Kinetics and Thermal Characterization of Epoxy-Amine Systems

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ABSTRACT: The curing behavior of epoxy resins was analyzed based on a simple kinetic model. We simulated the curing kinetics and found that it fits the experimental data well for both diglycidylether of bisphenol A–4,4′-methylene dianiline and diglycidylether of bisphenol A–carboxyl-terminated butadiene acrylonitrile–4,4′-methylene dianiline systems. The kinetic results showed the curing of epoxy resins involves different reactive process and reaction stages, and the value of activation energy is dependent on the degree of conversion. By analyzing the effect of vitrification, at low curing temperature, we found the curing reaction at the later stage was practically diffusion-controlled for unmodified resin, and the rubber component did not markedly decrease T_g at the early stage of reaction as would be expected. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2401–2408, 1999

Key words: degree of conversion; DSC; epoxy; vitrification; cure kinetics

INTRODUCTION

Epoxy resin is one of the most important polymeric materials, as polymer matrices for composite materials, and as adhesives. Curing kinetics of epoxy resins has been studied with different techniques. However, the reaction of curing epoxy resins is normally very complex because many reactive processes occur simultaneously, and there are other parameters that increase the complexity of the curing process, such as the phenomena of gelation and vitrification, the change from chemical kinetic control to control by diffusion in the advance of the curing.[1,2]

The kinetics of curing epoxy resins has been widely studied using isothermal or dynamic experiments with differential scanning calorimetry (DSC); experimental data are analyzed by the homogeneous reaction model, normally using autocatalytic or n order equation.[3–5] In these mod-

els, the whole reaction of curing was only considered as a single kinetic process, regardless of the different reactive processes or the different stages evolved in the system. When the profile of the rate curves is simple, this procedure normally gives a good fit of experimental data.

Recently, we analyzed the curing process of epoxy resins based on a morphological model,[6,7] where the kinetic parameters obtained were in good agreement with those reported in the literature. Several widely accepted models were used to evaluate the kinetic parameters and analyze the curing process for zeolite-filled epoxy systems.[8]

In the present work, we use an experimental model that does not require the knowledge of reaction rate equation $f(\alpha)$ and give the curing behavior at a different content of conversion for modified and unmodified epoxy resins. We found that the results simulated by this proposed model fit the experimental data better than that by the autocatalytic model, especially for a high-curing temperature and a low degree of conversion. The activation energy of curing is practically depen-

dent on conversion. Moreover, the effects of vitrification on the curing reaction will be discussed.

THEORETICAL ANALYSIS

All kinetic studies can start with the basic equation that relates the rate of conversion at constant temperature to some function of the concentration of reactants:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

or in the integrated form:

$$g(\alpha) = \int \frac{d\alpha}{f(\alpha)} = \int k \ dt \tag{2}$$

where $d\alpha/dt$ is the rate of cure, α is the fractional conversion at any time t, k is the Arrhenius rate constant, and $f(\alpha)$ is a function form of α that depends on the reaction mechanism.

Assuming the heat of reaction released at any time is proportional to the number of moles reacted at that time, the extent of cure α at any time is defined as:

$$\alpha = \frac{\Delta H}{\Delta H_I + \Delta H_R} \tag{3}$$

where ΔH is the partial area under the DSC curve up to the point of interest, ΔH_I is the total isothermal heat of cure, and ΔH_R is the heat evolved due to the residual isothermal reactivity of the sample at temperature T (it is determined by a dynamic postcuring after each isothermal experiment).

For the kinetic study, many authors consider that, during the curing process, the reaction mechanism does not change and the equation $f(\alpha)$ in eq. (1) has the same form. As previously described, the curing process in epoxy resins is complex and, in many cases, it is not correct to consider that the reaction mechanism remains constant during the whole process, or that there is a single activation energy associated with it.

Herein, we consider that $f(\alpha)$ has the same form, regardless of the temperature for the same degree of conversion α. By integrating eq. (2) for a curing time of $t = 0$, where $\alpha = 0$ to a time t with a degree of curing α, we obtain

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k \ dt = C = kt \tag{4}$$

where C is a constant. Equation (4) shows us how the time is inversely proportional to the reaction rate constant k for an α, regardless of the $f(\alpha)$ at a given temperature.

