Characteristics of Medical Polymer Based on an Epoxy Resin System—Curing Reaction Characteristics of Biphenol Epoxy Monomer with Phenolic Functional Hardeners

S. W. KIM,[1] M. G. LU,[1] M. J. SHIM[2]

[1] Department of Chemical Engineering, The University of Seoul, 90 Jeonnong-Dong, Dongdaemun-Gu, Seoul 130-743, Korea

[2] Department of Life Science, The University of Seoul, Seoul 130-743, Korea

ABSTRACT: The reaction kinetics of a biphenyl epoxy/polyol system was characterized by an isoconversional mode under dynamic conditions using differential scanning calorimetry (DSC) measurements. The results showed that the curing of epoxy resins involves different reaction stages and the values of activation energy is dependent on the degree of conversion. At the initial stage of cure, the phenol hydroxyl-epoxy reaction is predominant, then the hydroxyl group generated during curing can catalyze the reaction. The results were supported by the isothermal experiments. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1495–1503, 2001

Key words: curing of polymer; DSC; liquid–crystalline polymer; thermosets

INTRODUCTION

Epoxy–novolac systems have been widely used as the base material of epoxy molding compounds for integrated circuits packaging.[1,2] Currently, the trend in integrated circuits (IC) packaging is towards to the surface mount type. These packages are typically thinner than conventional packages; moreover, this surface mount technology allows for packages to be soldered to both sides of a circuit board, thus doubling the available space. The solders widely used for connecting electronic parts on the substrates are Pb-Sn eutectic solders. Although this eutectic solder has been suc-

cessfully developed environmental regulations can limit its use. Lead-free solders have been newly developed for this reason. In the soldering process, the whole package and the circuit board are exposed to the high temperature. As a result, the body of a surface mount package is rapidly heated to 215–260°C for up to 2 min compared to less than 150°C for the insertion-mounted package (only leads soldered). Due to the thermal mismatch between the silicon IC and the organic substrates, the temperature cycling excursions generate tremendous thermo-mechanical stress. Any moisture absorbed by the encapsulant exacerbates the package cracking problem because the moisture is rapidly turned to steam during the solder-reflow step, leading to package swelling and fracture of the mold compound (popcorning).[3–5]

Among the many factors that can influence package cracking, possible improvements in the molding compound have generated the most in-

terest. Most of the discussion has centered on improvements in three broad categories: increased high temperature strength, lower moisture absorption, and better adhesion. As known, mutifunctional resins can increase thermal resistance. However, they are difficult to handle as liquid because of their extremely high viscosity at room temperature. Hydrophobic resins and hardeners can lower moisture absorption, but it is done at the expense of high-temperature properties. Therefore, the largest benefit will result from the resin composition that have good thermal-mechanical property; at the same time, have low viscosity that allows the high filler loading to ensure the minimized moisture absorption.

In our previous work, we found that the biphenyl epoxy resins having a mesogen skeleton are excellent in heat resistance and mechanical strength, and with very low viscosity when melted associated with their liquid crystal structures,[6] so they can be used in a field of molding of semiconductor devices to improve the solder reflow resistance of epoxy resin composition. Recently, several results have been reported on the modification of biphenyl epoxy resins to prevent this crystalline resin from depositing out during kneading and extremely lowering its viscosity when melted.[7,8] However, it is necessary to conduct the systematic studies to optimize the resin composition, processing condition, and to find out the relationship between structure and property for the final industry applications.

Many studies have been done to clarify the reaction between epoxides and phenols, Shechter and Wynstra,[9] and Sorokin and Shode[10] studied the base-catalyzed epoxide/phenol reaciton in solvents. Banthia and McGrath[11] proposed a mechanism for the triphenylphosphine (TPP) catalysis of the reactions between epoxides and phenols, and concluded that little or no side reaction of epoxy with secondary hydroxyls took place. Biernath and Soane[12] developed a semiempirical rate law that describes the epoxy/phenol reaction catalyzed by TPP, and proposed a reaction mechanism for the curing process. In our previous work, we reported the LC phase change and curing reaction between biphenol epoxy and aromatic diamine.[13] Reaction kinetics of epoxy/novolac with and without a catalyst were also reported.[14]

However, in the previous work, the reaction kinetics were analyzed by the homogeneous reaction model, normally using autocatalytic or an *n*-order equation. In this model, 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. In this present article, the cure reaction of a biphenol epoxy/polyol system was characterized using an isoconversional model that does not require the knowledge of a reaction rate equation, and can give the curing behavior at a different content of conversion. We found that the experimental results from dynamic and isothermal conditions were fit well, and the activation energy of curing was practically dependent on the fractional conversion.

