Thermal Analysis of Curing Process of Epoxy Prepreg

LIANGFENG SUN,[1] SU-SENG PANG,[2] ARTHUR M. STERLING,[1] IOAN I. NEGULESCU,[3] MICHAEL A. STUBBLEFIELD[4]

[1] Department of Chemical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803

[2] Department of Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana 70803

[3] School of Human Ecology, Louisiana State University, Baton Rouge, Louisiana 70803

[4] Center for Energy and Environmental Studies, Southern University, Baton Rouge, Louisiana 70813

ABSTRACT: The curing process of epoxy prepreg was studied by means of differential scanning calorimetry analysis. The dynamic, isothermal, and combinations of dynamic and isothermal measurements were done over selected temperature ranges and isothermal cure temperatures. The heats of reaction for dynamic and isothermal cure were determined. The results show that the heat of the isothermal-cure reaction increased with the increment of temperature. The degree of cure was calculated from the heat of the isothermal-cure reaction. The complete cure reaction could be achieved at 220°C within a very short cure time. The changes of cure rate with time were given for the studied isothermal cure temperatures. To simulate the relationship between the cure rate and degree of cure, the autocatalytic model was used and the four parameters were calculated. Except in the late stage of the cure reaction, the model agrees well with the experimental data, especially at high temperatures. To account for the effect of diffusion on the cure rate, a diffusion factor was introduced into the model. The modified model greatly improved the predicted data at the late stage of cure reaction. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1074–1083, 2002

Key words: epoxy prepreg; cure kinetics; autocatalytic model; DSC

INTRODUCTION

Epoxy resins and epoxy prepreg are important thermosetting polymers. Their applications as composite materials are under continuing development in many fields. Various composite products are produced from epoxy prepregs. Epoxy prepregs are the fiber-reinforcing materials im- pregnated with epoxy resin, which are to be molded to the desired shape according to the needs of the final products, and cured by the application of heat.

A number of methods have been used to study the curing process of epoxy resin and epoxy prepreg.[1–4] Differential scanning calorimetry analysis was frequently reported in recently published studies.[5–7] It is assumed that the cure reaction heat equals the total area under the heat flow–time curve. The degree of cure is then determined from the cure reaction heat.

The simple model applied to the DSC data is the model from the *n*th order reaction mechanism. This model gave good fit to the experimental data only in the limited range of degree of

---

conversion.[8] A more complicated model for isothermal cure reaction assumed the autocatalytic mechanism.[9,10] The autocatalytic model may have different forms depending on whether the value of initial cure rate is zero or not. The results from the DSC analysis showed that the cure reaction of an epoxy resin system could be better described by an autocatalytic model.[11,12]

The studies on epoxy prepreg as joints to composite pipe systems by a heat-activated method were previously reported.[13] We are presently working to join composite-to-composite pipes with different joint configurations. To optimize the curing process for this application, it is necessary to understand the cure mechanism of epoxy prepreg in more detail. In this study, we analyzed the isothermal cure process of epoxy prepreg with the autocatalytic model at a series of cure temperatures with and without diffusion control.

EXPERIMENTAL

Materials

The commercial prepreg used as a sample in this study was 8552 Epoxy Matrix, which is an amine-cured epoxy resin system. It was supplied by Hexcel Corp. and contains about 33% resin with reinforcement of carbon fiber.

Methods

A differential scanning calorimeter (Seiko, Japan) was used to measure the heat flow change during the curing process. To prepare the samples, the prepreg was cut into very small pieces and put into an aluminum pan, after which the pan was sealed. By the recommendation of the Seiko instrument, the amount of sample was in the range of 7 to 10 mg. A larger sample size could increase the signal of the heat flow, but it would increase the temperature gradient inside the sample. The reference was an empty aluminum pan with cover. The purging gas was nitrogen. The flux of nitrogen was set to 100 mL/min. The sampling time was set to 6 s for all the isothermal runs in the temperature range between 100 and 200°C. The sampling time for the remaining runs was set to 3 s.
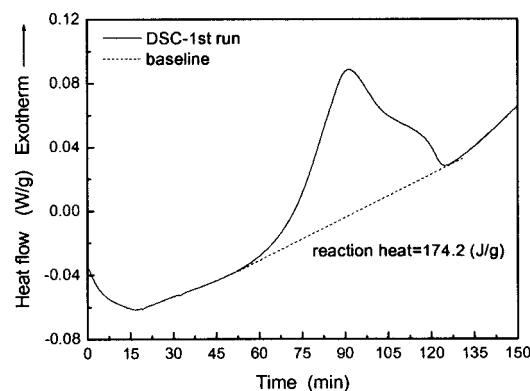
RESULTS AND DISCUSSION

Heat Flow Change with Time and Cure Reaction Heat

During the curing process, the instrument records the heat flow change with the cure time
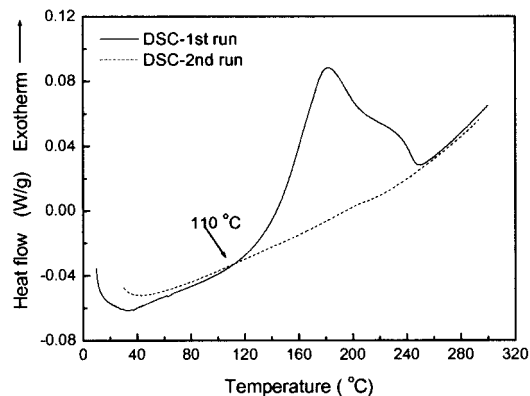
(a)

