Mechanism and Kinetics of Epoxy-Imidazole Cure Studied with Two Kinetic Methods

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ABSTRACT: Curing kinetics and mechanism of the diglycidyl ether of bisphenol-A (DGEBA) initiated with 2-ethyl-4-methylimidazole (EMI-2,4) were studied with two methods by using differential scanning calorimetry (DSC). Method I and Method 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 $49.03 \text{ kJ mol}^{-1}$, $e^{14.5}$ and 1.22, respectively. With Method II, E is proved to decrease initially, and then increase as the cure reaction proceeds, and the value of E spans from 34.3 to $63.84 \text{ kJ mol}^{-1}$. The variations of E were also used to study the cure reaction mechanism. Method I and Method 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 cure reactions, such as those of the DGEBA/EMI-2,4 system. [DOI 10.1295/polymj.37.833]

KEY WORDS Cure Reaction / DSC / Kinetic Method / DGEBA/EMI-2,4 System /

Imidazole-cured resins are widely used in the electronics industry as molding and sealing compounds because they exhibit a better heat resistance, a higher modulus, and a wider range of cure temperatures than amine-cured systems. The kinetics of imidazole/resin systems has been widely studied by using isothermal or dynamic DSC technique.^{1–5} But their studies were all based on the assumption of a constant E and the whole reaction of curing 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 system.

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

structure for DGEBA is shown in Figure 1. The curing agent used was EMI-2,4 supplied by Beijing Chemical Reagent Co. Other agents used were analytically pure grade and were supplied by Beijing Chemical Reagent Co.

Approximately 10 mg sample of the mixture of DGEBA and EMI-2,4 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; $\alpha\text{-Al}_2\text{O}_3$ 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 310 to 510 K at different heating rates of 5, 10, 15, 20°C/min . The reaction was considered to be complete when the rate curve leveled off to a baseline.

Theoretical Analysis

The curing mechanism of DGEBA/EMI-2,4 system, as shown in Figure 2, involves two stages consisting of the adduct and etherification reactions.^{1–3} 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 work⁵ showed that the formation of adduct 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. The objective criterion of meeting this specification is that the molar heat of the reac-

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Figure 1. Structure of DGEBA epoxy. **Figure 2.** Curing mechanism for the DGEBA/EMI-2,4 system.

tion 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 pph (parts per hundred, *i.e.*, 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 pph.⁸ In this work, the concentration of EMI-2,4 is 6 pph which falls within the range of 3–10 pph, moreover, only a main peak exotherm of the etherification reaction appears, as shown in Figure 3, that is to say, the heat of reaction for the etherification reaction peak is approximately the total heat of the curing reaction. Thus, in this work, ΔH can be considered as a constant over the whole cure reaction. Then, the rate of the cure reaction is $d\alpha/dt = (dH/dt)/\Delta H$ where dH/dt is the heat flow above the baseline. In other words, the rate of cure reaction is assumed to be pro-

Figure 3. DSC curing curves with different heating rates of the DGEBA/EMI-2,4(100:6 by weight ratio) system.

portional to the heat release rate.

From a dynamic DSC run, the total area S of the exothermal peak (the region between the exotherm and the baseline) is in direct proportion to ΔH released during the whole cure reaction. The fractional extent of conversion at a given temperature T can be expressed as:

$$\alpha = \Delta H_T / \Delta H = S_T / S \quad (0 \leq \alpha \leq 1)$$

where ΔH_T is the heat of reaction of partially cured samples heated up to the temperature T .

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:

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

where A is the frequency factor, E is the activation energy, $f(\alpha)$ is a function of the fractional extent of conversion α , 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.¹⁻³ In this work, as shown in Figure 4, each curve analyzed is typically parabolic, which is also indicative of an autocatalytic kinetics of the studied DGEBA/EMI-2,4 system.⁹

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.^{10,11}

Figure 4. Plots of $d\alpha/dt$ 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 °C/min heating rate is used as the total heat ΔH_{tot} .

RESULTS AND DISCUSSION

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.^{12,13} As shown in Figure 4, in this work, the fractional extent of conversion α at the peak exotherm is nearly a constant (~ 0.6); therefore, the relation between the heating rate and the peak exotherm temperature is of the form, Ozawa equation:¹³

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

where β is the heating rate in °C/min.

Figure 5 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 49.03 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

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

Eq 3 – Eq 4:

$$\text{value I} = \ln(d\alpha/dt) + E/RT - \ln[d(1 - \alpha)/dt] - E/RT' = (n - m) \ln[(1 - \alpha)/\alpha] \quad (5)$$

Figure 5. Plot of $-\ln \beta$ vs. $1000/T_p$.

Figure 6. Plot of Value I vs. $\ln[(1-\alpha)/\alpha]$ ($10^\circ\text{C}/\text{min}$ heating rate).

Figure 7. Plot of Value II vs. $\ln[\alpha(1-\alpha)]$ ($10^\circ\text{C}/\text{min}$ heating rate).

