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Comparative study on the curing kinetics and mechanism of a lignin-based-epoxy/anhydride resin system

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Abstract

Curing kinetics and mechanism of liquid lignin based epoxy resin (LEPL)—maleic anhydride (MA) system accelerated with benzyldimethylamine (BDMA) were studied by Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). In order to investigate the difference in the curing process, heating FTIR was used to study the change of the functional group. Complete consumption of the epoxides has been observed after the heating temperature was higher than 110 °C. E constant method and E variable method, to study the dynamic DSC curves, were deduced by assuming a constant and a variable activation energy, respectively. With E constant method, the cure reaction activation energy E, the frequency factor A and overall order of reaction $n+m$ are calculated to be 59.68 kJ mol^{-1}, e$^{20.6}$ and 1.462, respectively. With E variable method, E is proved to decrease initially, and then increases as the cure reaction proceeds. The value of E spans from 60.16 to 87.80 kJ mol^{-1}. With the E constant method, E variable method and heating FTIR spectra used together, we can have a comprehensive and profound understanding of the cure reactions of the LEPL—MA system.

Keywords: Curing kinetics; DSC; FTIR

1. Introduction

Lignin is a kind of abundant biomass resource. Its utilization has drawn attention for more than a century, however, only small portion of lignin and its derivatives has found application [1]. In recent decades, lignin based polymer has been more and more considered as potential way to use lignin reasonably in large scale [2–5]. Some researchers have also noticed lignin based epoxy. Zhao et al. [6] synthesized liquid lignin based epoxy resin (LEPL) by modifying lignin derivative to improve its reaction ability, followed by epoxidization. The mechanical properties of cured epoxy not only depend on its chemical component, preparation procedure, but also on its curing conditions. Hence knowledge of the rate and kinetics of cure of the LEPL is very important.

Kinetic investigations are one of the most important applications of thermal analysis. The DSC technique finds more applicability since the epoxy is exothermic process. The kinetics of epoxy cured system has been widely studied by using isothermal or dynamic DSC technologies [7–9]. Their study based on the assumption of a constant activation energy and the whole reaction of cure was considered as a single kinetic process (E constant method). The E constant method does not reflect the change of activation energy. The calculated activation energy by E constant method 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, and E changed momently. A simple and more reliable alternative is to use E variable method, which deduced without the assumption of constant activation energy [10,12]. The E variable method allows the activation energy to be determined as a function of the extent of conversion, and this dependence is determined without making any

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assumptions about the reaction model. The accuracy of determination of activation energy calculated by *E* variable method is determined by the amounts of dots in DSC curves, the more the dots, the higher the accuracy.

In this study the *E* constant method and *E* variable method were used to study the LEPL–MA (maleic anhydride) curing system. As a result with these two different kinetic methods we can have a comprehensive and profound understanding of the curing kinetics of the LEPL–MA system.

2. Experimental

Calcium lignosulfonate was provided by Guangzhou Pulp and Paper Industry, Guangzhou, P.R. China. Maleic anhydride (MA), benzyldimethylamine and other reagents were of analytically pure grade and purchased from Shanghai Chemical Co. The LEPL was synthesized by Zhao's method [6]. When calcium lignosulfonate was pretreated by sulfuric acid solution it turned into lignosulfonic acid solution. Excess phenol was then added into the stirred lignosulfonic acid solution, followed by the addition of sulfuric acid solution at 80 °C. The weight of both phenol and sulfuric acid solution was 40% of calcium lignosulfonate by weight, the concentration of phenol and sulfuric acid solution was 99.5% and 50%, respectively. After the system had reacted at 95 °C for 3 h, two phases were formed: an upper dark organic layer and a lower light acid solution layer. The dark organic layer was neutralized first and then distillated to remove phenol and to get a kind of black gel. The black gel can be divided into water-soluble part and water-insoluble part. The water-soluble part was applied as monomer to synthesize lignin based epoxy resin. The water-soluble part was mixed with epichlorohydrin and 20 wt% sodium hydroxide water solution was added as catalyst. The deep brown-red liquid lignin based epoxy resin (LEPL) was acquired. The important properties of LEPL are epoxy value of 0.47 mol/100 g and Mn = 365. Schematic of the LEPL, MA and benzyldimethylamine is shown in Fig. 1.

The FTIR measurements were carried out with a EQUNOX 55 (BRUKER Co. Germany). The sample was sandwiched between two pieces of double-polished silicon and then placed in-between a pair of KBr plates to avoid the possibility of KBr catalyzing epoxy cure reaction [13]. The background spectrum was collected with KBr and the polished silicon. The heating rate was 10 °C/min. A spectrum of the sample was taken every 5 °C to observe the change in chemical structure of the curing. The wavelength of spectrum was from 4000 $\mathrm{cm^{-1}}$ to 400 $\mathrm{cm^{-1}}$ with a resolution of 4 $\mathrm{cm^{-1}}$.

