Kinetics Analysis of the Curing Reaction of Fast Cure Epoxy Prepregs

L. F. YANG,¹ K. D. YAO,¹ W. KOH²

¹ Research Institute of Polymeric Materials, Tianjin University, Tianjin China, 300072

² Asian Manufacturing Research Center, Motorola China Electronics Ltd. No 10, 4th Avenue, TEDA, Tanggu, Tianjin, People's Republic of China, 300457

Received 14 July 1998; accepted 24 December 1998

ABSTRACT: In this article, the curing kinetics of two fast cure flip-chip epoxy encapsulants under both isothermal and nonisothermal conditions are investigated by differential scanning calorimetry. The method allows determination of the most suitable kinetic model and corresponding parameters. The kinetic analysis suggests that the two-parameter autocatalytic model is more appropriate to describe the kinetics of the curing reaction. There are certain differences between the kinetic data from isothermal and that from nonisothermal measurements. The apparent activation energy Ea and pre-exponential factor A of E-AB1 determined from nonisothermal experiments were higher than the isothermal values, whereas the Ea and A of E-RV2 determined from both methods are relatively close. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1501–1508, 1999

Key words: differential scanning calorimetry (DSC); epoxy resins; fast-cure; kinetic parameters

INTRODUCTION

The flip-chip solder bumped interconnection is typically packaged with underfill encapsulant. Epoxy encapsulants mechanically couple the chip and the substrate and decrease the stress in the solder joints, thereby enhancing solder fatigue life.^{1–3} The mechanical properties of the cured composites are determined by the degree of cure, which depends on the curing conditions. Therefore, a knowledge of cure rate is essential to get optimum cure conditions.

Many researchers have proposed various methods to study curing kinetics of epoxy systems. Differential scanning calorimetry (DSC) has been found to be a useful method with which to study

© 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/081501-08

exothermic curing reactions. Using DSC, kinetic analysis can be evaluated by isothermal and nonisothermal methods. By comparing the methods of kinetic analysis from isothermal and nonisothermal DSC measurements, it is evident that using the isothermal DSC experiment, the rate of the reaction as well as the extent of curing are monitored simultaneously during the course of the reaction. The kinetics parameters are calculated applying a simple method. However, it is a rather time-consuming method. The method using nonisothermal experiments is desirable because the kinetic data are obtained in a relatively short period of time. Nevertheless, there are some complications in the mathematical analysis of the temperature integral that are inherent to the nonisothermal approach.

Many articles have reported that there are certain differences between the kinetic data from isothermal and that from nonisothermal DSC

Correspondence to: K. D. Yao.

Journal of Applied Polymer Science, Vol. 73, 1501–1508 (1999)



Figure 1 Dynamic DSC thermal curves of the two samples.

methods. For example, Prime¹ found that for an epoxy-polyamide system, the apparent activation energy and pre-exponential factor determined from nonisothermal experiments were considerably higher than the isothermal values. However, rather good agreement between both isothermal and nonisothermal methods has been observed in other polymeric systems.^{2,3} There are few reports dealing with the comparative study on curing kinetics via the two methods.

In the present study, the curing kinetic of two epoxy encapsulants were investigated by both isothermal and nonisothermal DSC. This work will provide information for optimizing the curing conditions.

MATERIALS AND METHODS

The epoxy encapsulant samples were provided by Asian Manufacturing Research Center of Motorola China Electronics Ltd. The two materials are newly developed prepregs, which are being explored for applications in microelectronics. In



Figure 2 DSC curves of isothermal cure for E-AB1.



Figure 3 DSC curves of isothermal cure for E-RV2.

this study, the black sample will be termed E-AB1 and the red one will be termed E-RV2.

Values of the onset temperature (temperature where reactions occur) and reaction exotherm were measured using an American Perkin-Elmer Pyris 1 DSC analyzer at a heating rate of 10°C/min.

Isothermal Method

Isothermal DSC curves at curing temperatures of $130-170^{\circ}$ C were recorded directly in the calorimeter. The sample was placed in the DSC cell at ambient temperature and the temperature was increased at 60 K/min to the required curing temperature. After the isothermal curing measurements, the samples were scanned again at 10 K/min to obtain the residual heat.

Nonisothermal Method

Nonisothermal DSC curves were obtained at heating rates (5–30 K/min) from 50 to 300°C.

