

Studying on the curing kinetics of a DGEBA/EMI-2,4/nano-sized carborundum system with two curing kinetic methods

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Abstract

Curing kinetics of a bisphenol-A glycidol ether epoxy resin (DGEBA)/2-ethyl-4-methylimidazole (EMI-2,4)/nano-sized SiC(nano-SiC) system was investigated with two kinetic methods by means of differential scanning calorimetry (DSC). Methods I and II were deduced by assuming a constant E and a variable E , respectively. With method I, the cure reaction activation energy E , the frequency factor A and the overall order of reaction $m+n$ are calculated to be $71.75 \text{ kJ mol}^{-1}$, $e^{20.55}$ and 2.20, respectively. These results were used to have a simple qualitative comparison with the DGEBA/EMI-2,4 system. With method II, E is proved to decrease initially, and then increase as the cure reaction proceeds. The value of E spans from 42.4 to 95.8 kJ mol^{-1} . Furthermore, the variations of E were also used to study the cure reaction mechanism, and the shrinking core model was used to study the resin-particle reaction. Methods I and II are effective as long as they are used in proper aspects. With these two methods used all together, we can have a comprehensive and in-depth understanding of the curing kinetics of the DGEBA/EMI-2,4/nano-SiC system and the effect of nano-SiC particles on the curing kinetics of the DGEBA/EMI-2,4 system. © 2005 Published by Elsevier Ltd.

Keywords: DGEBA/EMI-2,4/nano-SiC system; Curing kinetics; Shrinking core model

1. Introduction

Nanocomposites have become promising materials. As the filler size decreases into nano length scale, the rheological, mechanical, and thermal mechanical properties of the composite change significantly. Therefore, studies on the properties of the nanocomposites have been developed rapidly, but there is a lack of study on the curing kinetics of the nanocomposites.

Because of the low coefficient of thermal expansion (CTE) and the high thermal conductivity of SiC, the SiC filled composite materials have attracted much attention in an attempt to reduce the CTE and the thermal resistivity of polymer composites. The particles may also affect the cure reactions in the epoxy system [1]. In the view of choosing the proper set of processing parameters for this thermoset-

inorganic particle system, the knowledge of curing kinetics is essential information.

The kinetics of curing epoxy resins has been widely studied by using isothermal or dynamic DSC technique and experimental data were analyzed by the homogeneous reaction method [2–5], in which E was considered as a constant and the whole cure reaction was considered as a single kinetic process (method I). Therefore, the calculated E is the apparent activation energy of the global reaction. However, the reaction of curing epoxy resins is normally very complex, such as the change from chemical kinetic control to diffusion control in the advance of the curing [6,7], and E changed momentarily.

In this work, another method deduced without the assumption of constant E (method II) was also employed to analyze the dynamic DSC data, then the interpretation of the dependence of E on the extent of reaction in the terms of the reaction mechanisms was also made. As a result, with these two different kinetic methods, which have their particular merits and demerits, used together, we can have a comprehensive and in-depth understanding of the curing kinetics of the DGEBA/EMI-2,4/nano-SiC system.

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2. Experimental

Epoxy resin used in this work was a nominally difunctional epoxy resin, Epon 828 supplied by Shanghai Resin Co. Epon 828 is, basically, DGEBA with the epoxy value of 0.48–0.52 mol/100 g. The curing agent used was EMI-2,4 supplied by Beijing Chemical Reagent Co. The nano-SiC particles with an average particle size of 50 nm were obtained from Karl Co. and treated with the silane coupling agent, γ -aminopropyl-triethoxysilane (A1100), from Shanghai Chemical Reagent Co. Other agents used were analytically pure grade and were supplied by Beijing Chemical Reagent Co.

Surface treatment of nano-SiC particles using silane involved (i) making a silane-absolute ethyl alcohol solution at a selected concentration, and the amount of silane coupling agent used was 10% by weight of the nano-SiC particles, (ii) adding nano-SiC particles to the solution and stirring with a magnetic stirrer for 30 min, (iii) heating at 333–353 K for 30 min, (iv) rinsing with alcohol by filtration, and (v) drying at 383 K for 12 h.