(b)

Figure 1 Dynamic cure from 30 to 300°C with heating rate of 2°C/min. (a) Heat flow as a function of temperature; (b) heat flow as a function of time.

based on the sample size. For the purpose of comparison, the heat flow for each run was normalized. Both dynamic and isothermal measurements were done to obtain more information about the curing process. For dynamic measurements, the sample was scanned with different heating rates from −5 to 300°C. Figure 1 gives the heat flow change at the heating rate of 2°C/min in the temperature range from 30 to 300°C. Figure 1(a) shows the difference between the first and second runs, as well as their changes with temperature. The sample for the second run was from the sample in the first run after it was cured. It was indicated that the appreciable cure reaction took place at about 110°C. Figure 1(b) shows the change of heat flow with time for the sample in the first run. A linear baseline between the onset and ending temperatures of the polymerization was selected relative to the peak, and the

area under the peak for the first run was then integrated by software. We assumed that the value of the area equals the reaction heat of dynamic cure. The dynamic reaction heat thus obtained is about 174.2 J/g, a value that is close to the reaction heat cured isothermally at 220°C (discussed later).

With information from the dynamic cure, a series of isothermal measurements were performed, starting from 110°C. Two runs were made on each sample. To achieve almost constant heat flow in the late cure stage, the measurement time was set long enough, from 100 min at 220°C to 720 min at 110°C. After the first run, the sample was left in the cell of the instrument to cool naturally to room temperature. The second run at each temperature was repeated with the same procedure and cure condition as for the first run. The heat flow was plotted against cure time for the first and second runs at each cure temperature. As shown in Figure 2, each curve for the first run exhibits a peak and finally becomes horizontal, whereas the curve for the second does not. Similar dynamic behavior between the two samples is seen in Figure 1. Except for the start-up of the isothermal measurement, the curve for the second run is almost horizontal over the whole cure time. This indicates that the isothermal cure reaction is almost complete after the first run at each cure temperature. The curve for the second run can be used as the baseline to the first run to integrate the area under the peak of the first run. This area is thought to be the isothermal cure reaction heat. The values for the isothermal cure reaction heat are also given in Figure 2.

It must be mentioned that the curve for the second run in Figure 2, at each temperature, was shifted along the heat flow axis and used as the baseline for the purpose of the calculation of the cure reaction heat only. Usually the curve for the second run needs to be shifted to have the same heat flow as the first runs at the end of their cure reactions. The experimental points in the last 10 min for both runs were averaged and the difference of the average values was calculated. The curve for the second run was then shifted up or down, depending on whether the average value in the last 10 min for the second run was greater or less than that for the first run. The magnitude of the shift at each temperature was different, ranging from -1.2 to 1.5×10^{-3} W/g or from -2.9 to 5.9% of the value to be shifted. Reasons to shift the curve for the second run are as follows:
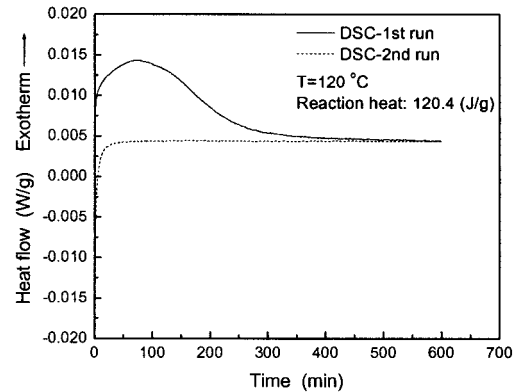
(a)
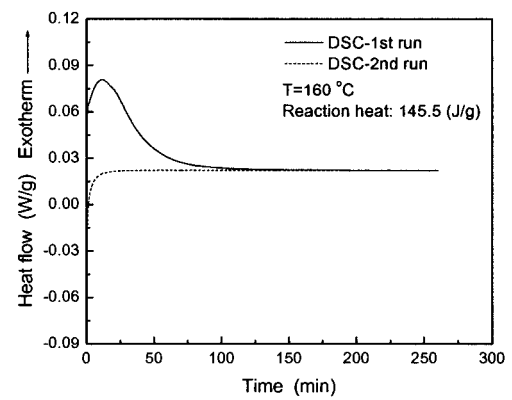
(b)
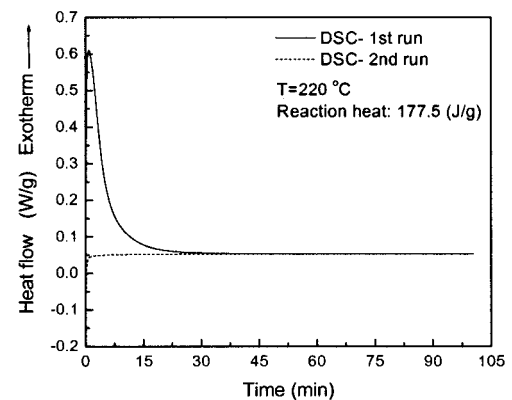
(c)

Figure 2   Isothermal cure of epoxy prepreg at different temperatures for varying times: (a) 120°C for 600 min with reaction heat of 120.4 J/g; (b) 160°C for 260 min with reaction heat of 145.5 J/g; (c) 220°C for 100 min with reaction heat of 177.5 J/g.