Eq 3 + Eq 4:

$$\begin{aligned} \text{value II} &= \ln(d\alpha/dt) + E/RT + \ln[d(1-\alpha)/dt] \\ &+ E/RT' = 2 \ln A + (m+n) \ln(\alpha - \alpha^2) \end{aligned} \quad (6)$$

DSC curing curve with the heating rate of $10^\circ\text{C}/\text{min}$ 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 Figure 6, is 0.802; the values of $m+n$ and $2 \ln A$ obtained from the slope and intercept of the plot of Value II vs. $\ln[\alpha(1-\alpha)]$, as shown in Figure 7, are 1.222 and 29, respectively.

Then we have:

$$n \approx 1.01; m \approx 0.21; A = e^{14.5}$$

Thus, the curing kinetic equation of this DGEBA/EMI-2,4(100:6 by weight ratio) system with Method I

Figure 8. Plots of $\ln(d\alpha/dt)$ vs. $1/T$.

can be expressed as:

$$d\alpha/dt = e^{14.5} e^{(-49.03/RT)} (1-\alpha)^{1.01} \alpha^{0.21}, \alpha \in [0, 1]$$

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 $Af(\alpha) = F(\alpha)$:

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

From eq 8, a plot of $\ln(d\alpha/dt)$ vs. $1/T$ values at the same fractional extent of conversion α from a series of DSC experiments at different heating rates would result in a straight line with a slope of $-E/R$ and an intercept of $\ln F(\alpha)$. Repeating this procedure, the E and $F(\alpha)$ 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 $F(\alpha)$ vs. α can be decided. Simulating these relationships, the kinetic equations of the cure reaction can be obtained.^{14,15}

Figure 8 is the plots of $\ln(d\alpha/dt)$ vs. $1/T$ for various values of α ($\alpha = 0.05, 0.10, 0.20, \dots, 0.90, 0.95$) covering the experimental range. Making fitted linear regression lines, then groups of E and $F(\alpha)$ values were obtained for each value of α . Figures 9 and 10 show plots of E and $\ln[Af(\alpha)]$ vs. α , respectively. The different values of E corresponding to different α confirms the conversion-dependence of E , viz., E is a variable. Different multiple regression equations were tried to fit the data in Figure 9, and it was found that quadratic polynomial can have enough goodness of fit. i.e., if high-order moments were utilized to fit the data in Figure 9, the coefficient of the items whose number

Figure 9. Plot of E vs. α .

Figure 10. Plot of $\ln[Af(\alpha)]$ vs. α .

of order are greater than or equal to 3 in the equations will be smaller than 10^{-5} , so quadratic polynomial is good enough. Data in Figure 10 were also fitted with different multiple regression equations and cubic polynomial was found to achieve the required precision. As shown in Figures 9 and 10, the fitted curves can represent dynamic DSC results in a major conversion range with goodness of fit.

The fitted multiple regression equations can be expressed as:

$$E(\alpha) = 63.837 - 1.085\alpha + 9.95E - 3\alpha^2 \quad (9)$$

$$\ln[Af(\alpha)] = 21.221 - 0.154\alpha + 3.501E - 3\alpha^2 - 2.530E - 5\alpha^3 \quad (10)$$

As discussed above, the studied system follows an autocatalytic kinetics, substitute eq 2 into eq 10,

$$\ln A + n \ln(1 - \alpha) + m \ln \alpha = 21.221 - 15.4\alpha$$

$$+ 35.01\alpha^2 - 25.30\alpha^3, \alpha \in (0, 1)$$

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

$$\ln A + n \ln 0.8 + m \ln 0.2 = 19.339$$

$$\ln A + n \ln 0.5 + m \ln 0.5 = 19.111$$

$$\ln A + n \ln 0.2 + m \ln 0.8 = 18.3538$$

Solving this equation set and the kinetic parameters are gained: $m \approx 0.24$, $n \approx 0.95$, $\ln A \approx 19.93$.

Therefore, the kinetic equation of cure reaction of this DGEBA/EMI-2,4(100:6 by weight ratio) system with Method II can be expressed as:

$$d\alpha/dt = e^{19.93}(1 - \alpha)^{0.95}\alpha^{0.24}e^{[-E(\alpha)/RT]}$$

with

$$E(\alpha) = 63.837 - 108.5\alpha + 99.5\alpha^2, \alpha \in (0, 1)$$

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

$$dE/d\alpha = -108.5 + 199\alpha, \alpha \in (0, 1)$$

As shown in Figure 9, the value of E spans from 34.3 to 63.84 KJ mol⁻¹. During the cure reaction, E initially decreases at low conversions ($\alpha < \sim 0.55$), and then increases as the cure progresses.