The reactants DGEBA, EMI-2,4 and surface treated nano-SiC particles were mixed in a 100:6:10 weight ratio, then the mixture was dispersed by sonication for 30 min to break down the agglomerations of the nano-SiC particles. Approximately 10 mg sample of the mixture was weighed accurately into an aluminum DSC sample pan and then covered with an aluminum lid. The entire operation was carried out in a dry chamber. DSC measurements were carried out by using a Perkin-Elmer DSC-7 system. The DSC was calibrated with high purity indium; α -Al₂O₃ was used as the reference material. Dynamic experiments were carried out under a nitrogen flow rate of 10 ml min⁻¹ and were performed at temperatures ranging from 323 to 553 K at different heating rates of 5, 10, 15, 20 °C min⁻¹. The reaction was considered to be complete when the rate curve leveled off to a baseline.

3. Theoretical analysis

The representative DSC curve displaying heat flow dH/dt against temperature T is shown in Fig. 1. The information that can be got directly from the curve is the onset temperature T_i , the peak temperature T_p , the terminal temperature T_f and the values of dH/dt of the points on the curve. The line between T_i and T_f is the baseline. Then the total area S of the exothermal peak (the region between the exotherm and the baseline), which is in direct proportion to the total quantity of heat ΔH released during the whole cure reaction, can be gained:

$$S = \frac{m\Delta H}{\xi}$$

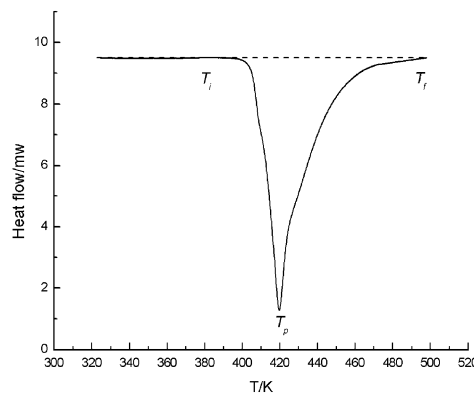


Fig. 1. Representative DSC curve of the thermosetting resin.

where m is the mass of reactive sample, ξ is the calibration coefficient which is independent of temperature [7].

The fractional extent of conversion α at a given temperature T can be expressed as:

$$\alpha = \frac{S_T}{S} = \frac{\Delta H_T}{\Delta H}$$

As is known, there were several coupling agent molecular layers on the surface of the nano-SiC particles after the surface treatment. One end of the coupling agent formed a hydrogen bond with the nano-SiC particles, and the other end of the coupling agent would enter in the epoxy macromolecule by means of chemical bond to form an interface layer between the nano-SiC particle and epoxy matrix during the subsequent cure reaction. In this work, the quantity of the nano-SiC particles in the system is small, thus the heat released during the chemical reaction between the coupling agent and the epoxy resins can be safely negligible.

The curing mechanism of DGEBA/EMI-2,4 system involves two stages consisting of the adduct and etherification reactions [8–10]. The adducts were believed to be the catalyst that initiated the etherification reactions which cross-link the epoxy resins and determine the final properties of the network. Previous work showed that the adduct formation was necessary prior to the etherification reaction. Thus, low EMI-2,4 concentrations can be used to analyze the etherification reactions by suppressing the adduct formation [9]. The objective criterion of meeting this specification is that the molar heat of the reaction ΔH approaches a constant. It is shown that the variation amplitude of the heat of reaction is small when the concentration of EMI-2,4 is between 3–10 wt% (gram mass of EMI-2,4 per 100 g mass of DGEBA), and the cure reaction is incomplete as the content of EMI-2,4 below 3 wt% [11]. In this work, the concentration of EMI-2,4 is 6 wt% which falls within the range of 3–10 wt%, moreover, only a main peak exotherm of the etherification reaction appears, as shown in Fig. 2, thus the heat of reaction for the etherification reaction peak is approximately the total heat

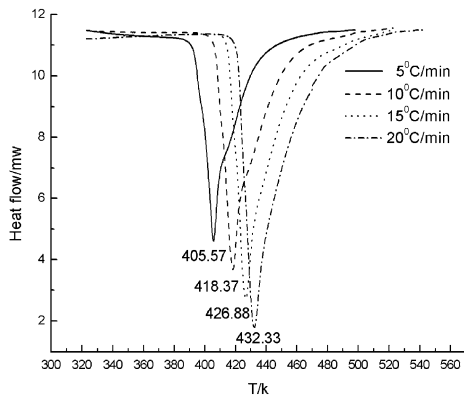


Fig. 2. DSC curing curves with different heating rates of the DGEBA/EMI-2,4/nano-SiC system.

of the curing reaction. In other words, ΔH can be considered as a constant over the whole cure reaction.