According to Equation 1, the degree of conversion, α , can be deduced from the DSC scans.

$$\alpha = 1 - \Delta H_R / \Delta H_T \tag{1}$$

where ΔH_R is the residual heat of reaction, ΔH_T is the total enthalpy of the reaction.

RESULTS AND DISCUSSION

An example of a 10° C min⁻¹ dynamic DSC thermal curves of the two samples are shown in Figure 1. The curve of E-AB1 shows a sharp exotherm that begins at ~ 143°C and ends at ~ 180°C, whereas E-RV2 shows a broader exotherm beginning at 120°C and ending at 180°C. However, the overall time for the reaction of E-RV2 is shorter than that of E-AB1.

Kinetic Analysis Using Isothermal Method

The kinetics of the curing reaction of two samples was investigated using isothermal DSC measure-

Table I	The Isothermall	y Curing Hea	t (ΔH iso) at Different	Temperatures
---------	-----------------	--------------	----------------------------------	--------------

			Curing Temperature (°C)					
		130	140	150	160	170	180	
The isothermally curing heat $(\Delta H iso, J/g)$	E-AB1 E-RV2	$\begin{array}{c} 125.1 \\ 62.9 \end{array}$	154.2 85	$151.6 \\ 109.6$	$160.4 \\ 105.6$	95.2 91	79.5 76.2	





Figure 4 Time dependencies of the isothermal cure degree for E-AB1.

ments. By this method, the rate of the reaction as well as the extent of curing are monitored simultaneously during the course of the reaction. Figures 2 and 3 display DSC of isothermal cure for the encapsulants. It can be seen that the cure rate of the systems increases with the reaction temperature. The curve pattern of E-RV2 is sharper than that of E-AB1. That means that the curing rate of E-RV2 is faster than that of E-AB1.

As listed in Table I, when the curing temperature was higher than 160°C, isothermal curing heat (ΔH iso) began to decrease. This may be because the reaction takes place very rapidly when

Table IIApparent Kinetic ParametersObtained from Isothermal Cure

		E-AE	31	E-RV2			
	m	n	$K \pmod{(\min^{-1})}$	m	n	$K \pmod{(\min^{-1})}$	
403	0.86	1.14	0.52	0.66	1.36	0.47	
413	0.74	1.26	0.87	0.56	1.44	0.56	
T423	0.72	1.28	1.55	0.52	1.48	1.16	
433	0.66	1.34	2.00	0.46	1.54	1.74	
443	0.6	1.4	3.75	0.4	1.6	2.53	
Ea	7	'1	66.51				
A	8.00E	2 + 08	$1.78E\ +\ 08$				

Figure 5 Time dependencies of the isothermal cure degree for E-RV2.

the temperature is too high, so that the heat evolved during the time required for temperature equilibration is not fully recorded in the DSC curves. Thus, it leads to a decrease in the values of ΔH iso. The maximum values of ΔH iso are obtained in the region of 150–160°C, which is the optimal range of curing temperature. In this range of temperatures, the values of (ΔH iso) are very close to those measured nonisothermally at 5 or 10 K/min.

Time dependencies of the isothermal curing degree calculated from calorimetric data are shown in Figures 4 and 5. The sigmoid shape of the curves reveals that the cure reaction follows an autocatalytic mechanism.⁴ By assuming the zero-initial cure rate, the autocatalytic cure rate equation is



Figure 6 The relationship of $\ln K \text{ vs } 1/T \times 10^3$.



Figure 7 DSC curves for the nonisothermal curing at different heating rates for E-AB1.

$$\frac{d\alpha}{dt} = K\alpha^m (1-\alpha)^n \tag{2}$$

be because the reaction mechanism varied with reaction temperatures since the epoxy resin system underwent a complex series of reactions.

$$\alpha_p = \frac{m}{m+n} \tag{3}$$

stant, and m, n are reaction orders. As listed in Table II, the reaction parameters K, m, and n could be calculated according to Equations 3, 4 and 5. The values of m, n varied within the temperature range studied. This might

where α is the degree of cure, K is the rate con-

where, α_p is the degree of cure at the exothermic peak.



Figure 8 DSC curves for the nonisothermal curing at different heating rates for E-RV2.