The dependence of the reaction constant on the temperature follows Arrhenius[7] Law:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{5}$$

By replacing eq. (5) in eq. (4) and taking logarithms, we will have:

$$\ln t = \frac{E}{RT} + A \tag{6}$$

where A is a constant. Equation (6), which makes a linear relation between the logarithm of the time needed to reach a conversion α and the inverse of temperature, will be used to study the curing kinetics of epoxy resins. The values of activation energy can be obtained from the slope of eq. (6). By extrapolating with these equation values outside the experimental range of temperatures, it is convenient to predict the time needed to reach a given conversion, and thus simulate curing kinetics.

EXPERIMENTAL

Materials

The epoxy resin systems used in this study consist of a diglycidylether of bisphenol A (DGEBA) resin (Shell Chemicals, Epon 828) and 4,4′-methylene dianiline (MDA) hardener (Fluka Chemie Co.) and a low molecular weight carboxyl-terminated butadiene-acrylonitrile (26%) copolymer (CTBN) (Kukdo Chemical Co.). These materials were used as supplied without further purification. The epoxide equivalent weight of the resin was taken as 184 and the concentration of CTBN is 10%. The resin was cured using stoichiometric quantities of diamine. The two systems are referred to as DGEBA-MDA and DGEBA-CTBN-MDA, respectively. The epoxy resin was mixed with CTBN and melted MDA under good stirring $\sim$ 80°C, then cooled rapidly to

room temperature. The resulting material was kept in a freezer at $-20°C$.

DSC Characterization

Samples consisting of the 4–8 mg mixture are placed in aluminum DSC pans and run on a SEIKO I-5000 series. In the isothermal scans, samples were heated to the test temperature at $100°C$ min^{-1} and measured at five temperatures between 80°–120°C. After all the isothermal curings, a dynamic scan is conducted from 20°–300°C at a heat rate of $10°C$ min^{-1} to determine the residual heat. Samples for measurement of glass transition temperature were placed in a thermostatic oven at different curing temperatures for various periods of curing time, or cured inside the DSC module if the curing time was < 3 h. DSC scans were conducted from -100 to $300°C$, at a heat rate of $10°C$ min^{-1}. The carrier gas is nitrogen at a flow of 50 mL min^{-1}. More details about the calibration procedure and thermal conditions can be found elsewhere.[6]

RESULTS AND DISCUSSION

Kinetic Analysis

The curing isotherms for the DGEBA-CTBN-MDA system was shown in Figure 1. A similar

Figure 1 Degree of conversion *versus* curing time at different temperatures for the DGEBA-CTBN-MDA system.

Figure 2 Correlation of the logarithm of time *versus* the inverse of the temperature for different conversions for the DGEBA-MDA system.

result was obtained for the DGEBA-MDA system. As would be expected, there is a higher extent of cure at the given curing temperature and time for the DGEBA-CTBN-MDA system. This kind of behavior has been frequently observed by other researchers[9,10] and showed that the cure reaction was accelerated at the early stage of cure due to the existence of CTBN. In our previous work, an appropriate interpretation was given by analyzing phase change theory.[6]

From Figure 1, we can obtain the curing times for a given degree of conversion, and it is possible to correlate the logarithm of curing time against the inverse of the temperature by using eq. (6). Figure 2 was a typical curve ln t *versus* $1/T_c$. For each degree of conversion at different temperatures for both systems, the values of activation energy can be obtained from the slope of these straight lines. Table I and Fig. 3 showed the comparative results of activation energies for both systems. As can be seen, the values of activation energy are not a constant, as supposed in many works throughout the whole curing process. At the early stage of cure reaction, the activation energy takes a maximum value, then decreases slightly, and remains practically constant—finally showing a certain tendency to decrease. However, some differences, especially in the early stage of cure, can be observed for DGEBA-CTBN-

Table I   Activation Energy at Different Degrees of Conversion for the DGEBA-MDA and DGEBA-CTBN-MDA Systems

| | E (kJ mol^{-1}) | | | | | | | | | |
| | Conversion (%) | | | | | | | | | |
	10	20	30	40	50	60	70	80	90	Average
DGEBA-MDA	39.4	42.7	42.9	43.0	42.5	41.9	40.9	39.8	37.2	41.1
DGEBA-CTBN-MDA	46.1	44.8	45.1	45.5	45.4	44.9	43.4	42.1	39.8	44.1