Theoretical Analysis

Differential scanning calorimetry (DSC) is an effective method to monitor the cure kinetics. Under the basic assumption that heat flow relative to the instrumental baseline is proportional to the reaction rate

$$\frac{dQ}{dt} = Q_{rxn} \frac{d\alpha}{dt} \tag{1}$$

where dQ/dt is a specific heat flow, Q_{rxn} is the total heat released when an uncured material is taken to complete cure, $d\alpha/dt$ is the cure rate, and α is the extent of cure. The value of Q_{rxn} can be determined by integrating a DSC peak

$$Q_{rxn} = \int_0^{t_f} \frac{dQ}{dt} dt \tag{2}$$

where t_f is the time to completion of cure. In fact, t_f is the time at which the heat flow drops below the sensitivity of a DSC instrument.

Therefore, the fractional conversion α can be defined as:

$$\alpha = \frac{1}{Q_{rxn}} \int_0^t \frac{dQ}{dt} dt \tag{3}$$

The obtained dependencies of $d\alpha/dt$ and/or α on t are used for kinetic analysis. Different models have been developed to describe the curing reactions of epoxides, including the *n*-th order reaction model, the autocatalytic reaction model, and the diffusion-control model. Recently, we have analyzed the curing process of both conventional epoxy and unsaturated polyester resins based on a isoconverional method, where it is not necessary

to assume a particular form of reaction model to evaluate the curing kinetics.

As known, 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:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{4}$$

or in the integrated form:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \tag{5}$$

where $k(T)$ is the rate constant. It can be described with the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \tag{6}$$

where A is the preexponential factor, E is the activation energy, and R is the gas constant. Then trivial rearrangements yield

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_i} \tag{7}$$

or in the integrated form:

$$-\ln t_{\alpha,i} = \ln\left[\frac{A_\alpha}{g_\alpha}\right] - \frac{E_\alpha}{RT_i} \tag{8}$$

Henceforth, the subscript α denotes the values related to a fixed conversion, and the subscript i is the ordinal number of an experiment.

EXPERIMENTAL

Materials

Epoxy resin used in this study is a mesogenic containing biphenyl epoxy obtained according to reported method previously by a base-catalyzed reaction of epichlorohydrin with the precursor dihydrobiphenyl.[15] The curing agent is a polyphenol compound obtained from phenol and p-hydroxybenzaldehyde using the known method as given below.[16]

Into a 1-liter four-neck flask equipped with a thermometer, a stirrer and a cooler were charged phenol (1 mol), p-hydroxybenzaldehyde (0.2 mol), and p-toluene sulfonic acid (1% mol of p-hydroxybenzaldehyde). The mixture was reacted at 150°C for 4 h, and further condensed under reduced pressure in the range of from 50 to 80 mmHg, while water and unreacted phenol was continuously removed. At the final stage, the reaction pressure was lowered to a value of 0.5 to 1 mmHg to completely remove excess phenol. A resulting product was obtained in a red-brown solid having a softening point of 118.6°C and a hydroxyl group equivalent of 99.

Sample Preparation

The stoichiometric ratio of epoxy to phenolic groups is 1 : 1. Benzyldimethylamine (1% mol) is used as a catalyst. The epoxy resin and curing agent were mixed thoroughly at 120°C until an homogeneous solution was obtained. This mixture was then cooled to 80°C, the catalyst was added, and stirred for about 30 s. The resulting sample was quenched immediately and stored in a refrigerator.

DSC Measurement

Approximately 10 mg samples of mixture were weighed accurately. Dynamic curing were performed in a Solomat DSC 4000 at different heating rates from 1 to 20°C/min under a nitrogen atmosphere. For isothermal experiments, the sample pan was placed in the DSC cell and heated at a high heating rate to the experimental temperatures. After all the isothermal curings a dynamic scan is conducted from 30–250°C at a heating rate of 10 K/min to determine the residual heat. More details about the calibration procedure and thermal conditions can be found elsewhere.[17]