Accordingly, the rate of conversion $d\alpha/dt$ at a given temperature T can be expressed as:

$$\frac{d\alpha}{dt} = \frac{(dH/dt)}{\Delta H}$$

All kinetic studies can start with the basic equation that relates the rate of conversion to some function of the concentration of reactants. For the thermosetting resins, $d\alpha/dt$ is usually expressed as:

$$\frac{d\alpha}{dt} = A e^{-E/RT} f(\alpha) \quad (1)$$

where A is the frequency factor, E is the activation energy, $f(\alpha)$ is a function of the fractional extent of conversion α and is associated with a certain reaction mechanism, R is the gas constant and T is the absolute temperature at time t .

It has been demonstrated that the DGEBA/EMI-2,4 system follows autocatalytic kinetics [8–10]. In this work, as shown in Fig. 3, each curve analyzed is typically parabolic, which is indicative of an autocatalytic kinetics of the studied DGEBA/EMI-2,4/nano-SiC system [12].

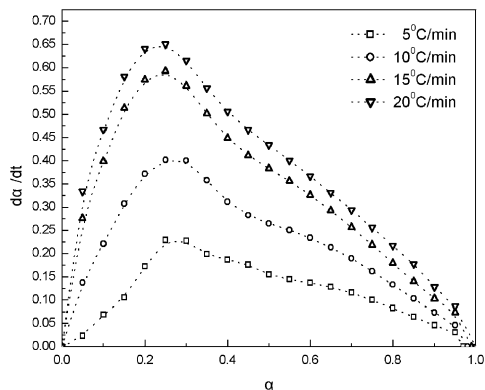


Fig. 3. Plots of da/dt vs. α for the cure reactions at different heating rates. Dotted lines are given only for showing the tendency. The heat released during the cure reaction at $20^\circ\text{C min}^{-1}$ heating rate is used as the total heat ΔH_{tot} .

Therefore, the addition of nano-SiC particles does not change the cure reaction mechanism.

For the thermosetting resins that follow autocatalytic kinetics, the expression of $f(\alpha)$, which excludes diffusion-controlled, fusion, and inversion-type reactions, is:

$$f(\alpha) = (1 - \alpha)^n \alpha^m \quad (2)$$

where $m+n$ is the overall order of reaction [13,14].

4. Results and discussion

4.1. Analysis of dynamic DSC data with method I (method with the assumption that E is constant)

As mentioned above, an assumption is usually made when dynamic DSC is used in studying the kinetics of the epoxy cure reaction, viz., $\alpha = \Delta H_T / \Delta H$. This implies that the fractional extent of conversion α at the peak exotherm is a constant, although the temperature at which the peak exotherm occurs depends on the heating rate [5,15]. As shown in Fig. 3, in this work, the fractional extent of conversion α at the peak exotherm is nearly a constant (~ 0.25); therefore, the relation between the heating rate and the peak exotherm temperature is of the form, Ozawa equation [15]:

$$\frac{d(-\ln \beta)}{d(1/T_p)} = \frac{1.052E}{R}$$

where β is the heating rate in $^\circ\text{C min}^{-1}$.

Fig. 4 shows the plot of $-\ln \beta$ vs. $1000/T_p$. A linear regression analysis suggests that, to a good agreement, the calculated value of E is $71.75 \text{ kJ mol}^{-1}$.

For the thermosetting resins that follow autocatalytic kinetics, we have:

$$\ln(d\alpha/dt) = \ln A - (E/RT) + n \ln(1 - \alpha) + m \ln \alpha \quad (3)$$

then

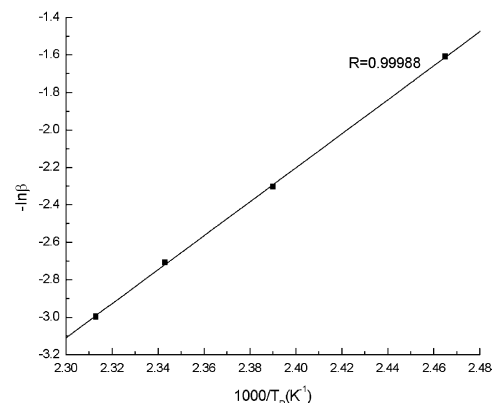


Fig. 4. Plot of $-\ln \beta$ vs. $1000/T_p$.