• At the end of the first run, the curve becomes almost horizontal; this means that the curing reaction is almost complete at the end of the first run at that temperature.
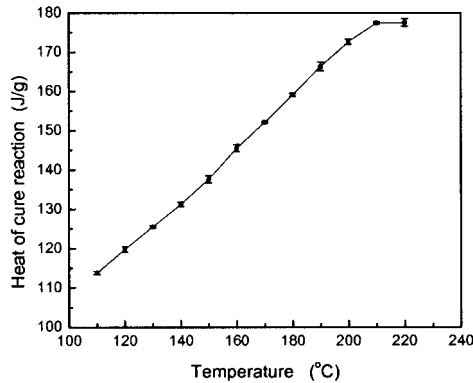
Figure 3 Heat of reaction for isothermal cure of epoxy prepreg as a function of temperature.

- For the second run, the sample has already been cured. The cured sample at the end of the first run should be the same as the sample in the second run, so they should have the same heat capacity and heat flow so long as the temperature profiles are the same.
- If there is a difference of heat flow between the end of the first run and the second run, it should result from the different initial conditions. It is difficult to control all conditions such that the same initial heat flow value will occur, even if all of the operating procedures at the start of the first and second runs are practically the same.

At different cure temperatures, the isothermal cure heat is different and its value increases with the increment of temperature. When the cure temperature was raised to 220°C, the cure heat was 177.5 J/g. This value is thought to be the total reaction heat of the isothermal cure because it is very close to the isothermal cure heat of 177.1 J/g at 210°C, which means that no additional cure heat was released and the cure reaction was complete at 220°C. This is supported by the experimental results from a combination of dynamic and isothermal cures, discussed next. All of the other values for reaction heats cured isothermally below 220°C were considered as the partial isothermal reaction heats. Figure 3 shows the relationship between reaction heat and cure temperature. The data were averaged from at least three separate measurements.

The experimental result obtained by the isothermal cure was confirmed by the combination of dynamic and isothermal cures. Several measurements with the combination of dynamic and iso-

thermal cures were done. The sample was first heated to the desired temperature at the rate of 1°C/min, held at that temperature for 80 min to allow the sample to achieve complete isothermal cure, then cooled down to 20°C, and finally reheated to 300°C at the same heating rate. Figure 4 shows the heat flow change with time. Each one has four or five positive peaks and three negative peaks. The first positive peak is from the normal cure reaction, which is an exothermic peak. The fifth positive peak, if it exists, comes from the residual cure reaction, which is also an exothermic peak. The other positive and negative peaks result from the sudden changes of the heating rate, which consequently cause the sudden changes of the heat flow. So they are not actually the exothermic or endothermic peaks. The residual reaction heat was calculated by integrating the area under the peak with the linear baseline between the onset and ending temperatures of polymerization. The sample after the isothermal cure at 180°C has the residual reaction heat of 18.6 J/g. This value is very close to 18.1 J/g, the difference of isothermal reaction heats at 180 and 220°C. The residual reaction heats after cure at 190 and 200°C are 12.3 and 6.1 J/g, respectively. The differences of isothermal reaction heat at 190 and 200°C to that at 220°C are 10.4 and 5.3 J/g, respectively. After isothermal cure at 220°C, the residual reaction heat is zero. This proves that the complete isothermal cure reaction could be achieved at 220°C and that the cure reaction heat obtained by the above method is reliable.