RESULTS AND DISCUSSION

Dynamic Curing

The dynamic and isothermal scans of epoxy/polyol reaction at different heating rates and isothermal temperatures are shown in Figures 1 and 2. The reaction enthalpies Q_{rxn} can be estimated from a series of nonisothermal runs, which are conducted at 1, 5, 10, and 20 K/min. The curing reaction heats at different heating rates are listed
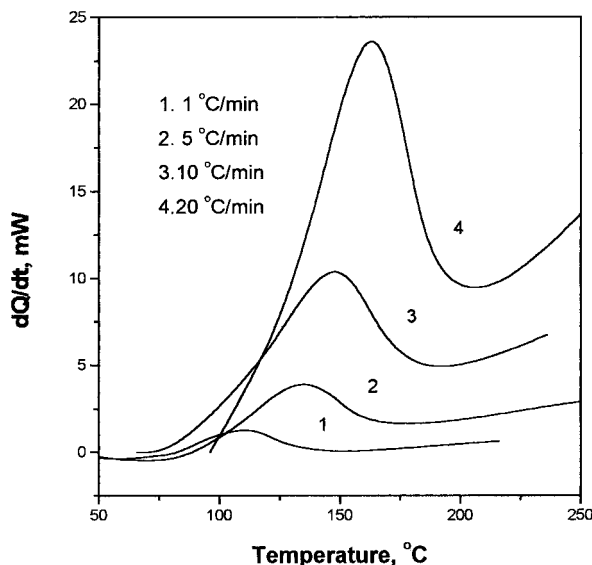
Figure 1 Dynamic scans at different heating rates.

Table I Reaction Heats at Different Heating Rates

Heating Rate, °C min^{-1}	Reaction Heat. Jg^{-1}
1	491.2
5	512.3
10	505.6
20	515.2

in Table I. Because the dynamically cured samples have not shown any noticeable residual heat upon the second heating, we assume that the cure reaction almost reaches completion under those nonisothermal conditions. The average value of Q_{rxn} was estimated to be 506 J/g.

The values of reaction heat under isothermal conditions were 346, 390, 425, and 481 J/g at temperatures of 100, 120, 140, and 160°C, respectively. This means that the ultimate conversion, α_c, under these curing conditions equals to 0.68,
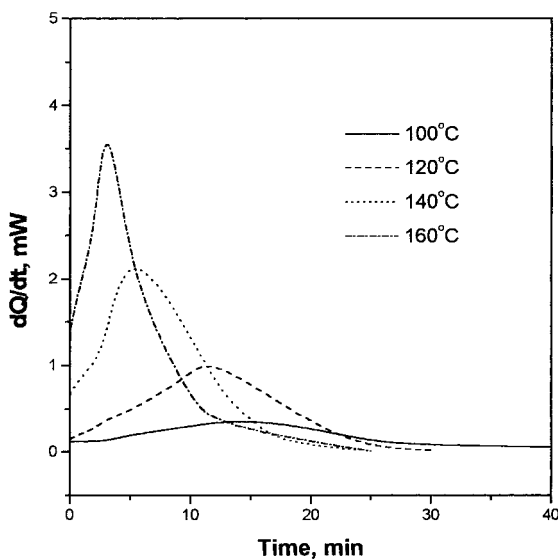

Figure 2 Isothermal curings at different temperatures.

0.77, 0.84, and 0.95, respectively. At the low temperatures, the curing did not reach completion. However, it should be mentioned that the values of conversion used in this study is relative extents of the cure, which can be obtained by dividing the absolute extent of cure α for each temperature over the corresponding value of the ultimate conversion, α_c, that is

$$\alpha' = \frac{1}{Q_T} \int_0^t \frac{dQ}{dt}\, dt \qquad (9)$$

where Q_T is the integrated heat release from a system cured at low temperature ($T < T_{g,\infty}$). Prime[18] pointed out that the use of the relative conversion instead of the absolute value may affect the kinetic evaluations. For isoconversional method, Salla and Ramis[19] have experimentally observed that the activation energy evaluated from the absolute and relative conversions are very close for the initial stage of cure (low conversion). For the incomplete cure, the effect is negligible when the relative conversion is used instead of the absolute value.