After mixing the epoxy components the samples (7–9 mg) were sealed in an aluminum DSC sample pan and then covered with an aluminum lid and equilibrated at 50 °C for 1–3 min. Curing studies were conducted on a TA Instruments DSC Q-10 in standard DSC mode under nitrogen atmosphere at a flow rate of 50 ml $\mathrm{min^{-1}}$. The DSC measurements were performed at different heating rates of 2.5, 5, 7.5, 10 °C/min. The reaction was considered to be complete when the rate curve leveled off to a baseline. The DSC instrument was calibrated for temperature and heat flow using indium metal standard (MP = 156.6 °C, $\Delta H = 28.45\ \mathrm{J\,g^{-1}}$).

3. Theoretical analysis

The DSC exothermic curves were used to evaluate the heat of cure (ΔH) and kinetic parameter of the cure reaction.

The representative DSC curve displaying heat flow dH/dt against temperature T is shown in Fig. 2. The onset temperature T_i, the peak temperature T_p, the terminal temperature T_f and the values of dH/dt of the point on the curve can be obtained directly from the curve. The line between T_i and T_f is baseline. The whole area S of the exothermal peak is directly proportional to the total quantity of heat ΔH released during the completion of cure reaction, then S can be gained:

$$S = m\Delta H/\xi$$

where m is the mass of reactive sample and ξ is the calibration coefficient which is independent of temperature [12].

The DSC peaks for nonisothermal curing of epoxy–anhydride systems are shown in Fig. 3. These peaks have been used to estimate the total heat release of cure ΔH. The heating FTIR spectra, as shown in Fig. 4, indicate that the

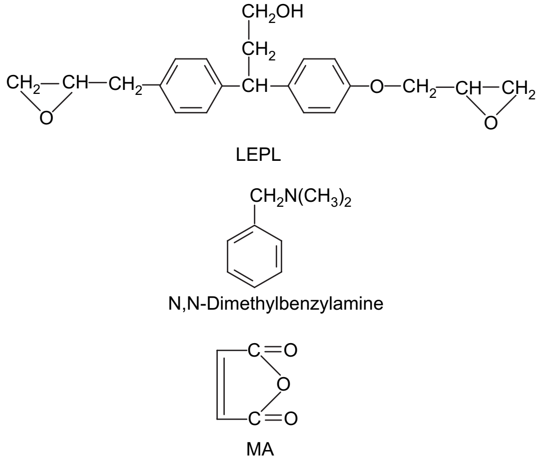

Fig. 1. Molecular structure of the reagents.

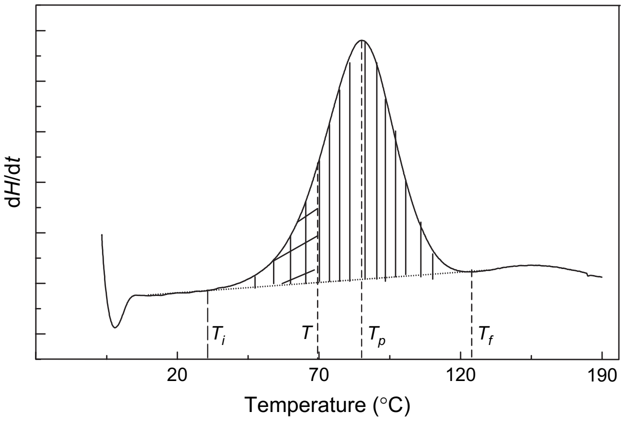

Fig. 2. Representative dynamic DSC curve of the thermosettting resin.

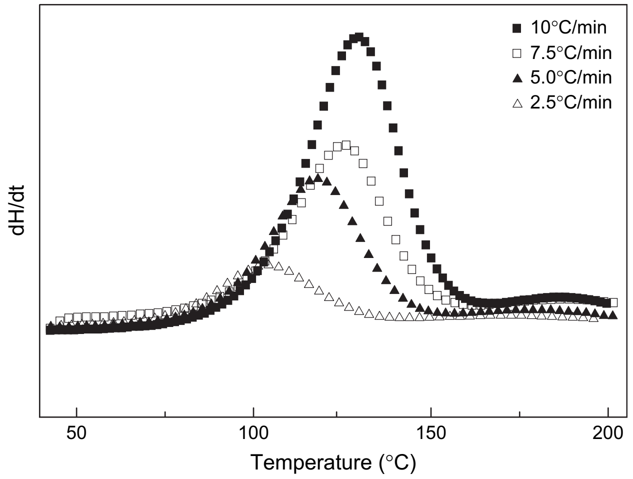

Fig. 3. DSC curves of LEPL–MA curing system with different heating rates.

epoxy groups' absorption (peak at 913 cm^{-1}) disappears in a temperature zone 110–140 °C. This means that the cure reaction is completed. That is to say the heat of ΔH is approximately the total heat of the cure reaction. Thus ΔH can be considered as a constant over the whole cure reaction. The heat of cure is directly proportional to the area under the DSC cure. The fractional conversion α calculated from the fractional and total areas under the DSC curve was used for the computation of the kinetic parameters.