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.¹⁶

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.¹⁻³ 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 (A2), which contains the nucleophilic alkoxide ion, was believed to be the catalyst that initiated the etherification reaction. Unlike the 1:1 adduct (A1), 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 Figure 9, as compared to the very beginning of the process where the nonautocatalyzed reaction occurs.¹⁷

As the cure reaction proceeds, the system under-

Table I. Curing kinetic parameters of the DGEBA/EMI-2,4 system resulting from Method I and Method II

Curing kinetic equation	$d\alpha/dt = A(1 - \alpha)^n \alpha^m e^{-E/RT}$	
	Method I (10 °C/min heating rate)	Method II
E	49.03 KJ mol ⁻¹	$63.837 - 108.5\alpha + 99.5\alpha^2$, $\alpha \in (0, 1)$
$dE/d\alpha$	0	$-108.5 + 199\alpha$, $\alpha \in (0, 1)$
Variation of $dE/d\alpha$	/	$0 < \alpha < 0.55$, $dE/d\alpha < 0$; $\alpha = 0.55$, $dE/d\alpha = 0$; $0.55 < \alpha < 1$, $dE/d\alpha > 0$
$\ln A$	14.5	19.93
$m + n$	1.22	1.19
n	1.01	0.95
m	0.21	0.24

goes 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.¹⁷ The increase in E at higher conversions for the system can be understood in terms of cooperative motion of the chain segments.¹⁸ 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 .

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(100:6 by weight ratio) system, obtained by Method I and Method II, were tabulated in Table I.

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 49.03 KJ mol⁻¹, which is the apparent activation energy of the global reaction of the DGEBA/EMI-2,4(100:6 by weight ratio) system. This value is much lower than the results obtained in previous work^{5,19} in which E is also assumed to be constant and Fourier Transform Infrared Spectroscopy (FTIR) or DSC technique is used. Moreover, this value falls within the range of 34.3–63.84 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(100:8 by weight ratio) system is 41.28 KJ mol⁻¹, which is lower than that of the DGEBA/EMI-2,4(100:6 by weight ratio) system.

As shown in Table I, 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.

To demonstrate the applicability of these two kinetic methods, the kinetic methods results were compared with the experimental data of 5 and 20 °C/min heating rate, as shown in Figures 11 and 12. It can be seen that the results with 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 °C/min heating rate at higher conversions. Meanwhile, the kinetic method results are in good agreement with the experimental data of 20 °C/min heating rate in the whole tested conversions

Figure 11. Comparison of experimental data with the kinetic method results (5 °C/min heating rate).

Figure 12. Comparison of experimental data with the kinetic method results (20 °C/min heating rate).

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.²⁰ When the cure reaction kinetics becomes diffusion controlled, the reaction is hard to proceed which leads to incomplete ultimate conversion, *viz.*, $\alpha_{ult} < 1$.

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} .

CONCLUSIONS

The curing kinetic parameters of the DGEBA/EMI-2,4 system were obtained by Method I and Method 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 49.03 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 34.3 to 63.84 KJ mol⁻¹. The value of $\ln A$ and $m + n$ obtained by Method I is 14.5 and 1.22, respectively. Meanwhile, the corresponding values obtained by Method II are 19.93 and 1.19. $m + n > 1$ 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. On the other hand, although Method I can not 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 different DGEBA/EMI-2,4 systems.

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 system, with these two methods used all together.

REFERENCES

1. A. Farkas and P. F. Strohm, *J. Appl. Polym. Sci.*, **12**, 159

- (1968).
2. M. S. Heise and G. C. Martin, *J. Polym. Sci.*, **26**, 153 (1988).
 3. M. S. Heise and G. C. Martin, *Macromolecules*, **22**, 99 (1989).
 4. J. M. Bartion and P. M. Shepard, *Makromol. Chem.*, **176**, 199 (1975).
 5. M. S. Heise and G. C. Martin, *J. Appl. Polym. Sci.*, **39**, 721 (1990).
 6. T. Ooshi and M. Fujimoto, *J. Polym. Sci.*, **30**, 1821 (1992).
 7. E. A. Turi, ed., "Thermal Characterization of Polymeric Materials," Academic Press, New York, 1981.
 8. D. ZHANG, *China Adhesive*, **6**, 38 (1997).
 9. O. Levenspiel, ed., "Chemical Reaction Engineering," 2nd ed., Wiley & Sons, New York, 1972.
 10. W. W. Wendlandt, ed., "Thermal analysis," 3rd ed., Wiley & Sons, New York, 1986.
 11. M. R. Kamal and S. Sourour, *Polym. Eng. Sci.*, **13**, 59 (1973).
 12. T. Donnellan and D. Roylance, *Polym. Eng. Sci.*, **22**, 821 (1982).
 13. T. Ozawa, *Bull. Chem. Soc. Jpn.*, **38**, 1881 (1965).
 14. H. Friedman, *J. Polym. Sci.*, **50**, 183 (1965).
 15. J. H. Flynn, *J. Therm. Anal.*, **37**, 293 (1991).
 16. S. Vyazovkin, *Int. Rev. Phys. Chem.*, **19**, 45 (2000).
 17. S. Vyazovkin and N. Sbirrazzuoli, *Macromolecules*, **29**, 1867 (1996).
 18. S. Vyazovkin, N. Sbirrazzuoli, and I. Dranca, *Macromol. Rapid Commun.*, **25**, 1708 (2004).
 19. D. ZHANG and Y. C. Gongyi, *Aerospace Materials & Technology*, **5**, 31 (1994).
 20. K. C. Cole, J. J. Hechler, and D. Noel, *Macromolecules*, **24**, 3098 (1991).