For nonisothermal conditions, when the temperature varies with time with a constant heating rate, $\beta = dT/dt$, eq. (4) is represented as follows:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (10)$$

Isoconversional kinetic analysis offers a viable alternative in this situation. The basic idea of this type of analysis is that $f(\alpha)$ has the same form regardless of the temperature for the same degree of conversion α, or say, the reaction rate at a constant conversion depends only on the temperature. For the differential isoconversional method [eq. (7)], the activation energy is determined as the logarithmic derivative of the cure rate at a fixed conversion over the reciprocal temperature
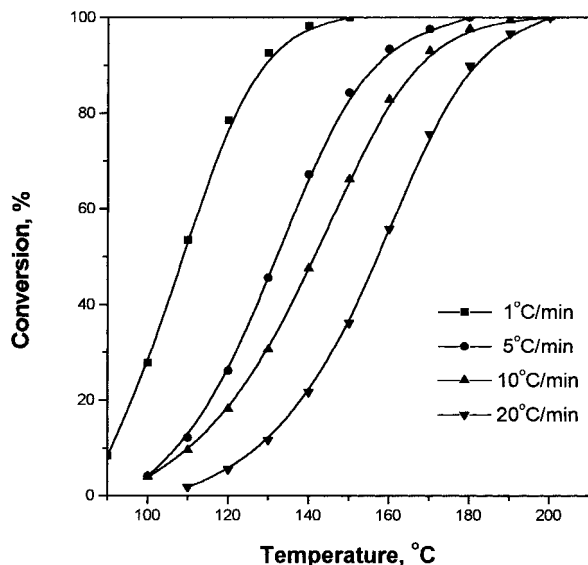
Figure 3 Fractional conversion as a function of temperature for various heating rates.

$$E_\alpha = -R \frac{d \ln(d\alpha/dt)_\alpha}{dT^{-1}}$$

$$= -R \left[\frac{d \ln k(T)}{dT^{-1}}\right]_\alpha + \frac{RT^2}{f(\alpha)} \left[\frac{df(\alpha)}{dt}\right]_\alpha \qquad (11)$$

where E_α is the effective activation energy at a given conversion. For a single-step process, E_α is independent of α and may have the meaning of the intrinsic activation energy. Multistep processes reveal the dependence of E_α and α, the analysis of which helps not only to disclose the complexity of a process but also to identify its kinetic scheme.[20]

The second term of the sum includes the temperature derivative of the reaction model at a constant conversion. It is clear that the value of the second term is always positive, which means that the respective E_α values should always be greater than the actual values of the activation energy. This deviation is expected to increase sharply at the fractional conversion close to α_e (the ultimate conversion) when $f(\alpha)$ approaches zero turning the second term of the sum in eq. (11) into infinity. However, the systematic error can be eliminated by replacing the absolute extent of cure with the relative value α'.

In practical, it is more convenient to use the integral forms of eq. (11). The derivative modes from Ozawa, Flynn, and Wall, and Dole[21–24] can be used to give the E_α from the plot $\ln(\beta_i/T_{\alpha,i}{}^2)$ or

$\ln\beta_i$ vs. $T_{\alpha i}{}^{-1}$ (here i is ordial number of DSC runs performed at different heating rate, β_i). The Kissinger mode was used to obtain the relationship of $E_\alpha \sim \alpha$.

The fractional conversion at different heating rates can be calculated by integrating the heating release. The relationship between conversion and curing temperature was shown in Figure 3. The isoconversonal plots by Kissinger mode were given in Figure 4, and the dependence of E_α and α for this epoxy/polyol system is presented in Figure 5 and listed in Table II. 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 sharply, and finally remains practically constant.

The dependence of activation energy on conversion clearly revealed the autocatalytic reaction that occurred in this system. At the initial stage of cure, the phenol hydroxyl-epoxy reaction is predominant; etherification occurs only at elevated temperatures once most phenol hydroxyls are exhausted. Therefore, the high activation energy value (107 kJ mol^{-1} at $\alpha \to 0$) at the lower conversion are attributed to phenol-epoxy addition. This value is markedly higher than the activation energy reported in the literature, where the activation energy was supposed to be constant throughout the entire cure process.[25–27] Because the hydroxyl groups formed during the cure facil-
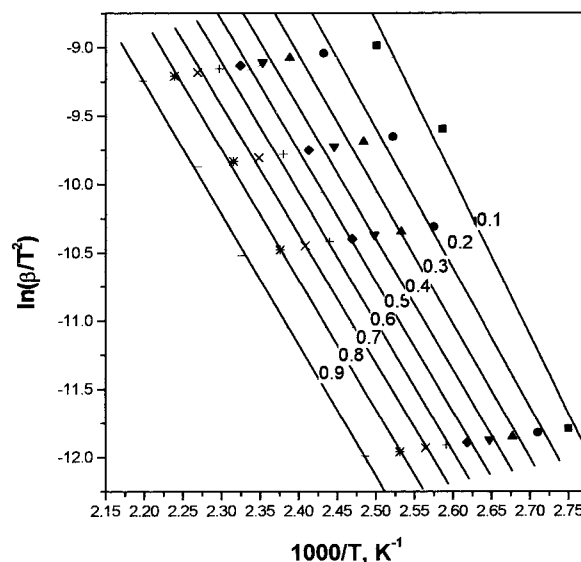