$$\begin{aligned} \ln[d(1 - \alpha)/dt] \\ = \ln A - (E/RT') + n \ln \alpha + m \ln(1 - \alpha) \end{aligned} \quad (4)$$

Eq. (3)–Eq. (4):

$$\begin{aligned} \text{Value I} &= [(E/RT) + \ln(d\alpha/dt)] - [E/RT'] \\ &\quad + \ln(d\alpha_1/dt)] \\ &= (n - m)\ln[(1 - \alpha)/\alpha] \end{aligned} \quad (5)$$

Eq. (3)+Eq. (4):

$$\begin{aligned} \text{Value II} &= [(E/RT) + \ln(d\alpha/dt)] + [(E/RT') \\ &\quad + \ln(d\alpha_1/dt)] \\ &= 2 \ln A + (m + n)\ln(\alpha - \alpha^2) \end{aligned} \quad (6)$$

DSC curing curve with the heating rate of 10 °C min⁻¹ was studied. The value of *n*–*m* obtained from the slope of the plot of Value I vs. ln[(1–α)/α], as shown in Fig. 5, is 1.447; the values of *m*+*n* and 2 ln *A* obtained from the slope and intercept of the plot of Value II vs. ln[α(1–α)], as shown in Fig. 6, are 2.202 and 41.098, respectively.

Then we have:

$$n \approx 1.82; \quad m \approx 0.38; \quad A = e^{20.55}$$

Thus, the curing kinetic equation of the DGEBA/EMI-2,4/nano-SiC system with method I can be expressed as:

$$\frac{d\alpha}{dt} = e^{20.55} e^{(-71.75/RT)} (1 - \alpha)^{1.82} \alpha^{0.38}, \quad \alpha \in [0, 1]$$

4.2. Analysis of dynamic DSC data with method II (method without the assumption of constant *E*)

From Eq. (1):

$$\ln(d\alpha/dt) = \ln A - (E/RT) + \ln f(\alpha) \quad (7)$$

let *Af*(α)=*F*(α):

$$\ln(d\alpha/dt) = (-E/RT) + \ln F(\alpha) \quad (8)$$

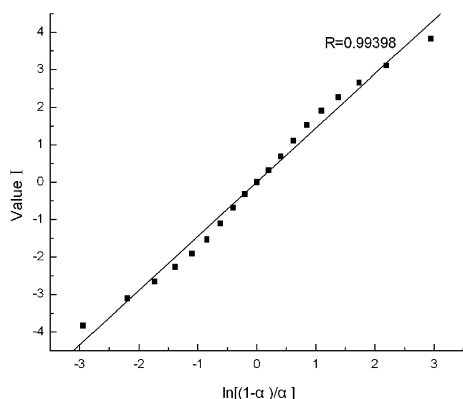


Fig. 5. Plot of Value I vs. ln[(1–α)/α].

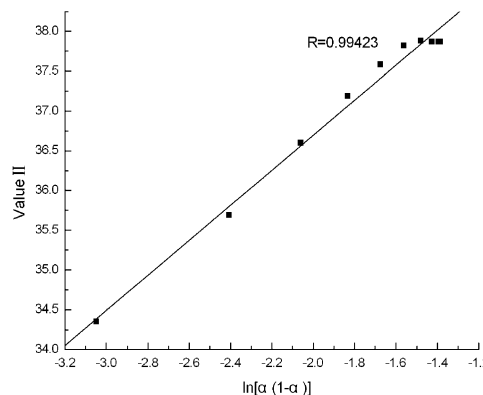


Fig. 6. Plot of Value II vs. ln[α(1–α)].

From Eq. (8), a plot of ln(dα/dt) vs. 1/*T* values at the same fractional extent of conversion α from a series of dynamic DSC experiments at different heating rates would result in a straight line with a slope of –*E*/*R* and an intercept of ln *F*(α). Repeating this procedure, the *E* and *F*(α) values corresponding to different α from the DSC curing curves of different heating rates can be obtained. That is to say, the relationship of *E* vs. α and *F*(α) vs. α can be decided. Simulating these relationships, the kinetic equations of the cure reaction can be obtained [16,17].