MDA. The difference can be attributed to the so-called autocatalysis caused by the initial hydroxyl concentration and the addition of catalysts, such as the impurities. It is consistent with the results reported in the literature.[9,10] It is worthy to note herein that such autocatalysis only affects the curing reaction through the Arrhenius frequency factor, such as increasing the reaction rate, but not decreasing the activation energy as observed in many catalytic reactions. Detailed mechanisms are still not clear. This catalysis can also result from some kinds of fillers in epoxy resins.[11,12] It was attributed to the presence of chemical complexes. In fact, a further investigation will be necessary to elucidate the curing reaction responsible for these observed experimental effects. The decrease in activation energy at the final period of cure obviously represented the change of curing mechanism from chemical kinetic control to con-

trol by diffusion due to the phenomena of gelification, vitrification, and high viscosity existed in the reaction medium. Similar results have been frequently observed in heterogeneous reactions.[13] Therefore, in a more pragmatic sense, the activation energy is a time-temperature factor and as such it is useful in predicating behavior of thermosets in real processes.

For a special case, the given extent of cure is 50% and the time $t_{1/2}$ that often used as a parameter to analyze the reaction kinetics can be expressed as:

For the DGEBA-CTBN-MDA system

$$t_{1/2} = 1.06 \times 10^{-5} \exp\left(\frac{45.4 \times 10^3}{RT}\right) \qquad (7)$$

For the DGEBA-MDA system

$$t_{1/2} = 3.72 \times 10^{-5} \exp\left(\frac{42.5 \times 10^3}{RT}\right) \qquad (8)$$

Normally, it is to be expected that the reaction rate decreases with time, because the concentrations of reactive species decrease as the conversion increases. But, in this type of process, the reaction rate increases as the reaction advances due to the effect of autoacceleration. At higher conversions, the rate may decrease again due to the effect of vitrification, which is very pronounced at low-curing temperatures. This effect may overlap with the sharp increase in viscosity at high conversions, which also leads to the decrease in the reaction rate.[14]

In fact, whether due to the viscosity of the medium, to the phenomenon of vitrification, or to the process of the end of the reaction, the decrease of reaction rate has been detected at the high degree of conversion. This can be seen in Figure 4, which shows the reaction rate according to the

Figure 3   Activation energy *versus* degree of conversion for both systems.

Figure 4 Reaction rate *versus* degree of conversion at different temperatures for DGEBA-MDA.

Figure 5 Comparison between experimental curves and data from extrapolation of the kinetic equation for DGEBA-MDA.

degree of conversion for the DGEBA-MDA system. Similar results can also been observed in the DGEBA-CTBN-MDA system.

Due to the good linearity obtained in the curves ln *t versus* $1/T$ (see Fig. 2), it is possible to calculate the time needed to reach a given temperature inside or outside the range of experimental measurements, thus to simulate the curves' degree of conversion *versus* curing time. Figure 5 compares the curves simulated with the kinetic model and the results obtained experimentally with DSC for the DGEBA-MDA system. Similar results can also be obtained for the DGEBA-CTBN-MDA system. To establish the kinetics of the process according to eq. (6), we used a range of experimental temperatures between 80° and 120°C. As can be seen in Figure 7, in this interval of temperatures, the fit between the experimental and calculated values is very good. At temperatures of 60° and 150°C, outside the range of temperatures used to establish the kinetic equation, the fit is also quite good at the low-curing temperature. However, in the case of high temperature, the fit is not very good, probably due to the fact that, at this temperature, the curing process is too rapid and some of the reaction heat is released before the calorimeter can detect it. In these cases, we think that the simulation shows more correct results than the experimental ones. Therefore, the isothermal method used in this work may be very useful to predict curing kinetics and curing times for rapid

process at high temperatures, where the calorimeter does not have time to detect the start of the reaction.[15] From Figures 5 and 6, we can find that the results simulated by extrapolation of the eq. (6) fit the experimental data better than that by autocatalytical model, especially for high-curing

Figure 6 Comparison between experimental curves and data from the autocatalytic model for DGEBA-MDA.