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

$$\alpha = S_T/S = \Delta H_T/\Delta H$$

where ΔH_T is the heat of reaction of partially cured samples heated up to the temperature T. Then, the rate of the cure reaction is $\mathrm{d}\alpha/\mathrm{d}t = (\mathrm{d}H/\mathrm{d}t)/\Delta H$ where $\mathrm{d}H/\mathrm{d}t$ is the heat flow above the baseline.

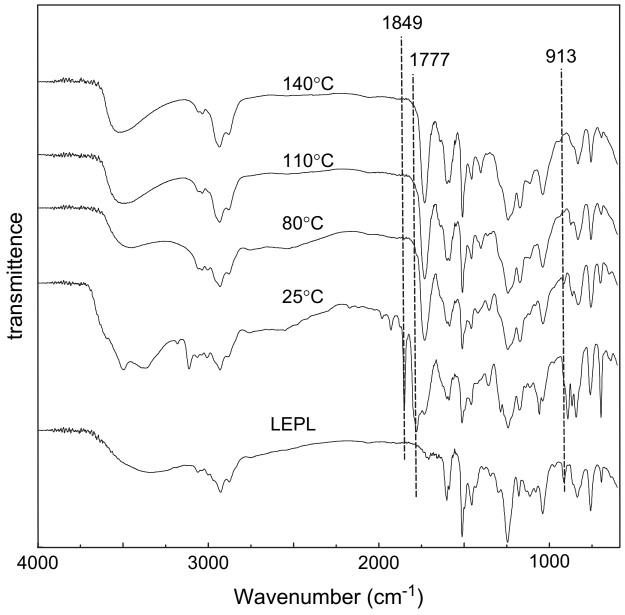

Fig. 4. Heating FTIR spectra of LEPL–MA curing system.

All kinetic studies start with a basic rate equation, which relates $\mathrm{d}\alpha/\mathrm{d}t$ to a function of the concentrations of the reactants [$f(\alpha)$] through a rate constant (k):

$$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha) \tag{1}$$

where α is the chemical conversion or extent of reaction and $f(\alpha)$ is assumed to be independent of temperature. k is assumed to follow an Arrhenius equation, thus $\mathrm{d}\alpha/\mathrm{d}t$ is expressed as:

$$\mathrm{d}\alpha/\mathrm{d}t = A\mathrm{e}^{-E/RT}f(\alpha) \tag{2}$$

where E is the activation energy, R is the gas constant ($8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$), T is the absolute temperature, A is the pre-exponential of frequency factor and $f(\alpha)$ is a function of the fractional extent of conversion α.

It has been demonstrated that the epoxy–anhydride systems follow nth-order autocatalytic kinetics [14,15]. No matter what the kinetics is, the function $f(\alpha)$ can be expressed in the form of one equation:

$$f(\alpha) = (1-\alpha)^n\alpha^m \tag{3}$$

where $n+m$ is the overall order of reaction.

Therefore, the objective of the kinetic study of the curing process is to determine the reaction equation, the reaction orders (m and n), E, and A. If $m = 0$, the reaction follows nth-order kinetics; if $m \neq 0$, the reaction follows autocatalytic kinetics.

4. Results and discussion

4.1. Heating FTIR spectral analysis

The reaction mechanism can be described by FTIR analysis. The FTIR spectral analysis is based on the band intensity change of functional groups during the reaction period. Fig. 4 shows the heating FTIR spectrum of LEPL–anhydride curing system at various reaction temperatures at the heating rate of 10 °C/min. The LEPL–anhydride cure reaction is the reaction between epoxy and the anhydride (esterification). As shown in Fig. 5, in the reaction between epoxy and anhydride, epoxy can be considered as a tetra-functional monomer while anhydride is bi-functional. This reaction produces ester linkage in the cured resins. FTIR was used to observe the change of the functional groups during the LEPL–anhydride process.