Fig. 7 is the plots of ln(dα/dt) vs. 1/*T* for various values of α (α=0.05, 0.10, 0.20, ..., 0.90, 0.95) covering the experimental range. Making fitted linear regression lines, then groups of *E* and *F*(α) values were obtained for each value of α. Figs. 8 and 9 show plots of *E* and ln[*Af*(α)] vs. α, respectively. The different value of *E* corresponding to different α confirms the conversion-dependence of *E*, viz. *E* is a variable. Trying different multiple regression equations to fit the data in Fig. 8, we found cubic polynomial can have enough goodness of fit, i.e. if high-order moments were utilized to fit the data in Fig. 8, the coefficient of the items whose number of order are greater than or equal to 4 in the equations will be smaller than 10⁻⁵, so cubic polynomial is good enough. Data in Fig. 9 were also fitted and cubic polynomial also can achieve the required precision. As shown in Figs. 8 and 9, the fitted curves can represent

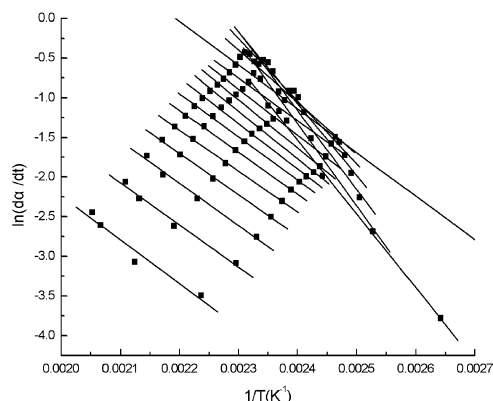
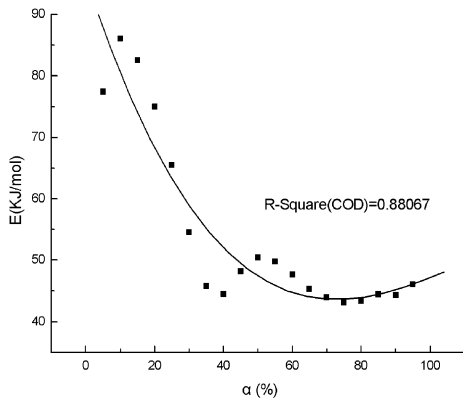


Fig. 7. Plots of ln(dα/dt) vs. 1/*T*.

Fig. 8. Plot of E vs. α .

dynamic DSC results in a major conversion range with goodness of fit.

The fitted multiple regression equations can be expressed as:

$$E(\alpha) = 95.842 - 1.703\alpha + 0.017\alpha^2 - 5.049E - 5\alpha^3 \quad (9)$$

$$\ln[Af(\alpha)] = 26.177 - 0.247\alpha + 5.66E - 3\alpha^2 - 4.153E - 5\alpha^3 \quad (10)$$

As discussed above, the studied system follows an autocatalytic kinetics, substitute Eq. (2) into Eq. (10),

$$\ln A + n \ln(1 - \alpha) + m \ln \alpha = 26.177 - 24.7\alpha + 56.6\alpha^2 - 41.53\alpha^3, \quad \alpha \in (0, 1)$$

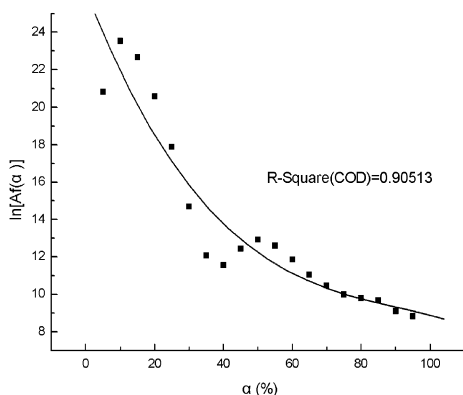
Let $\alpha = 0.2, 0.5$ and 0.8 , a equation set with three-element can be obtained:

$$\ln A + n \ln 0.8 + m \ln 0.2 = 23.169$$

$$\ln A + n \ln 0.5 + m \ln 0.5 = 22.786$$

$$\ln A + n \ln 0.2 + m \ln 0.8 = 21.378$$

Solving this equation set and the kinetic parameters are gained: $m \approx 0.51$, $n \approx 1.78$, $\ln A \approx 24.36$.

Fig. 9. Plot of $\ln[Af(\alpha)]$ vs. α .