Degree of Cure and Cure Rate

The curing process is an exothermic reaction. The cumulative heat generated during the process of reaction is usually related to the degree of cure. It is assumed that the degree of cure is proportional to the reaction heat. One commonly used method assumes that the degree of cure equals the ratio of the difference between total and residual reaction heat to the total reaction heat. The sample is prepared and partially cured for a series of times at a certain temperature before measurement. Its residual heats are then measured. This method takes much time to prepare the partially cured sample. In our experiments, the sample used was fresh and uncured. Its reaction heat at each sampling time was determined by integrating the curve of heat flow from the beginning to the determined time, so the degree of cure can be di-
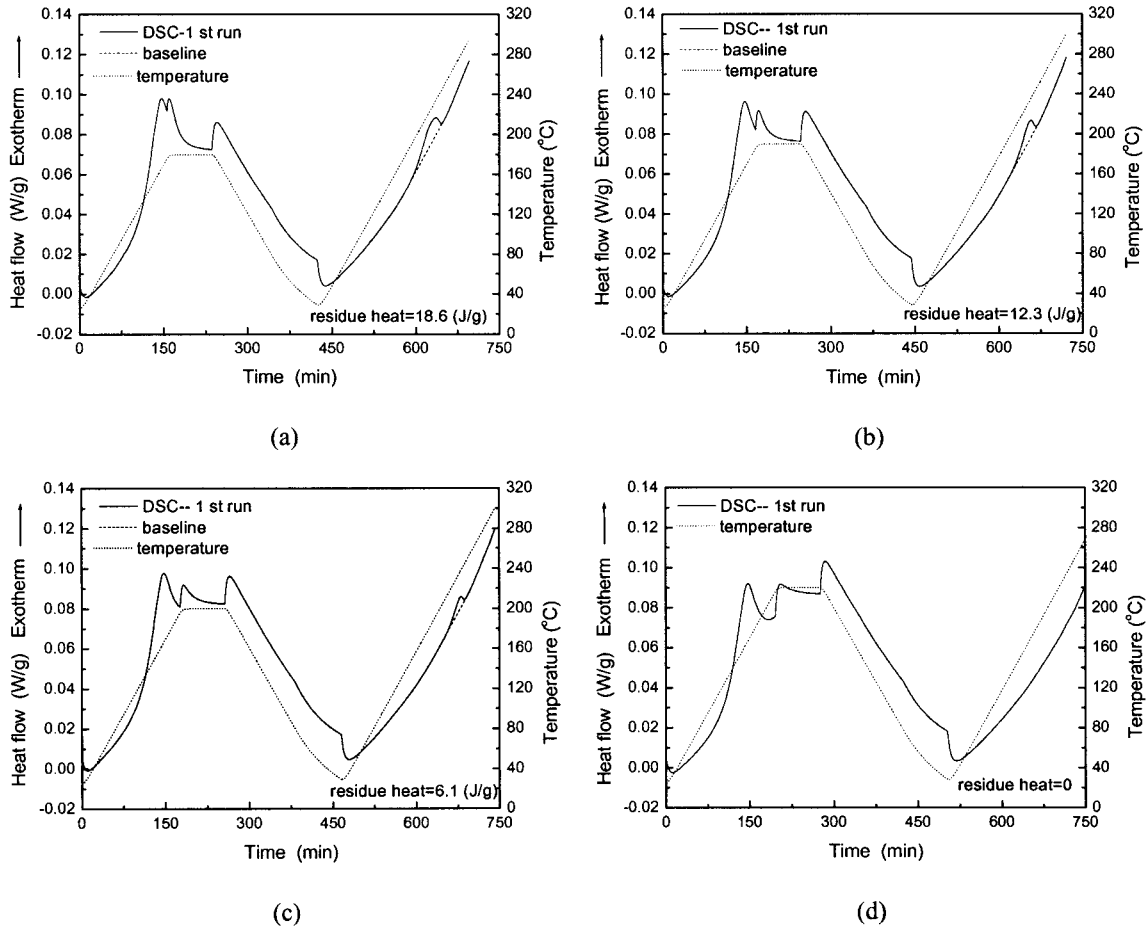
(a)

(b)

(c)

(d)

Figure 4 Combinations of dynamic and isothermal cure of epoxy prepreg at different isothermal temperatures: (a) Cure from 30 to 180°C (heating), holding 80 min, 180 to 30°C (cooling), and 30 to 300°C (reheating); (b) cure from 30 to 190°C (heating), holding 80 min, 190 to 30°C (cooling), and 30 to 300°C (reheating); (c) cure from 30 to 200°C (heating), holding 80 min, 200 to 30°C (cooling), and 30 to 300°C (reheating); (d) cure from 30 to 220°C (heating), holding 80 min, 220 to 30°C (cooling), and 30 to 300°C (reheating)

rectly calculated from the partial reaction heat. It is expressed by the following[14]:

$$\alpha = \frac{\Delta H_t}{\Delta H_{\text{total}}} \qquad (1)$$

where α is the degree of cure, ΔH_t is the partial heat of reaction at time t, and ΔH_{total} is the total heat of reaction. As discussed earlier, the total reaction heat of the studied sample was 177.5 J/g.

Once the partial reaction heats at each sampling time and temperature have been measured, the degree of cure can be easily calculated by eq. (1). Its relationship to cure time at the temperature range from 110 to 220°C is shown in Figure

5. Compared to the value of 1 at 220°C, the final degree of cure at 110°C is only about 0.64. The time needed to reach the final degree of cure is also much different, depending on the isothermal cure temperature.

The cure rate at each sampling time and temperature can be calculated by differentiating the degree of cure to time. The changes of cure rate with time at each isothermal temperature from 110 to 220°C are shown in Figure 6. In the early stages of the cure reaction, the cure rate at a higher temperature is faster than that at a lower temperature; in the late stages, however, the cure rate is slower at the higher cure temperature. Note that for the lower temperature range of 110
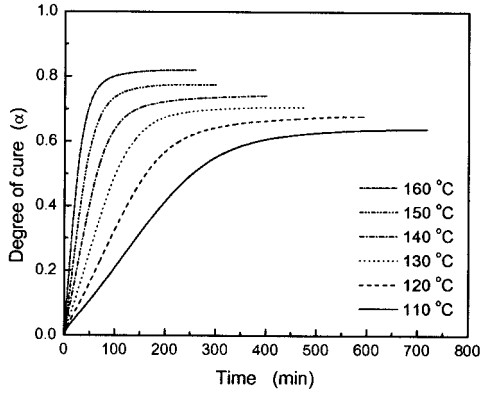
(a)
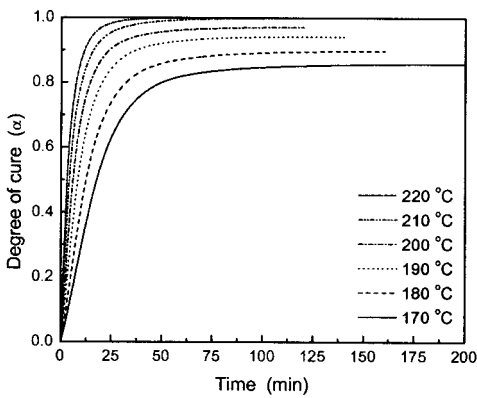
(b)

Figure 5 Degree of cure as a function of time at different isothermal temperatures: (a) 110–160°C; (b) 170–220°C.

to 160°C, the slope of the cure rate curve is negative near time zero. This agrees with the auto-catalytic model (to be discussed next) when the reaction order m is greater than 1.