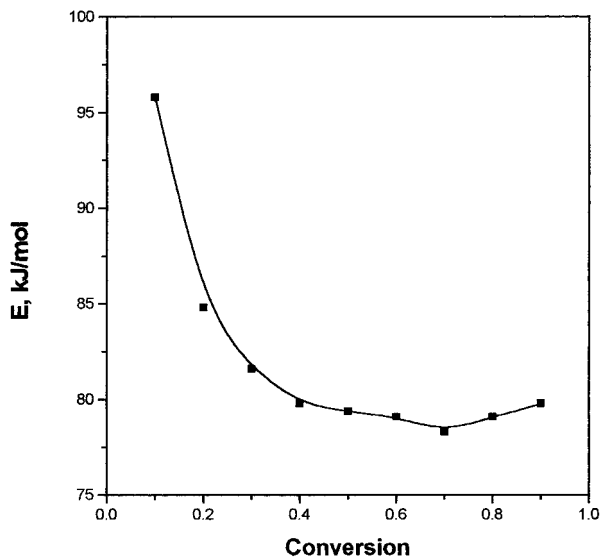**Figure 4** Isoconversional plots from different heating rates.

Figure 5 Activation energy as a function of conversion.

Figure 6 Kissinger plot from the maximum curing rates.

itate a ring opening, it is reasonable to expect a decrease in the activation energy compared with the very beginning of the cure where nonautocatalytic reaction occurs. Therefore, the constant activation energy value of 80 kJ mol^{-1} is associated with the autocatalytic reaction. It starts at a conversion of around 0.4. 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. In other kinetic models, the epoxy addition was considered as a single step so that the activation energy was supposed to be a constant. This

Table II   Kinetic Parameters Analyzed by the Iso-conversional Model

Conversion, %	Activation Energy E_a, kJ mol^{-1}	Preexponential Factor[28] A^a, min^{-1}
0.1	95.8	4.80×10^8
0.2	84.8	8.12×10^6
0.3	81.6	1.96×10^6
0.4	79.8	7.96×10^5
0.5	79.4	5.24×10^5
0.6	79.1	3.45×10^5
0.7	78.6	2.11×10^5
0.8	79.1	1.87×10^5
0.9	79.8	1.40×10^5
Average	81.9	—

^{a} $A = \beta E_{a,p} \exp(E_{\alpha,a}/RT_\alpha)/RT_\alpha^2$.

does not correspond to the autocatalytic mechanism of process. The reported low values of the activation energy are some practically average values between the activation energies of noncatalyzed and autocatalyzed reactions, being closer to the latter value. Vyazovkin et al.[29] studied the kinetic of the epoxy-novolac/amine system by the isoconversional model and observed the same tendency in change of activation energy with conversion. In our previously works,[30] a diffusion-control process was observed for a conventional bisphenol A epoxy/amine system at the final stage of curing ($\alpha > 0.8$) where the activation energy was decreased deeply. It may be associated with the mesogenic structure of epoxy resin. It is reported that the LC phase facilitate the decrease of viscosity.[13]

The preexponential factor can be calculated using the method given in ASTM E 698.[31] It assumes the extent of the reaction at the exotherm peak, α_p, is constant and independent of a heating rate. Based on the obtained linear relationship (Fig. 6) between the reciprocal of exotherm peak temperature (T_p) and the logarithm of the heating rate ($\ln\beta/T_p^2$), the activation energy can be obtained from the slope of the straight line, and preexponential factor be calculated:

$$A = \frac{\beta_i E_{a,p}}{RT_{p,i}^2} \exp\left(\frac{E_{a,p}}{RT_{p,i}}\right) \tag{12}$$

where T_p is the temperature at which maximum conversion rate occurs on DSC curve.