			Heating Rate (K/min)							
		2.5	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
The nonisothermally curing heat $(\Delta H$ niso, J/g)	E-AB1 E-RV2	167.1 83.9	123.5 78.7	118.5 75.6	112.6 67.7	103.8 65.8	$\begin{array}{c} 100.8\\ 63.5\end{array}$	98.6 55.5	$95.8 \\ 55.1$	94.5 58.4

Table III The Nonisothermally Curing Heat (ΔH niso) at Different Heat Rates

$$m+n=2\tag{4}$$

$$\frac{d\alpha_p}{dt} = K \frac{m^m n^n}{(m+n)^{(m+n)}} \tag{5}$$

As plotted in Figure 6, the relationship of K against 1/T is fitted well with the Arrhenius equation (Eq. 6). The activation energy Ea and pre-exponential factor A can be deduced from the equation (Seen in Table II).

$$LnK = A - Ea/RT \tag{6}$$

Kinetic Analysis Using Nonisothermal Method

The apparent kinetic parameters were also determined from the nonisothermal DSC curves applying Kissinger's methods.⁸ Figures 7 and 8 illustrate the DSC curves of the two uncured resins at different heating rates. It is observed that the peak temperature (Tp) of the exothermal curve tends to increase as the heating rate declines. The total enthalpy of curing (ΔH_{niso}) evaluated from the DSC curves are listed in Table III. It tends to increase as the heating rate declines, which coincides with other kinds of epoxy resins.⁴ This phenomena occurs because the reaction takes place very rapidly at higher curing temperatures. The curing heat evolved during the time required for temperature equilibration is not fully recorded in the DSC curves, which leads to a decrease in the value of (ΔH_{niso}) .

According to Kissinger's method, which follows from Equation 6, the overall apparent activation energy was determined via the peak temperatures of nonisothermal DSC curves at different heating rates (as shown in Fig. 9).

$$\frac{d\left[\ln\left(\frac{\phi}{Tp^2}\right)\right]}{d\left[\frac{1}{Tp}\right]} = -\frac{Ea}{R}$$
(7)

where ϕ is the heating rate, Tp is the peak temperature of the exothermal curve, Ea is the overall apparent activation energy, and R is the universal gas constant.

Once the activation energy has been known, the kinetic model from the nonisothermal DSC curves can be obtained based on Malek's method.⁹ The DSC data displayed in Figure 7 were converted to $y(\alpha)$ and $z(\alpha)$ functions, following Equations 8 and 9. These data normalized within the $\langle 0, 1 \rangle$ interval are plotted in Figure 10.

$$y(\alpha) = \phi e^x \tag{8}$$

$$z(\alpha) = \pi(x)\phi T/\beta \tag{9}$$

where, ϕ is the rate of heat flow, x = E/RT, $\pi(x)$ denotes an approximation of the temperature integral,⁶ β represents the heating rate, and *T* is the curing temperature.

As described in Stephan et al.,⁶ the shape of the $y(\alpha)$ function allows selection of the kinetic model. It is evident that the shape of all these functions is independent of the heating rate and the maximum is located in the interval $0.05 < \alpha_M$ $< \alpha_p$ (α_p being the conversion degree at the peak



Figure 9 Kissinger's method applied to the samples.



Figure 10 Normalized $y(\alpha)$ function. (a) and $z(\alpha)$ function (b) for E-AB1.

of the DSC curve.) The pattern of $y(\alpha)$ shown in Figures 10 and 11, together with the data in Table IV, indicate that the two-parameter auto-catalytic model is better for describing the curing reaction than the reaction order model.

As for the SB (m, n) model, the kinetic parameter ratio P can be calculated from Equation 10,

whereas the parameter *n* corresponds to the slope of the linear dependence $\ln[(d\alpha/dt)e^x]$ vs $\ln[\alpha_p(1 - \alpha)]$ for $\alpha \in (0.5, 0.9)$ according to Equation 11, and at the same time, the pre-exponential factor *A* was also obtained. Then the second kinetic exponent *m* was calculated from m = pn.

$$P = \alpha_M / (1 - \alpha_M) = m/n \tag{10}$$



Figure 11 Normalized $y(\alpha)$ function. (a) and $z(\alpha)$ function (b) for E-RV2.