Cure Reaction Modeling

The autocatalytic model for the cure reaction is as follows[10]:

$$r = (k_1 + k_2 \alpha^m)(1 - \alpha)^n \qquad (2)$$

where r is the cure rate, m and n are the orders of cure reaction, and k_1 and k_2 are the rate constants. The different methods to calculate kinetic parameters in eq. (2) were previously reported.[6,8,11,15]

Equation (2) can be differentiated to give eq. (3):

$$\frac{dr}{d\alpha} = (1 - \alpha)^{(n-1)}[m k_2 \alpha^{(m-1)}(1 - \alpha)$$
$$- n(k_1 + k_2 \alpha^m)] \qquad (3)$$

If $m > 1$ and $\alpha = 0$, we have

$$\frac{dr}{d\alpha} = -n k_1 \qquad (4)$$

The rate constant k_1 can be obtained by extrapolating the curve of cure rate versus degree of cure and its value equals the cure rate at $\alpha = 0$. From eq. (4), we know that the value of $n k_1$ equals the negative derivative of cure rate to degree of cure when the degree of cure is zero. Thus the reaction order n can be easily calculated. Theoretically, if the cure reaction order m is greater than 1, the derivatives of cure rate to degree of cure should be
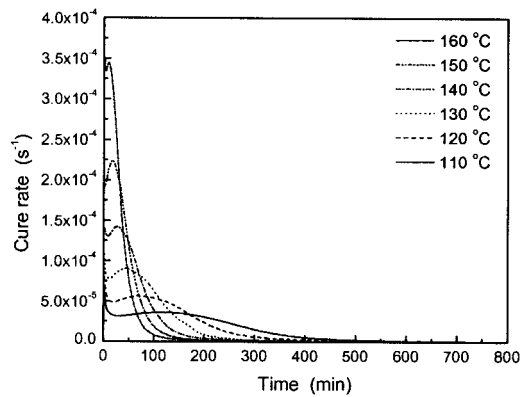
(a)
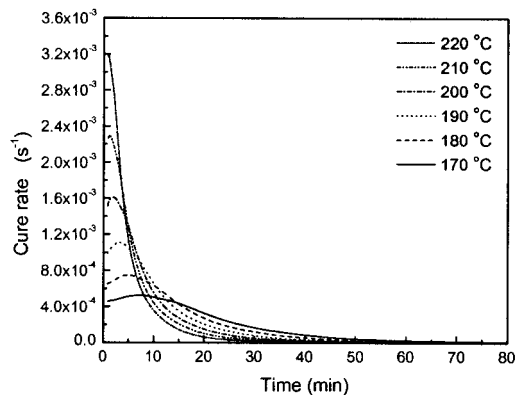
(b)

Figure 6 Cure rate as a function of time at different isothermal temperatures: (a) 110–160°C; (b) 170–220°C.

negative. Our experimental data indicate that in the low-temperature ranges from 110 to 160°C, the derivatives of cure rate to degree of cure are indeed negative when the degree of cure nears zero.

Once the rate constant k_1 and reaction order n are known, eq. (2) can be expressed as follows:

$$\left[\frac{r}{(1-\alpha)^n} - k_1\right] = k_2\alpha^m \qquad (5)$$

By eq. (5), we make a logarithmic plot of $\{[r/(1-\alpha)^n] - k_1\}$ to the degree of cure. The rate constant k_2 and reaction order m can be easily obtained.

With the above method, we analyzed the experimental data at 160°C. The rate constant k_1 equals $3.40 \times 10^{-4} \pm 2.1 \times 10^{-6}$ s^{-1}. The derivative of cure rate to degree of cure at $\alpha = 0$ is $-8.20 \times 10^{-4} \pm 2.6 \times 10^{-6}$ s^{-1}. The value of the cure reaction order n was then calculated to be 2.41. The relationship between $\{[r/(1-\alpha)^n] - k_1\}$ and the degree of cure α, and their linear fitting are given in Figure 7. The calculated values for rate constant k_2 and reaction order m are 2.63 $\times 10^{-3} \pm 6.59 \times 10^{-6}$ s^{-1} and 1.46 $\pm$ 0.002, respectively. It was found that the values of the four parameters obtained by this method are close to those obtained through nonlinear least-square regressions, discussed next.