The kinetic equation of cure reaction of the DGEBA/EMI-2,4/nano-SiC system with method II can be expressed as:

$$\frac{d\alpha}{dt} = e^{24.36}(1 - \alpha)^{1.78} \alpha^{0.51} e^{-E(\alpha)/RT}$$

with

$$E(\alpha) = 95.842 - 170.3\alpha + 170\alpha^2 - 50.49\alpha^3, \quad \alpha \in (0, 1)$$

Making the differential equation of $E(\alpha)$, viz. $dE/d\alpha$,

$$dE/d\alpha = -170.3 + 340\alpha - 151.47\alpha^2, \quad \alpha \in (0, 1)$$

$$= 151.47[(\alpha - 1.122)^2 - 0.368^2]$$

As shown in Fig. 8, the value of E spans from 42.4 to 95.8 kJ mol^{-1} . During the cure reaction, E initially decreases at low conversions ($\alpha < \sim 0.75$), and then increases as the cure progresses.

4.3. Analysis of the variation of E and the cure reaction mechanism with method II results

Method II is deduced without the assumption of constant E and started with the basic equation, therefore, the kinetic equations of the cure reaction calculated with method II should be more suitable to real situation than method I does. With method II results, the variations in E on the extent of reaction can be used to study the cure reaction mechanism [18].

As far as the curing kinetics of DGEBA initiated with EMI-2,4 is concerned, the process of cure has been demonstrated to be autocatalytic [8–10]. The first step in the curing process of DGEBA/EMI-2,4 system is the formation of both 1:1 and 2:1 adducts. The 2:1 adduct, which contains the nucleophilic alkoxide ion, was believed to be the catalyst that initiated the etherification reaction. The activated 2:1 adduct is not consumed since the alkoxide ion is continually regenerated during the etherification reaction. As discussed above, in this work, the heat released of the curing reaction is principally due to the etherification reaction. Therefore, it is reasonable to expect a decrease in E of the epoxy-imidazole cure, as shown in Fig. 8, as compared to the very beginning of the process where the nonautocatalyzed reaction occurs [19].

As the cure reaction proceeds, the system undergoes gelation (liquid-to-rubber) and vitrification (rubber-to-glass) transitions. Intensive cross-linking occurs and reduces molecular mobility, then the cure changes from a kinetic to a diffusion regime [19]. The increase in E at higher conversions for the system can be understood in terms of cooperative motion of the chain segments [20]. At the early stages of the transition, the packing is loose, which allows the chain segments to move independently (i.e. with a lower degree of cooperativity). As the cure reaction proceeds, the free volume decreases. At the glassy state, the

small amount of free volume only allows for local motions of the chain segments. To initiate translational motion of the segments, it requires a great degree of cooperativity between the chain segments, which is associated with a large energy barrier to the segmental motion as reflected in the great value of E at later cure stages, i.e. at higher values of α . As a result, the energetic constraints are intensified which is reflected in an increase of E .

Furthermore, the effect of nano-SiC particles on the cure reaction of the DGEBA/EMI-2,4 system can be studied with the shrinking core model (SCM) [21–23], which is the best simple representation for the majority of reacting fluid–particle systems despite its limitation.

As is known, during the cure reaction, one end of the silane coupling agent, which has formed a hydrogen bond with the nano-SiC particles after the surface treatment, would enter in the epoxy macromolecule by means of chemical bond to form an interface layer between the nano-SiC particle and epoxy matrix. The reaction occurs first at the outer skin of the particle, and then the zone of reaction would move into the particle and leave behind the reacted layer. There are three steps occurring in succession during reaction: (i) diffusion of epoxy macromolecule through the liquid film surrounding the particle to the surface of the particle, (ii) penetration and diffusion of epoxy macromolecule through the reacted layer to the surface of the unreacted core, (iii) reaction of epoxy macromolecule with the unreacted coupling agent layer at this interface of the reacted layer and unreacted core. The resistance of the different steps usually varies greatly one from the other; in such cases we may consider that step with the highest resistance to be rate-controlling. According to the shrinking core model, the progressive reaction of the resin–particle system is chemical reaction, reacted layer diffusion, and film diffusion in turn control. These resistances act in series, and the total resistance increases as the reaction proceeds, which also contribute to the increase of E .

4.4. Comparison of the two methods and the calculated curing kinetic parameters obtained with them

The resulting curing kinetic parameters of the DGEBA/EMI-2,4/nano-SiC system, obtained by methods I and II, were tabulated in Table 1.