Figure 7 Plots of reduced rate against degree of conversion for DGEBA-MDA at different temperatures.

temperature and a low degree of conversion. We compared the experimental curves with data calculated from a simple autocatalytical model[16]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1 - \alpha) \tag{9}$$

or

$$\frac{1}{1 - \alpha}\frac{d\alpha}{dt} = k_1 + k_2\alpha \tag{10}$$

Figure 7 shows that a linear relationship between the reduced rate and extent of reaction exists up to ~ 70% conversion for neat resin in our experiment. Similar curing behavior was observed for the sample contained in the CTBN component. Values of the preexponential factor and activation energy can be obtained. The kinetic parameters of the autocatalytic model was given as:

For the DGEBA-MDA system

$$k_1 = 4.58 \times 10^7 \exp\left(-\frac{65.5 \times 10^3}{RT}\right)$$

$$k_2 = 3.86 \times 10^4 \exp\left(-\frac{34.8 \times 10^3}{RT}\right) \tag{11}$$

For the DGEBA-CTBN-MDA system

$$k_1 = 3.86 \times 10^6 \exp\left(-\frac{52.4 \times 10^3}{RT}\right)$$

$$k_2 = 7.84 \times 10^4 \exp\left(-\frac{24.4 \times 10^3}{RT}\right) \tag{12}$$

It is interesting to note that there is no falloff in reduced rate observed as described by many researchers due to the onset of vitrification. After ~ 70% conversion, the curves deviated from the model equation. At higher curing temperatures, the graphs shows a slight retardation in rate followed by a sudden increase in the gradient. With decreasing the curing temperature, this deviation appears early. It may be attributed to the differences in the relative reactivities of primary and secondary amines or may be ascribed to the reaction no longer fitting the autocatalytic model.

Effect of Vitrification

As described previously, the reactive system can vitrify for the low-curing temperatures, which dramatically affects the progress of the curing reaction, because the reaction process becomes practically diffusion-controlled.

Vitrification involved a physical transformation from a liquid or rubbery state to a glass state as a result of an increase in crosslinking density of the sample. It is well known that this phenomenon occurs when the glass transition temperature, T_g, becomes equal to the curing temperature, T_c.[12,17] For a given curing temperature, as would be expected, the T_g increases and the residual heat of curings decreases with the curing time as a consequence of the increase in the degree of crosslink. The higher the curing temperature, the shorter the time required to reach the maximum glass transition temperature, $T_{g\infty}$, of the resin will be. Figure 8 is a plot of T_g to curing time at curing temperatures of 80°C and 120°C. The reaction time and degree of conversion required to reach $T_g = T_c$ is defined as vitrification time t_v and α_v. The values of t_v at different T_c can be obtained from T_g *versus* time as shown in Figure 8, and α_v was calculated from the residual heat involved at t_v. It is clear from Table II that vitrification was practically involved in the curing temperature of 80°C, because the degree of cure is only ~ 0.76 when vitrification occurs. For the high-curing temperature, vitrification is negligible because the curing reaction at t_v is approximately completed, although the curing tempera-

Figure 8 Dependence of T_g on curing time at different temperatures for both systems.

Figure 9 Logarithm of time to fixed T_g versus $1/T_c$.

ture is still lower than the maximum glass transition temperature, $T_{g\infty}$.

In the rubber (CTBN)-modified epoxy system, microphase separation usually occurs before gelation and vitrification (reaction-reduced phase separation).[18,19] A decrease in glass transition temperature was observed because part of the rubber remained dissolved in the matrix at the end of the phase separation (i.e., complete exhaustion of the rubber was not possible). However, from Figure 8 and Table II, we can find, for the DGEBA-CTBN-MDA system, the glass transition temperatures at the different curing temperatures are higher than that in DGEBA-MDA at the early stage of reaction, especially at the low-curing temperature. This result certified that the rubber component (CTBN) markedly accelerates the curing reaction as described previously, thus increasing the crosslinking degree. Meanwhile, as shown in Table II, the glass transition temperatures ($T_{g\infty}$) under isothermal

scans were always lower than that by dynamic cure. It can be attributed to the slight degradation of samples cured in isothermal conditions, because a relatively long time is necessary to complete the final cure.