Another easier and efficient way to analyze the data is by the nonlinear regressions of the experimental data. In our data analysis, we employed Origin software to do nonlinear least-squares curve fitting to the experimental data. To successfully obtain the four parameters in the autocatalytic model, the selection of initial values for the parameters and ranges of experimental data is very important. During the process of nonlinear regressions, the sum of the squares of the derivations of the theoretical values from the experimental values, which is called χ^2, decreases and the parameters change. The nonlinear regressions stop when χ^2 values are minimum and the parameters do not change with additional iterations. The values for the parameters thus obtained are the best values for the model to describe the experimental data. Figure 8 provides the fitting curves and experimental data at different isothermal temperatures. Except for data in the late stage of cure reactions, the fitting curves agree well with the experimental data. The values for the rate constants and reaction orders at
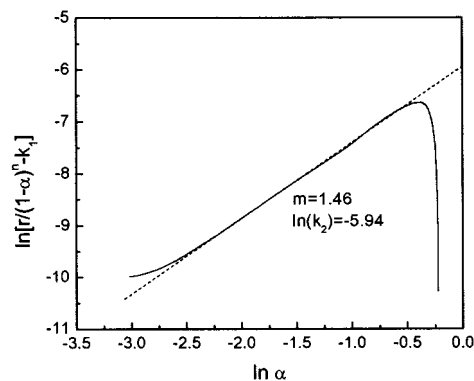

Figure 7   Logarithm plot of $\{[r/(1-\alpha)^n] - k_1\}$ against α at 160°C, where $k_1 = 3.40 \times 10^{-4}$ s^{-1} and $n = 2.41$.

different temperatures are listed in Table I. The cure reaction orders m and n decrease with the increment of temperature. The rate constants k_1 and k_2 increase with the increment of temperature and can be expressed by the following Arrhenius equation:

$$k = Ae^{-(E_a/RT)} \qquad (6)$$

By eq. (6), the plots of $\ln(k_1)$ versus $1/T$ and $\ln(k_2)$ versus $1/T$ with their linear regression curves, shown in Figure 9, are provided. From the intercepts and slopes of the regression curves, the preexponential factors A_1 and A_2 and activation energies E_{a1} and E_{a2} can be determined. Their values are also given in Table I. The cure temperature has more effect on rate constant k_1 than it does on k_2.

In the late stage of the curing process, the sample approaches the solid state. The movement of the reacting groups and the products is greatly limited and thus the rate of reaction is not controlled by the chemical kinetics but, rather, by the diffusion of the reacting groups and products. From Figure 8, it is noticed that there exist large derivations of theoretical values from experimental data in the late cure stage, especially at low temperatures. To account for the effect of the diffusion on the rate of cure reaction, the diffusion factor introduced by Chern et al.[16] is included in the expression of the cure rate. Thus the total rate of reaction is expressed as follows:

$$r = f(\alpha)(k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (7)$$

where $f(\alpha)$ is the diffusion factor, which may be expressed in the following form:
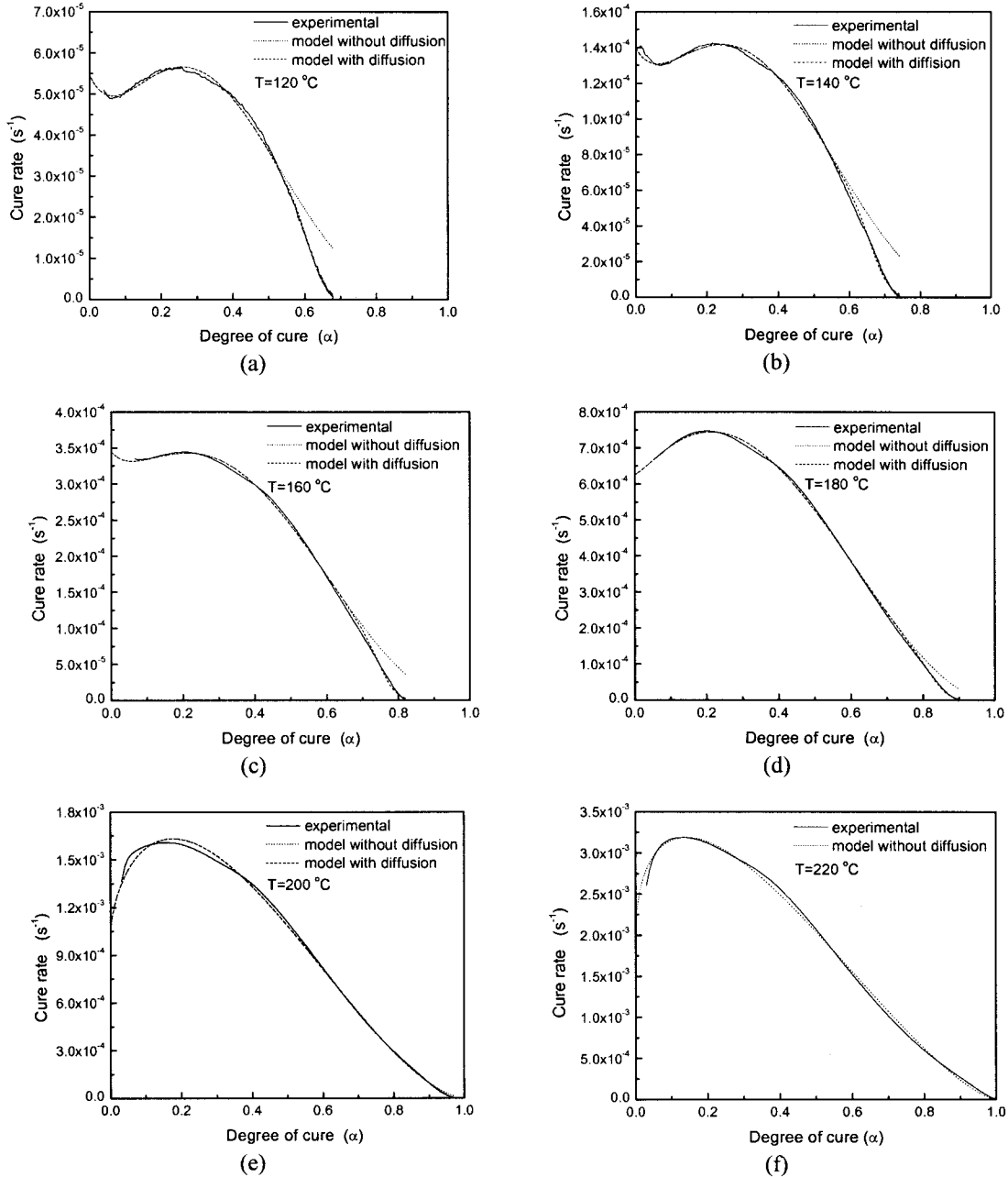
Figure 8 Comparisons of experimental data with those of the autocatalytic model at select isothermal cure temperatures: (a) 120°C; (b) 140°C; (c) 160°C; (d) 180°C; (e) 200°C; (f) 220°C.