The analysis of FTIR spectra is based on the peak intensity variation of the anhydride groups' absorption at 1979, 1927, 1849 cm^{-1}. The continual decreasing of anhydride band intensity at 1979, 1927, 1849 cm^{-1} and that of the epoxy band at 913 cm^{-1} shows that there is progressive consumption of the anhydride and epoxy during the cure reaction. In addition, an increase of the intensity of the ester band at 1732 cm^{-1} is observed. All these changes indicate that the main reaction of curing is a polyaddition esterification reaction. The mechanism of LEPL–MA curing system is similar to

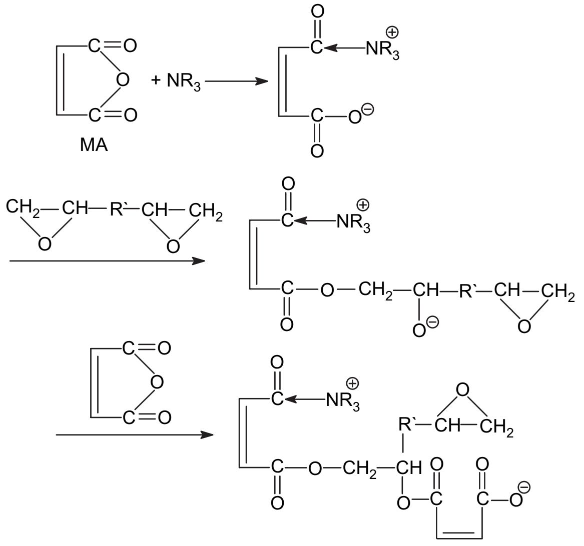

Fig. 5. Reaction between LEPL and MA under catalyst.

LEPL–MTHPA, the only difference is that the band intensity at 1979, 1927 and 690 cm^{-1} disappeared, which attributes to unsaturated carbon atoms of MA, during the LEPL–MA curing process. This indicated that unsaturated carbon atoms of MA were consumed in the process.

Moreover, as shown in Fig. 4, the FTIR spectrum has no significant changes when the temperature was higher than 110 °C. This means the cure reaction was completed at the temperature zone higher than 110 °C. The reaction completed at 110 °C is corresponding to the exothermal peak position of the DSC curves as shown in Fig. 3 in which the peaks' temperature zone is 100–130 °C.

4.2. Analysis of dynamic DSC data with E constant method

The multiple heating rate Ozawa method [16] was used to calculate the kinetic parameters. The reactions were conducted at four different heating rates: 2.5, 5.0, 7.5, and 10.0 °C/min. Based on Ozawa method, E can be calculated with the peak temperature (T_p) and heating rate β as follows:

$$\mathrm{d}(-\ln\beta)/\mathrm{d}(1/T_\mathrm{p}) = 1.502E/R$$

where β is the heating rate in °C/min and R is the gas constant ($8.314\ \mathrm{J\,mol^{-1}\,K^{-1}}$).

Fig. 6 shows the plot of $-\ln\beta$ *vs.* $1000/T_\mathrm{p}$. A linear regression suggests that, to a good agreement ($R = 0.99933$), the activation energy E calculated by Ozawa method is $59.68\ \mathrm{kJ\,mol^{-1}}$.

For the thermosetting resins we have:

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln A - E/RT + n\ln(1-\alpha) + m\ln\alpha \tag{4}$$

Then

$$\ln[\mathrm{d}(1-\alpha)/\mathrm{d}t] = \ln A - E/RT' + n\ln\alpha + m\ln(1-\alpha) \tag{5}$$

Eq. (4) – Eq. (5):

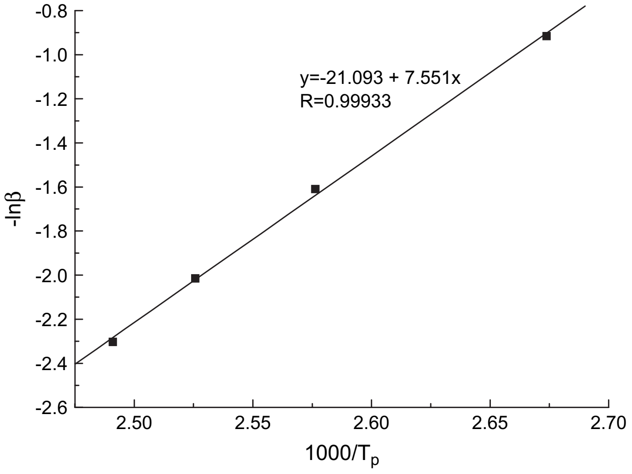

Fig. 6. Relation between ln β with $1000/T_\mathrm{p}$ of LEPL–MA curing system.

$$\begin{aligned}\text{Value I} &= \ln(\mathrm{d}\alpha/\mathrm{d}t) + E/RT - \ln[\mathrm{d}(1-\alpha)/\mathrm{d}t] - E/RT' \\ &= (n-m)\ln[(1-\alpha)/\alpha]\end{aligned} \tag{6}$$