Encapsulants	$lpha_M$	α_p	$lpha_p^{\infty}$
E-RV2 E-AB1	$\begin{array}{c} 0.39\\ 0.43\end{array}$	$\begin{array}{c} 0.47 \\ 0.53 \end{array}$	$0.57 \\ 0.6$

Table IV Average Values of α at the Maximum of the $y(\alpha)$ Function (α_M) and $z(\alpha)$ Function (α_n^{α}) for the Encapsulants

$$\ln[(d\alpha/dt)e^x] = \ln A - n \,\ln[\alpha^p(1-\alpha)] \quad (11)$$

Then the rate constant of curing was determined following the Arrhenius equation.¹⁰ The results are listed in Tables V and VI.

CONCLUSIONS

From these results, the following conclusions are drawn:

- 1. The two encapsulants can be fully cured in less than 10 min at 160°C.
- 2. The curing process of two fast cure encapsulants was monitored by different methods. The sigmoid shape of the time dependencies of isothermal curing degree implied that the processes could be described by a two-parameter auto-catalytic model, which coincides with the kinetic analysis from the nonisothermal DSC curves.
- 3. Certain differences between the kinetic data from isothermal and nonisothermal measurements have been observed. How-

Table VApparent Kinetic Parameters ofCuring Obtained from Nonisothermal Cure

		E-AB1			E-RV2		
		m	n	${{\rm Ln} A\over ({\rm min}^{-1})}$	т	n	${{\rm Ln} A\over ({\rm min}^{-1})}$
Heating rate (β, K/min)	5.0 10 20 30	0.76 0.74 0.63 0.91	1.17 1.19 1.35 1.02	$22.3 \\ 22.2 \\ 21.8 \\ 21.4$	0.33 0.47 0.53 0.41	0.82 0.7 0.76 0.73	$22.2 \\ 17.9 \\ 18.2 \\ 22.4$
Mean		0.76	1.19	21.9	0.43	0.75	20.2

Table VIThe Apparent Kinetic Parameters ofthe Nonisothermal Cure

Encapsulant	Ea (kJ/mol)	A (min	$1^{-1})$	k ₂₅ (min	$^{\circ C}$	$\underset{(\min^{-1})}{\overset{k_{160^{\circ}\mathrm{C}}}{\mathrm{(min^{-1})}}}$
E-RV2 E-AB1	$65.79 \\ 74.95$	5.93E - 3.24E -	+ 08 + 09	1.54E 4.03E	- 04 - 05	$\begin{array}{c} 0.61 \\ 0.5 \end{array}$

ever, the relationship between the kinetic parameters from isothermal and dynamic experiments is dependent on different epoxy systems. The apparent activity energy Ea determined from the isothermal DSC curves are 66.51 kJ/mol for E-RV2 and 71 kJ/mol for E-AB1, respectively, and those obtained from the nonisothermal DSC curves are 65.79 kJ/mol for E-RV2 and 74.95 kJ/mol for E-AB1, respectively. The pre-exponential factor A are 1.78E + 08 for E-RV2 and 8E + 08 for E-AB1 and those obtained from the nonisothermal DSC curves are 5.93E + 08 for E-RV2 and 3.24E + 09 for E-AB1.

The commercial epoxy prepolymers and equipment were kindly donated by Motorola (China) electronic company.

REFERENCES

- 1. Prime, R. B. Polym Eng Sci 1973, 13, 365-370.
- Gonzalez-Romero, V. M.; Casillas, N. Polym Eng Sci 1989, 29, 295–302.
- Kenny, J. M.; Trivisano, A. Polym Eng Sci 1991, 31, 1426–1430.
- Lee, J. Y.; Shim, M. J.; Kim, S. W. Mater Chem Phys 1997, 48, 36–40.
- Park, C. E.; Han, B. J.; Bair, H. E.; Raju, V. R. J Mater Sci Lett 1997, 16, 1027–1029.
- Stephan, F.; Fit, A.; Duteurtre, X. Polym Eng Sci 1997, 37, 436–449.
- Montserrat, S.; Andreu, G.; Cortes, P., et al. J Appl Polym Sci 1996, 61, 1663–1674.
- 8. Kissinger, H. E. Anal Chem 1957, 29, 1702-1710.
- 9. Malek, J. Thermochim Acta 1992, 200, 257-263.
- Crane, L. W. J Polym Sci, Polym Lett 1973, 11, 533–541.