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (8)$$

where C and α_c are the two empirical constants, which are temperature dependent. α_c is called the critical degree of cure.

By combining eqs. (7) and (8), eq. (2) with diffusion control can be reexpressed by the following:

$$r = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} (k_1 + k_2 \alpha^m)(1 - \alpha)^n \quad (9)$$

There are six parameters in eq. (9). In the data analysis using eq. (9), the rate constants k_1 and k_2 and the reaction orders m and n have already been determined. To determine the remaining two constants C and α_c, we again used the same software to do the nonlinear least-square regres-

Table I   Kinetic Parameters of the Autocatalytic Model Obtained from Isothermal Cure

Temperature (°C)	k_1 ($\times 10^{-4}$ s^{-1})	SE ($\times 10^{-7}$ s^{-1})	k_2 ($\times 10^{-3}$ s^{-1})	SE ($\times 10^{-5}$ s^{-1})	m	SE ($\times 10^{-2}$)	n	SE ($\times 10^{-2}$)
110	0.36	1	1.22	2	1.98	0.73	3.97	1.3
120	0.55	2	1.40	3	1.87	1.01	3.60	1.69
130	0.85	5	1.76	4	1.77	1.38	3.34	2.00
140	1.40	7	2.04	5	1.68	1.39	3.02	2.02
150	2.02	0	2.51	4	1.53	0.72	2.82	1.23
160	3.45	0	2.77	4	1.50	0.60	2.45	1.11
170	4.47	0	3.11	6	1.25	0.85	2.25	1.23
180	6.27	0	3.58	7	1.16	0.86	2.08	1.40
190	9.03	0	3.76	9	0.99	1.05	1.82	1.61
200	10.3	0	3.88	4	0.66	0.53	1.68	0.58
210	14.3	0	4.09	2	0.52	0.26	1.51	0.28
220	19.4	0	5.14	16	0.47	1.18	1.47	1.70

E_{a1} (J/mol)	SE (J/mol)	A_1 (s^{-1})	SE (s^{-1})	E_{a2} (J/mol)	SE (J/mol)	A_2 (s^{-1})	SE (s^{-1})
5.73×10^4	1.05×10^3	2416	714.1	1.96×10^4	8.84×10^2	0.60	0.149

sions. During the regression process, χ^2 values decrease and C and α_c are kept to change only until χ^2 values, C, and α_c remain unchanged with more iterations of regressions. The regression curves with diffusion factor at different temperatures are also provided in Figure 8 for comparisons. It can be observed that the model with a diffusion factor has very good agreement with the experimental data.

The values for constant C and critical degree of cure α_c at different temperatures are listed in Table II. The critical values for degree of cure increase with the increment of temperature. Figure 10 shows the relationship between the diffusion factor and the degree of cure at different temperatures. It can be shown that the diffusion factor remains almost unchanged with values close to 1 in the early cure stage. In the late cure stage, however, it decreases significantly until it approaches zero.

CONCLUSIONS

The DSC measurement of epoxy prepreg is very useful in elucidating the curing process and in determining the kinetic parameters for the model. Its results can be used to optimize the curing process of epoxy prepreg in its applications as joints to composite pipe systems. The dynamic measurement shows that the appreciable cure re-
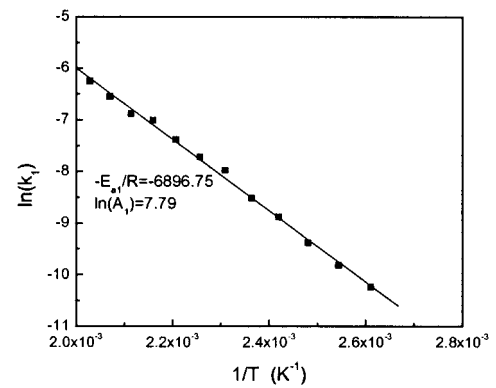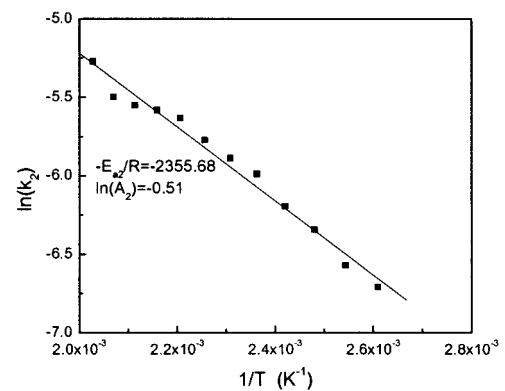
Figure 9   Rate constants k_1 and k_2 as a function of temperature: (a) $\ln(k_1)$ versus $1/T$; (b) $\ln(k_2)$ versus $1/T$.