Eq. (4) + Eq. (5):

$$\begin{aligned}\text{Value II} &= \ln(\mathrm{d}\alpha/\mathrm{d}t) + E/RT + \ln[\mathrm{d}(1-\alpha)/\mathrm{d}t] + E/RT' \\ &= 2\ln A + (n+m)\ln[\alpha(1-\alpha)]\end{aligned} \tag{7}$$

DSC curing curve with the heating rate of 10 °C/min was studied. The value of $n-m$ determined from the slope of the plot of value I *vs.* $\ln[(1-\alpha)/\alpha]$, as shown in Fig. 7, is 1.02; the values of $n+m$ and $2\ln A$ obtained from the slope and intercept of the plot of value II *vs.* $\ln[\alpha(1-\alpha)]$, as shown in Fig. 8, are 1.46 and 41.2, respectively. Then we have:

$n \approx 1.024$; $m \approx 0.22$; $A = \mathrm{e}^{20.6}$

Thus, the curing kinetic equation of the LEPL–MA system with E constant method can be expressed as:

$$\mathrm{d}\alpha/\mathrm{d}t = \mathrm{e}^{20.6}\mathrm{e}^{(-59.68/RT)}(1-\alpha)^{1.24}\alpha^{0.22}, \quad \alpha \in [0,1]$$

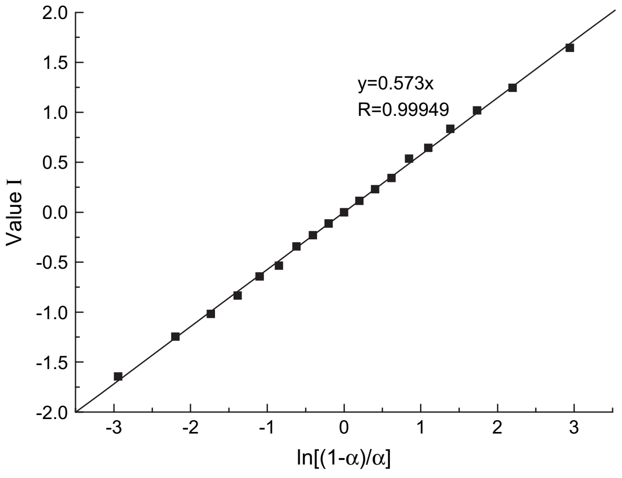

Fig. 7. Plot of value I *vs.* $\ln[(1-\alpha)/\alpha]$ (heating rate of 10 °C/min).

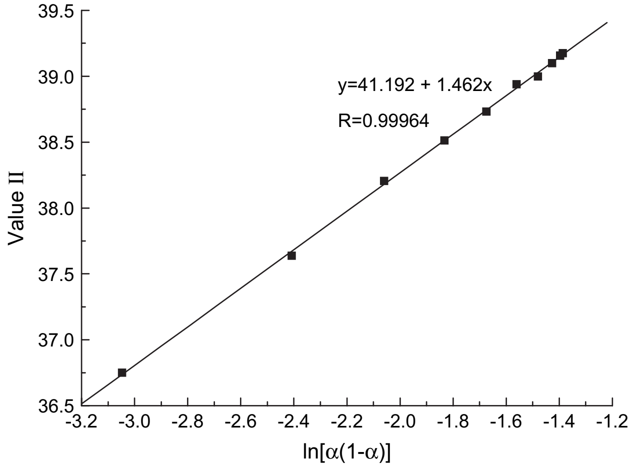

Fig. 8. Plot of value II *vs.* $\ln[\alpha(1-\alpha)]$ (heating rate of 10 °C/min).

4.3. Analysis of dynamic DSC data with E variable method

From Eq. (2):

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln A - (E/RT) + \ln f(\alpha) \quad (8)$$

Let $Af(\alpha) = F(\alpha)$, then

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = -(E/RT) + \ln F(\alpha) \quad (9)$$

From Eq. (9) a plot of Plots of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *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 beeline with a slope of $-E/R$ and an intercept of $\ln F(\alpha)$. The E and $F(\alpha)$ values corresponding to different α from the DSC curves of different heating rates can be obtained by repeating this procedure. Thus the relationship of E *vs.* α and $F(\alpha)$ *vs.* α can be decided. Simulating these relationships, the kinetic equations of the cure reaction can be obtained [17].

Fig. 9 is the plot of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $1/T$ for various values of α ($\alpha = 0.05, 0.10, \ldots, 0.90, 0.95$) covering the experimental data range. Making fitted linear regression lines, then groups of E and $F(\alpha)$ values were obtained for each value of α. Figs. 10 and 11 show plots of E and $\ln[F(\alpha)]$ *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. 10, cubic polynomial can have enough goodness of fit. Data in Fig. 11 were also fitted and cubic polynomial also can achieve the required precision. As shown in Figs. 8 and 9, the fitted curves can represent dynamic results in a major conversion range with goodness of fit.