Table III   Calculation of Arrhenius Parameters by the ASTM E698-79 Method

β, K min^{-1}	T_p, K	α_p	10^{-8} A, min^{-1}	$E_{a,p}$, kJ mol^{-1}
1	383.9	0.52	5.69	
5	407.7	0.52	6.55	
				88.2
10	420.2	0.57	6.55	
20	436.5	0.58	5.53	

The preexponential factor generally reflects the collision frequency of the reactant molecules. During the early stages of the reaction, the monomer concentration is expected to be higher, and thus the preexponential factor is also higher. Higher temperature induces higher motion speed of molecules, and thus increases the possibility of collision and reaction rate. Equation (12) was also used to approximately calculate the preexponential factors at other different conversions.

The data from ASTM E698 are given in Table III. As can be seen, the activation energy obtained by this method seems to be a little lower than that by the iso-conversional analysis. This is not surprising, because the conversions at the exotherm peak are not a constant, as supposed, and the ASTM E698 method treats the complex cure process as a single-step reaction of the first order. Compared to the results of iso-conversional analysis, the activation energy evaluated by this method is a single point to the dependence of E on a at $\alpha = \alpha_p$.

Isothermal Curing

This LC epoxy-polyol system cured under dynamic conditions has shown an autocatalytic reaction mechanism. The kinetic can be simply described with the following expression.

The analysis of the reduced rate vs. fractional conversion can be used to check the validity of the assumed kinetic model

$$\text{Reduced rate} = \frac{1}{(1-\alpha)^2}\frac{d\alpha}{dt} = k_1 + k_2\alpha \qquad (13)$$

where k_1 is the reaction constant related to non-autocatalytic reaction, k_2 is the reaction constant related to autocatalytic reaction.

The relationship between the reduced rate and the fractional conversion is given in Figure 7. The plot shows three different regions. A first linear region followed by a second one with increased slope, and finally a third region with an abrupt decrease in the values of reduced rate. It is interesting to note that there is no fall-off in the reduced rate observed as described by many researchers due to the onset of vitrification. The detailed mechanism is still not clear now. It may be attributed to the transformation of reaction process. Under isothermal conditions, the reaction became diffusion-control, and the kinetic equation may not be suitable. Similar results have been found in the conventional epoxy resin systems when a high content of the filler was used.[17]

The reduced rate change with fractional conversion is in good agreement with the results by isoconversional analysis. The first linear segment in the curves indicates the epoxy/phenol group reaction until a fractional conversion of approximately 0.3–0.45. Then, the reaction rate increases due to the autocatalytic reaction until the reaction becomes diffusion controlled after the conversion of 0.7–0.8. The data from isothermal experiments were given in Table IV, where α_1 represents the beginning of autocatalytic reaction, and α_2 is the value of the fractional conversion from which eq. (13) is not suitable. It should be noted that the rate constants listed in Table III were the average values in the range of $\alpha = 0$
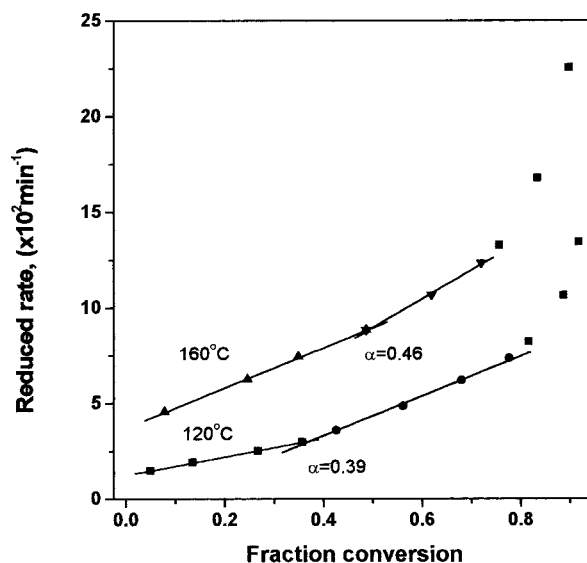

Figure 7   Reduced rate as a function of fractional conversion.

Table IV   Kinetic Parameters from Isothermal Experiments

Temp. °C	α_1	α_2	Rate Constant[a]	
			k_1, (min^{-1})	k_2, (min^{-1})
100	0.35	0.72		
120	0.39	0.78	7.35×10^6	7.96×10^9
			$\exp(-58.7/RT)$	$\exp(-86.1/RT)$
140	0.44	0.81		
160	0.46	0.75		

[a] The unit of the activation energy is kJ mol^{-1}.