action begins at about 110°C. The epoxy prepreg was measured isothermally from 110 to 220°C. The determination of cure reaction heat under isothermal conditions can be improved by introducing the heat flow for the second DSC run as the baseline to integrate the heat flow for the first DSC run. The isothermal cure reaction heat increases with the increment of cure temperature. The maximum reaction heat of isothermal cure can be achieved at 220°C. The results from the isothermal cure process were partially supported by the data from the combination of dynamic and isothermal measurements. The degree of cure at isothermal cure temperatures below 220°C is less than 1. In the earlier stage of isothermal cure reaction, the cure rate at the higher temperatures is faster than the cure rate at the lower temperatures, whereas in the late cure stage, the cure rate is lower at the higher temperatures. The relationship between cure rate and degree of cure was simulated by the autocatalytic four-parameter model. Except in the late cure stage, the model can provide a good predication in the large range of experimental data, especially at a high isothermal cure temperature. The kinetic rate constants k_1 and k_2 increase with the increment of cure temperature, whereas the orders of reaction m and n decrease. In the late stage of cure reaction, the effect of diffusion on the cure rate is apparent, especially at low isothermal cure temperatures. The modified autocatalytic four-parameter model, including the diffusion factor, was used to simulate the experimental data again. The simulated results with the modified model were greatly improved in the late cure stage.

Table II   Values of the Constant C and Critical Degree of Cure α_c for Autocatalytic Model at Different Temperatures

Temperature (°C)	C	SE	α_c	SE ($\times 10^{-4}$)
110	50.0	0.167	0.5980	0.8
120	41.4	0.139	0.6247	0.9
130	57.7	0.359	0.6641	1.4
140	38.2	0.180	0.6783	1.6
150	49.7	0.396	0.7276	2.1
160	42.3	0.314	0.7637	2.3
170	43.1	0.350	0.8039	2.4
180	39.3	0.380	0.8485	2.8
190	50.1	0.821	0.9070	3.7
200	75.7	3.548	0.9523	6.7
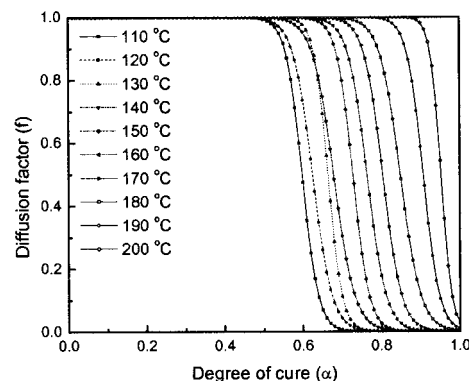
Figure 10   Variation of diffusion factor with degree of cure at different temperatures.

REFERENCES

1. Grenier Loustalot, M. F.; Grenier, P. Polymer 1992, 33, 1187.
2. Laza, J. M.; Julian, C. A.; Larrauri, E.; Rodriguez, M.; Leon, L. M. Polymer 1998, 40, 35.
3. Poisson, N.; Maazouz, A.; Sautereau, H.; Taha, M.; Gambert, X. J Appl Polym Sci 1998, 69, 2487.
4. Xu, L.; Schlup, J. R. J Appl Polym Sci 1998, 67, 895.
5. Barton, J. M.; Hamerton, I.; Howlin, B. J.; Jones, J. R.; Liu, S. Polymer 1998, 39, 1929.
6. Han, S.; Kim, W. G.; Yoon, H. G.; Moon, T. J. J Polym Sci Part A Polym Chem 1998, 36, 773.
7. Gualpa, M. C.; Riccardi, C. C.; Vazquez, A. Polymer 1998, 39, 2247.
8. Barton, J. M.; Greenfield, D. C. L. Polymer 1992, 33, 1177.
9. Gonis, J.; Simon, G. P.; Cook, W. D. J Appl Polym Sci 1999, 72, 1479.
10. Horie, K.; Hiura, H.; Sawada, M.; Mita, I.; Kambe, H. J Polym Sci A-1 1970, 8, 1357.
11. Yang, F.; Yao, K. D.; Koh, W. J Appl Polym Sci 1999, 73, 1501.
12. Han, S.; Yoon, H. G.; Suh, K. S.; Kim, W. D.; Moon, T. J. J Polym Sci Part A Polym Chem 1999, 37, 713.
13. Stubblefield, M. A.; Yang, C.; Pang, S.-S.; Lea, R. H. Polym Eng Sci 1998, 38, 143.
14. Morancho, J. M.; Salla, J. M. Polymer 1999, 40, 2821.
15. Han, S.; Kim, W. G.; Yoon, H. G.; Moon, T. J. J Appl Polym Sci 1998, 68, 1125.
16. Chern, C. S.; Poehlein, G. W. Polym Eng Sci 1987, 27, 782.