As mentioned above, method II is deduced without the assumption of constant E and started with the basic equation, therefore, the results with method II should give a better fit to the real situation than those calculated with method I. That is to say, it can be used to test whether E is constant or not and the variation of E can be used to study the mechanism of cure reaction. Moreover, the thing must be especially noticed is that method I only uses the values at the peak temperatures of the curing curves, whereas, method II uses most of the information in the curing curves, so the results with method II are more creditable than method I. In addition, an important advantage of method II for determining E over other methods is that it is a model-free method which allows E to be independently determined without assuming any reaction model. It is known that an incorrect model will give a grossly incorrect value for E . However, the demerit of method II is that the calculation process is much complex.

The activation energy calculated with method I is $71.75 \text{ kJ mol}^{-1}$, which is the apparent activation energy of the global reaction of the DGEBA/EMI-2,4/nano-SiC system. This value falls within the range of $42.4\text{--}95.8 \text{ kJ mol}^{-1}$ obtained with method II. Although method I can not be used in studying cure reactions in detail, it is really a simple and effective method in qualitative comparison among different curing systems. The activation energy calculated with method I of the DGEBA/EMI-2,4 system is $49.03 \text{ kJ mol}^{-1}$, which is lower than that of the DGEBA/EMI-2,4/nano-SiC system. This result indicates that the nano-SiC particles inhibit the curing process.

As shown in Table 1, the value of $\ln A$ and $m+n$ obtained by these two methods are similar and $m+n > 1$ demonstrates that the cure reaction of the studied system is complex which is also proved by the variation of E during the whole curing process. Meanwhile, these kinetics parameters of the DGEBA/EMI-2,4 system calculated with method I are 14.5 and 1.22, respectively, which indicates that the presence of nano-SiC particles can enhance the frequency factor and the overall order of the reaction.

To demonstrate the applicability of these two kinetic methods, the kinetic methods results were compared with the experimental data of 5 and $20 \text{ }^\circ\text{C min}^{-1}$ heating rate, as shown in Figs. 10 and 11. It can be seen that the results with

Table 1
Curing kinetic parameters of the DGEBA/EMI-2,4/nano-SiC system resulting from methods I and II

Curing kinetic equation	$d\alpha/dt = e^{\ln[Af(\alpha)]} e^{-E(\alpha)/RT}$	
	Method I	Method II
E	$71.75 \text{ kJ mol}^{-1}$	$95.842 - 170.3\alpha + 170\alpha^2 - 50.49\alpha^3, \alpha \in (0,1)$
$dE/d\alpha$	0	$-170.3 + 340\alpha - 151.47\alpha^2, \alpha \in (0,1)$
Variation of $dE/d\alpha$	–	$0 < \alpha < 0.75, dE/d\alpha < 0; \alpha = 0.75, dE/d\alpha = 0; 0.75 < \alpha < 1, dE/d\alpha > 0$
$\ln A$	20.55	24.36
$m+n$	2.20	2.29
n	1.82	1.78
m	0.38	0.51

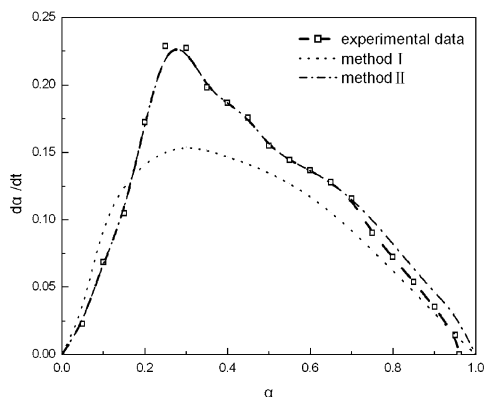


Fig. 10. Comparison of experimental data with the kinetic method results ($5\text{ }^{\circ}\text{C min}^{-1}$ heating rate).

method II are in better agreement with the experimental data than method I. Furthermore, as far as the kinetic method results with method II is concerned, differences between model predictions and experimental data are observed to be smaller when the heating rate increases. The kinetic method results diverge obviously from the experimental results of $5\text{ }^{\circ}\text{C min}^{-1}$ heating rate at higher conversions. Meanwhile, the kinetic method results are in good agreement with the experimental data of $20\text{ }^{\circ}\text{C min}^{-1}$ heating rate in the whole tested conversions range.