Correlation between curing time and corresponding curing temperature for a given glass transition was obtained by DSC scans of partially cured samples. A log plot curing time t as a function of curing temperature is given in Figure 9. The observed dependence of t and T_c can be described by the following exponential equation. The same relationship between T_g and curing temperature T_c was also observed.

$$t = 7.76 \times 10^{-11}\exp(3.67 \times 10^4/RT_c) \quad (11)$$

$$T_g = 1.32 \times 10^{10}\exp(-2.86 \times 10^4/RT_c) \quad (12)$$

CONCLUSIONS

In this work, the isothermal cure behavior has been investigated for the DGEBA-MDA and

Table II   Effect of Curing Conditions on Vitrification

	80°C		100°C		120°C		Dynamic Condition
	$T_{g\alpha}$ (°C)	α_v	$T_{g\infty}$ (°C)	α_v	$T_{g\infty}$ (°C)	α_v	T_g (°C)
DGEBA-MDA	116.4	0.76	134.2	0.89	155.2	0.96	165.4
DGEBA-CTBN-MDA	113.5	0.86	123.6	0.93	149.4	0.97	156.5

DGEBA-CTBN-MDA systems. The results lead to the following conclusions.

The kinetic results showed that curing of epoxy resins involves different reactive processes and reaction stages for both systems. The value of activation energy is dependent on the degree of conversion. Although a single activation energy as a descriptive parameter of the kinetics of the curing process is obtained, the autocatalysis and the change in mechanism from chemical kinetic control by diffusion can be reflected in the results obtained from this proposed model. Moreover, the curing kinetics fit the experimental data well and can predict the values of curing time for a given conversion inside or outside the range of experimental temperatures, and makes it possible to characterize the curing in the different stages through which it passes even if at a high-curing temperature. The rubber component did not decrease T_g as generally expected at low-curing temperatures, especially at the early stage of reaction, because it effectively accelerates the curing reaction and increases the crosslinking degree.

REFERENCES

1. Oishi, T.; Fujimoto, M. J Polym Sci Part A 1992, 30, 1821.
2. Turi, E. A. Thermal Characterization of Polymer Materials; Macmillan Publishing Company, Inc.: New York, 1987.
3. Prime, R. B. Polym Eng Sci 1973, 13, 365.
4. Horie, K.; Hiura, H.; Sawada, M.; Mita, I.; Kambe, H. J Polym Sci A-1 1970, 8, 1357.
5. Ryan, M. E.; Dutta, A. Polymer 1979, 20, 203.
6. Kim, S. W.; Lu, M. G.; Shim, M. J. Polymer J 1998, 38, 80.
7. Lu, M. G.; Shim, M. J.; Kim, S. W. Thermochem Acta 1998, 323, 37.
8. Lu, M. G.; Shim, M. J.; Kim, S. W. Polym Eng Sci, to appear.
9. Sourour, S.; Kamal, M. R. Thermochim Acta 1976, 14, 41.
10. Rozenberg, B. A. Adv Polym Sci 1967, 11, 2343.
11. Dutta, A.; Ryan, M. E. J Appl Polym Sci 1979, 24, 635.
12. Bajaj, P.; Jha, N. K.; Kumar, R. A. J Appl Polym Sci 1990, 40, 203.
13. Hill, C. G. An Introduction to Chemical Engineering Kinetics and Reactor Design; Wiley: New York, 1977; Chapter 12.
14. Kretzschmar, K.; Hoffmann, K. W. Thermochim Acta 1985, 94, 105.
15. Salla, J. M.; Ramis, X. J Appl Polym Sci 1995, 51, 453.
16. Barton, J. M. Adv Polym Sci 1985, 72, 111.
17. Gillham, J. K. Polym Eng Sci 1987, 26, 1429.
18. Montarnal, L. T.; Gillham, J. K.; McPherson, C. A. J Appl Polym Sci 1981, 26, 889.
19. Chen, T. K.; Jan, Y. H. J Mater Sci 1992, 27, 111.