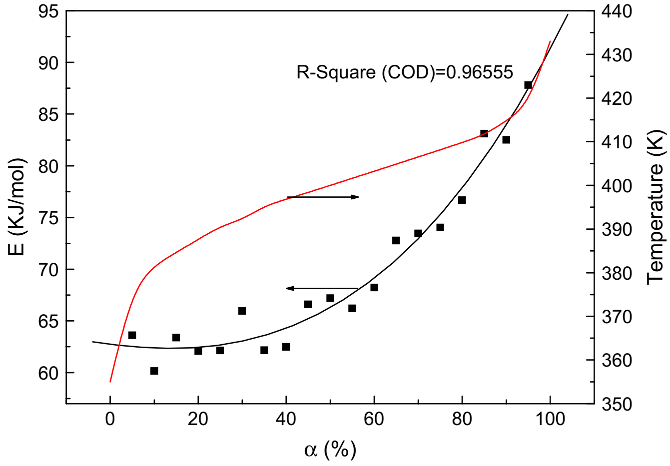

Fig. 10. Dependence of activation energy on the extent of conversion and the dependence of the extent of conversion on temperature at the heating rate of 10 °C/min of LEPL–MA system.

The fitted multiple regression equations can be expressed as:

$$E(\alpha) = 62.73 - 0.0532\alpha + 0.0016\alpha^2 + 1.8071E - 5\alpha^3$$

$$F(\alpha) = 20.162 - 0.00271\alpha + 6.4718E - 4\alpha^2$$

The kinetic equation of cure reaction of the LEPL–MTHPA curing system with E variable method can be expressed as:

$$\mathrm{d}\alpha/\mathrm{d}t = F(\alpha)\exp(-E(\alpha)/RT)$$

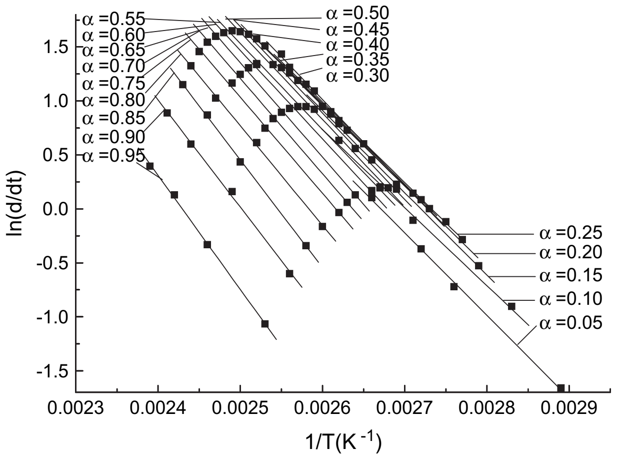

Fig. 9. Plots of $\ln(\mathrm{d}\alpha/\mathrm{d}t)$ *vs.* $1/T$.

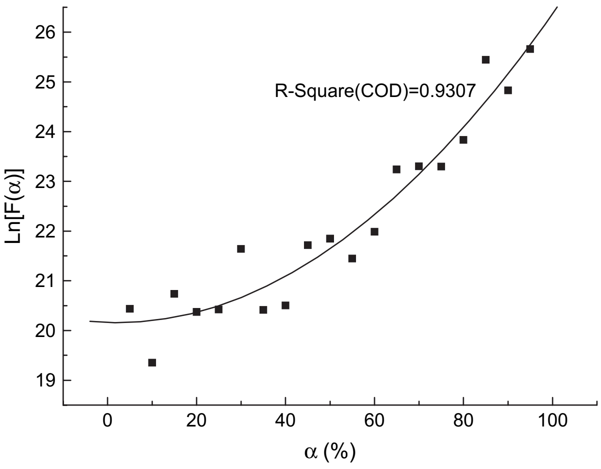

Fig. 11. Plot of $F(\alpha)$ *vs.* α.

$$E(\alpha) = 62.73 - 5.323\alpha + 15.823\alpha^2 + 18.071\alpha^3, \quad \alpha \in (0,1)$$

$$\ln[F(\alpha)] = 20.162 - 0.271\alpha + 6.472\alpha^2, \quad \alpha \in (0,1)$$

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

$$\mathrm{d}E/\mathrm{d}\alpha = 54.213\left[(\alpha + 0.292)^2 - 0.428^2\right]$$

$$\mathrm{d}E/\mathrm{d}\alpha = 0(\alpha \approx 0.14)$$

Thus the minimum of $E(\alpha)$ is $E = 60.16$, ($\alpha \approx 0.14$).