The neglect of diffusion factor as the kinetic method is deduced may be responsible for the deviation of the experimental data at higher conversions from the kinetic method results. At early stages of cure, before gelation and vitrification, the reaction takes place in the liquid phase and is controlled by chemical kinetics. So, the kinetic behavior described by this model coincides with the experimental data. As the reaction progresses, a deviation appears due to the onset of gelation and vitrification where the mobility of reactive groups is hindered, the rate of conversion is controlled by diffusion rather than by kinetic factors and the values predicted by the model are higher than the experimental data [24]. When the cure reaction kinetics becomes diffusion controlled, the reaction is hard to proceed

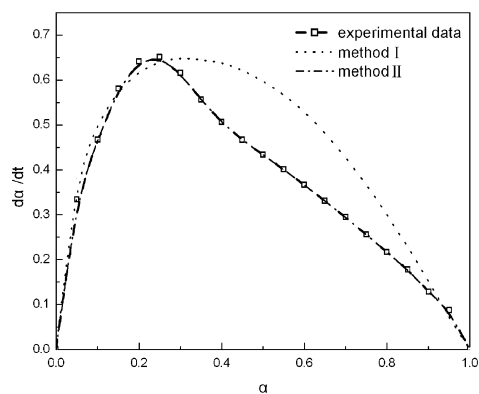


Fig. 11. Comparison of experimental data with the kinetic method results ($20\text{ }^{\circ}\text{C min}^{-1}$ heating rate).

which leads to incomplete ultimate conversion, viz., $\alpha_{\text{ult}} < 1$.

The better degree of agreement of kinetic method results with the experimental data at higher heating rate indicates the temperature-dependence of the diffusion and the reaction rate. For the dynamic DSC, the higher the heating rate, the higher the temperature range the cure reaction occurs. Since the mobility of the reacting groups is less hindered in high temperature, vitrification would occur until high conversions, which leading to a high α_{ult} .

5. Conclusion

The cure reaction of the DGEBA/EMI-2,4/nano-SiC system obeys an autocatalytic mechanism and the addition of nano-SiC particles does not change the reaction mechanism.

The curing kinetic parameters of the DGEBA/EMI-2,4/nano-SiC system were obtained by methods I and II, which were deduced by assuming a constant E and a variable E , respectively. With method I, the cure reaction activation energy E is calculated to be 71.75 kJ mol^{-1} . With method II, E is proved to decrease initially, and then increase as the cure reaction proceeds. The value of E spans from 42.4 to 95.8 kJ mol^{-1} , and approaches 71.75 kJ mol^{-1} as the conversion comes up to 0.17 . The value of $\ln A$ and $m+n$ obtained by method I is 20.55 and 2.20 , respectively. Meanwhile, the corresponding values obtained by method II are 24.36 and 2.29 . $m+n > 1$ demonstrates that the cure reaction of the studied system is complex which is also proved by the variation of E .

With method II, the variation of E can be obtained in detail, which can be used to have a in-depth study on the cure reaction mechanism, however, the calculation process is much complex. In this work, the shrinking core model was also used to discuss the resin-particle reaction. On the other hand, although method I can not to be used in studying E in detail, it is really a simple and effective method in qualitative comparison among different curing systems. With method I, we can have a simple qualitative comparison between the curing kinetics of the DGEBA/EMI-2,4/nano-SiC system and the DGEBA/EMI-2,4 system. It shows that the E , A and $m+n$ values of the DGEBA/EMI-2,4/nano-SiC system are higher than those parameters of the DGEBA/EMI-2,4 system. This phenomenon is believed to be the effect of nano-SiC particles on the curing kinetics of the DGEBA/EMI-2,4 system.

It is also shown that the results by using method II are in better agreement with the experimental data than method I. Moreover, as far as the kinetic method results by using method II is concerned, differences between model predictions and experimental data are observed to be smaller when the heating rate increases.

It can be seen from above analyses that these two methods have their particular merits and demerits,

consequently, both of them are effective as long as they are used in proper aspects. In practice, we can have a comprehensive and in-depth understanding of the cure reactions, such as the cure reactions of the DGEBA/EMI-2,4/nano-SiC system, the effect of nano-SiC particles on the curing kinetics of the DGEBA/EMI-2,4 system, with these two methods used all together.

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