then to check the validity of the used kinetic analysis approach. The results showed that the model gave a good description of the curing reaction before diffusion being the main process. However, at a specific conversion region, the cure reaction of the system is controlled by a diffusion control reaction rather than an autocatalytic reaction. When diffusion control took place, the curing kinetics is described by Chern and Poehlein's equation. By employing a general mathematical equation referred to iso-conversional kinetic analysis, the dependency of activation energy on conversion is illustrated. The form of this dependency verifies that in the conversion range of 0.3–0.7, the curing reaction is diffusion controlled; the result is clearly confirmed using the Kamal kinetic analysis.

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