At first, value of E is 62.73 kJ mol^{-1} ($\alpha = 0$), then decreases to 60.16 kJ mol^{-1} ($\alpha \approx 0.14$), thereafter increases to 87.80 kJ mol^{-1} ($\alpha = 1$). As can be seen in Fig. 10, the variable E spans from 62.73 to 60.16 at first stage then from 60.16 to 87.80 kJ mol^{-1} at second stage. During the cure reaction, E initially decreases ($\alpha \lesssim 0.14$) and increases at high conversions ($\alpha \gtrsim 0.14$).

4.4. Analysis of the variation of E and the cure reaction mechanism with E variable method

E variable method allows the activation energy to be determined as a function of the extent of conversion α without assumption of constant E and started with the basic equation. And the E dependence on α is determined without any assumption about the reaction model. Therefore the kinetic equations of the cure reaction deduced from E variable method should be more suitable to real situation than E constant method. The changes in the cure mechanism can be detected by using E variable method if these changes are associated with the changes in the activation energy [18].

Based on the heating FTIR spectral results, in this work, the heat released from the cure reaction is principally due to the esterification reaction. Therefore, it is reasonable to expect a decrease in E of the epoxy–anhydride cure, as shown in Fig. 10, as compared to the very beginning of the process where no catalyzed reaction occurs. The system undergoes gelation and vitrification transitions as the cure reaction proceeds. Intensive cross-linking occurs and reduces molecular mobility, for epoxy systems, vitrification causes the change from chemical to diffusion control [19].

For the LEPL–MA curing system at early stages ($\alpha \lesssim 0.14$) E decreases. This can be understood in terms of cooperative motion of the chain segments [20]. The packing is loose at the early stages; the loose packing allows the chain segments to move independently. So E decreases with the conversion increase. For the LEPL–MA curing system at later stages ($\alpha \gtrsim 0.14$) E increases. As the cure reaction proceeds, conversion increases, the free volume decreases. At the glassy state, the small amount of free volume only allows for local motions of the chain segments. It requires a great degree of cooperativity between the chain segments to initiate translational motion of the segments. The cooperativity between the chain segments results in a large energy barrier to the segmental motion as reflected in the value E at later cure stages. As reflected in an increase of E the energetic constrains are intensified.

The change to diffusion control is accompanied markedly by slowing down the cure rate. The effect of diffusion control on the cure kinetics is very profound when vitrification occurs at later cure stages ($\alpha \gtrsim 0.14$). The vitrification induced diffusion control can be recognized by a higher value of the activation energy at the final cure stages. As shown in Fig. 10, the E increases as the conversion α increases ($\alpha \gtrsim 0.14$). Therefore it is reasonable to believe that diffusion control has a profound effect on the over all kinetics of the LEPL–MA system because its vitrification occurs at early stages of the cure process.

4.5. Comparison of the E constant method and E variable method

E variable method is deduced without assumption of a particular of the reaction model and without assuming a constant E. Moreover, E variable method started with the basic equation, thus the results obtained by E variable method should give a better fit to the real situation than those calculated by E constant method. This means E variable method allows for evaluating an effective activation energy, E, as a function of the extent of reaction, α. Moreover, it must be noticed that E constant method only uses the values at the peak values of the curing DSC curves, whereas, E variable method uses most of the values in the DSC cures.

When calculating dα/dt of the curing, E constant method only uses one DSC cure, thus there exists a temperature effect on the calculations because different heating rates result in different dα/dt ~ α curves [11], while E variable method has no temperature effect on the calculations because the calculated results used all the four DSC cures. So the results obtained by E variable method are more authentic than E constant method. Especially, E variable is a model-free method which allows E to be determined without assuming any reaction model. Changes in the cure mechanism that are associated with the changes in the activation energy that can be deterred by E variable method. This is an important advantage of E variable method to deter E over the other methods. As known, in epoxy cure study, an incorrect model will give a grossly deviant value of E. Compared to its advantages, the disadvantages of E variable method in the calculation process is very complex.

The activation energy calculated with E constant method is 59.68 kJ mol^{-1}, which is the apparent activation energy of the entire reaction of the LEPL–MA system. The calculated E of LEPL–MA curing system is lower than LEPL–MTHPA system in which E value is 78.93 kJ mol^{-1} [21]. Moreover, this value falls near the range of 60.16–87.80 kJ mol^{-1} obtained by E variable method. E constant method is a simple and effective method in qualitative comparison among different curing systems, though E constant method cannot be used in studying cure reactions in detail.