$\sim \alpha_2$. The average values of activation energy for k_1, k_2 were 59 and 86 kJ mol^{-1}, respectively. It is resonable that the transformation of reaction rates shifted to higher fractional conversion as the isothermal temperature increased because the diffusion restriction occurs early at a lower temperature. Therefore, it would be expected that a better kinetic result can be completed using dynamic DSC measurements because they provide kinetic information over a larger temperature range, and there are no precure and vitrification problems as in the case with isothermal experiments.[32]

CONCLUSIONS

The kinetic results showed that the curing process of biphenol epoxy/polyol can be described using an isoconverisonal mode, and the effective activation energy is dependent on the conversion. At the early stage of cure, the reaction is mainly controlled by epoxy/phenol addition, then followed the autocatalytic process. It is in good agreement with the results from isothermal experiments. However, the diffusion-control step for this studied system was only observed in isothermal conditions.

REFERENCES

1. Tummala, R. R.; Rymaszewski, H. Y.; Klopfenstein, A. Microelectronics Packaging Handbook; Chapman and Hall, New York, 1997, p. 76, vol. 1.
2. Wong, C. P. Polymers for Electronic and Photonic Applications; Academic: San Diego, CA, 1993, p. 195.
3. Yang, W.-Li; Yin, D. M. S. Proc. 49th ECTC; 1999, p. 721.
4. Fukuzawa, I.; Ishiguro, S.; Nanbu, S. Proc. 26rd Int. Reli. Phys. Symp. 1988, p. 95.
5. Leong, T.; Beng, L. IEEE Singapore, IPFA, 1993, p. 170.
6. Lu, M. G.; Shim, M. J.; Kim, S. W. J Appl Polym Sci 2000 77, 1568.
7. U.S. Pat. 5,840,824 (1998).
8. U.S. Pat. 5,578,660, (1996).
9. Shechter, L.; Wynstra, J. J Ind Eng Chem 1948, 48, 86.
10. Sorokin, M. F.; Shode, L. G. Zh Org Khim 1966, 2, 1463.
11. Banthia, A. K.; McGrath, J. E. Polym Prepr 1979, 20, 629.
12. Biernath, R. W.; Soane, D. W. In Contemporary Topics in Polymer Science; Salamone, J. C.; Riffle, J., Eds.; Plenum Press: New York, 1992, p. 103, vol. 7.
13. Lu, M. G.; Shim, M. J.; Kim, S. W. Macromol Chem Phys 2001, 202, 223.
14. Gualpa, M. C.; Riccardi, C. C.; Vazquez, A. Polymer 1998, 11, 2247.
15. Lu, M. G.; Shim, M. J.; Kim, S. W. Kor Polym J 1999, 7, 304.
16. U.S. Pat. 5,149,730 (1992).
17. Lu, M. G.; Shim, M. J.; Kim, S. W. Polym Eng Sci 1999, 39, 274.
18. Prime, R. B. In Thermal Characterization of Polymeric Materials; Turi, E. A., Ed.; Academic Press: New York, 1997, p. 1380, 2nd ed.
19. Salla, J. M.; Ramis, X. Polym Eng Sci 1996, 36, 835.
20. Barton, J. M. Polymer 1980, 21, 604.
21. Irabien, A.; Santiago, C.; Araiz, A. J Therm Anal 1984, 29, 1131.
22. Ozawa, T. Bull Chem Soc Jpn 1965, 38, 1881.

23. Flynn, J. H. J Therm Anal 1983, 27, 95.
24. Doyle, L. D. Nature 1965, 207, 290.
25. Apicella, A.; Nicolais, L.; Iannone, M. J Appl Polym Sci 1984, 29, 2083.
26. Mijovic, J.; Fishbain, A.; Wijaya, J. Macromolecules 1992, 25, 986.
27. Chiao, L. Macromolecules 1990, 23, 1286.
28. Li, Y. S.; Li, M. S.; Chang, F. C. J Polym Sci Part A Polym Chem 1999, 37, 3614.
29. Vyazovkin, S.; Sbirrazzuoli, N. Macromolecules 1996, 29, 1867.
30. Lu, M. G.; Kim, S. W. J Appl Polym Sci 1999, 71, 2401.
31. Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials (ANSI/ASTM E698–79); ASTM: Philadelphia, 1979.
32. Lu, M. G.; Shim, M. J.; Kim, S. W. J Therm Anal Calor 1999, 58, 701.