The kinetic methods' results were compared with experimental data of 2.5 and 10 °C/min heating rate to demonstrate the applicability of the two kinetic methods. As can be seen in Fig. 12, the results with E variable method are in better agreement with the experimental data than that of E constant

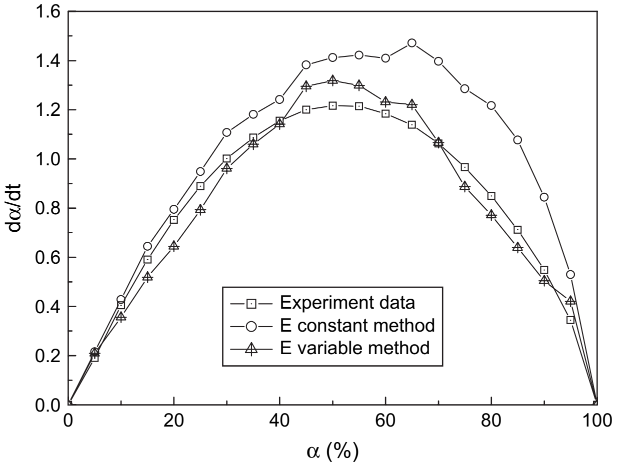

Fig. 12. Comparison of experimental data with the kinetic method results (heating rate: 2.5 °C/min).

method. As shown in Fig. 13, the *E* constant method is a little more agreeable one with the experimental data than that of *E* variable method. This is because when calculating dα/dt of the curing, *E* constant method only uses one DSC cure at heating rate of 10 °C/min, while *E* variable method has no heating rate dependence on the calculations because the calculated results used all the four DSC cures. Furthermore, as far as the kinetic method results with *E* variable is concerned, there is no obvious difference between model predictions and experimental data when the heating rate decreases. There is obvious difference between model predictions obtained by *E* constant method and experimental data when the heating rate decreases. This means the *E* variable method have more applicability than *E* constant method. The discrepancy between results of *E* variable method and experimental data mainly occurs at the middle range of conversion α. The neglect of the synthesis of chemical and diffusion as the kinetic method is deduced may be responsible for the discrepancy. At early cure stages, before gelation and vitrification the reaction occurs in the liquid phase and is controlled by chemical kinetics. At later cure stages, the cure reaction kinetics becomes diffusion controlled, thus the kinetic behavior described by this model coincides with the experimental data, when the cure process is controlled by typical chemical or diffusion. At the middle range of the cure extent, the rate of conversion is controlled by the synthesis of chemical and diffusion and the values predicted by the model are higher than that of the experimental data.

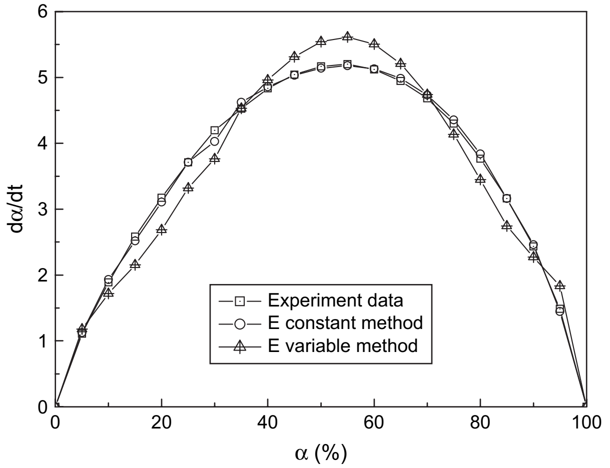

Fig. 13. Comparison of experimental data with the kinetic method results (heating rate: 10 °C/min).

5. Conclusions

Epoxy resins were obtained by the reaction of the lignin based epoxy resin with maleic anhydride in the presence of a catalytic benzyldimethylamine. The curing process of the LEPL with MA was studied using DSC at different heating rates. Heating FTIR was used to study the change of the functional group. Complete consumption of the epoxides has been observed after the heating temperature was higher than 110 °C. The curing kinetic parameters of the LEPL–MA system were obtained by *E* constant method and *E* variable method. With *E* constant method, the cure reaction activation energy *E* is 59.68 $\mathrm{kJ\,mol^{-1}}$. The value of $\ln A$ and $n+m$ obtained by *E* constant method is 20.6 and 1.46, respectively. With *E* variable method, *E* is proved to decrease initially, and then increases as the cure reaction proceeds. The value of *E* spans from 60.16 to 87.80 $\mathrm{kJ\,mol^{-1}}$. The value $n+m=1.46>1$ demonstrates that the cure reaction of the studied system is complex which is also proved by the variation of *E* during the whole process. With *E* variable method, the obtained variation *E* can be used to have a profound study on the cure reaction mechanism. But the calculation process is very complex. The *E* constant method is a simple and effective method in qualitative comparison among different curing system though it cannot be used in studying *E* in detail. The comparison between different methods and experimental data indicates that the results by using *E* variable method are in better agreement with the experimental data than *E* constant method. With the *E* constant method, *E* variable method and heating FTIR spectra used together, we have a comprehensive and profound understanding of the cure reactions of the LEPL–MA system.

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