Comparison of the Curing Kinetics of the RTM6 Epoxy Resin System Using Differential Scanning Calorimetry and a Microwave-Heated Calorimeter

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ABSTRACT: The cure of a commercial epoxy resin system, RTM6, was investigated using a conventional differential scanning calorimeter and a microwave-heated calorimeter. Two curing methods, dynamic and isothermal, were carried out and the degree of cure and the reaction rates were compared. Several kinetics models ranging from a simple nth order model to more complicated models comprising nth order and autocatalytic kinetics models were used to describe the curing processes. The results showed that the resin cured isothermally showed similar cure times and final degree of cure using both conventional and microwave heating methods, suggesting similar curing mechanisms using both heating methods. The dynamic curing data were, however, different using two heating methods, possibly suggesting different curing mechanisms. Near-infrared spectroscopy showed that in the dynamic curing of RTM6 using microwave heating, the epoxy-amine reaction proceeded more rapidly than did the epoxy-hydroxyl reaction. This was not the case during conventional curing of this resin. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3658–3668, 2006

Key words: epoxy; kinetics; microwave; calorimetry; infrared

INTRODUCTION

Epoxy resins are widely used in major industrial applications, such as preparation of composites. The physical and mechanical properties of the epoxy resins largely depend upon the extent of cure, while their processability is dependent on the rate of polymerization under the curing conditions. Kinetics analysis of the resin is, therefore, important both for a better understanding of structure–property relationships and for optimizing the processing conditions.[1]

The kinetics of epoxy resin cure has been widely investigated in the literature under conventional thermal processing conditions.[2–5] The increasing need for faster and more efficient alternatives to conventional thermal heating for processing composites has led to an interest in the use of microwave heating. It is important to know whether microwave processing can alter the mechanism and kinetics of the chemical reactions involved. For instance, a preferential orientation of dipoles in the microwave field may alter the rates of reactions taking place during curing. Many studies have been reported in the literature on the effect of microwave curing of epoxy resins. Some of these studies[6–8] report higher reaction rates using microwave heating when compared with those obtained using conventional heating, whereas other studies[9,10] report the same kinetics using both methods. There also have been reports of a slight retardation in the curing reaction using microwave heating.[11] Comparative studies can be hindered by a number of factors. First, comparable experimental techniques may not be available, and therefore it is difficult to eliminate effects due to the techniques used. Second, reactions are not always followed in situ, but rather samples are removed from processing equipment and analyzed separately.[7–9,11] Exceptions include investigations of microwave and thermal cure kinetics using in situ real time infrared spectroscopy[10] and dielectric measurements.[6]

A common method for following chemical reactions is differential scanning calorimetry (DSC). This method, however, cannot be applied directly to microwave processing using conventional DSC equipment. A microwave-heated calorimeter has been developed that is capable of making measurements analogous to DSC, allowing direct comparison of microwave and thermal curing processes.[12,13] This article presents the
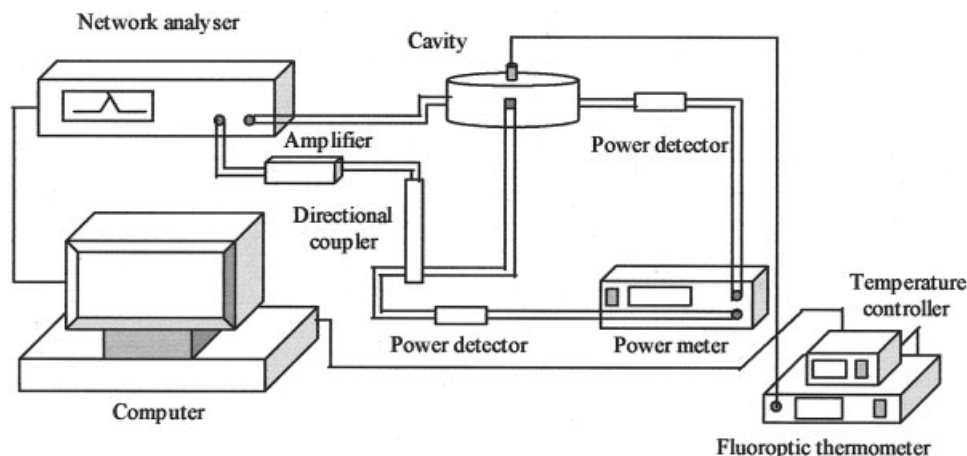
Figure 1 Schematic representation of the microwave-heated calorimeter.

results of calorimetric studies of the cure of an epoxy-amine system (RTM6) using conventional and microwave heating.

EXPERIMENTAL

Materials

The epoxy resin system used was RTM6 supplied by Hexcel Composites (Duxford, UK). RTM6 is a premixed epoxy-amine system developed for the resin transfer molding process.

Curing procedure

Thermal curing was conducted using a PerkinElmer Pyris 1 DSC. Curing of samples 5–10 mg in size placed in aluminum sample pans was carried out in a nitrogen atmosphere at heating rates of 2, 5, 10, and 15°C min^{-1} and isothermal temperatures of 160, 170, 180, and 190°C. For isothermal curing, samples were heated at a rate of 300°C min^{-1} from room temperature to the isothermal temperature and were then held at this temperature for the duration of cure. Measurements were started after 2 min from the beginning of heating to allow thermal equilibrium to be reached by the sample.

The microwave calorimeter is described in detail elsewhere,[13] and therefore, only a brief outline of the equipment is presented in this article. Figure 1 shows a schematic diagram of the microwave-heated calorimeter. Microwave curing was carried out in a cylindrical brass, single mode cavity operating in TE111 mode designed to give maximum field strength at the center of the cavity. Microwaves were generated at a frequency of 2.45 GHz by a Hewlett–Packard 8720ET network analyzer and were amplified using a solid state amplifier (Microwave Amplifiers Ltd.), which produced a maximum power of ~30 W. Transmitted

and reflected powers were measured using an Anritsu ML4238A power meter. The power required for heating the sample was calculated by subtracting the transmitted and reflected powers from the amplifier power. This power is analogous to the heat flow to a DSC sample cell in that any exothermic reaction taking place in the sample will lead to a decrease in the power needed for heating and any endothermic reaction will have the opposite effect. Time, temperature, and power were measured and recorded at a rate of 4 measurements per second and used for calorimetric studies.

The epoxy resin samples (0.3–0.4 g) were cured in glass test tubes placed in the center of the cavity. The temperature of the sample was monitored using a fluoroptic thermometer (Luxtron 790) inserted in a 1.5-mm-diameter glass tube placed in the test tube. The thermometer was connected to a CAL 9500P temperature controller, which was programmed to maintain the desired heating rate or isothermal temperature. Dynamic curing was carried out at heating rates of 2, 5, 10, and 15°C min^{-1} and isothermal curing was performed at 160, 170, 180, and 190°C. As in the DSC measurements, the samples were heated at a high heating rate (~100°C min^{-1}) to the isothermal temperature and measurements were started 2 min after the start of the heating.

Transmission near-infrared spectra were recorded in situ during microwave heating using a Fourier transform infrared spectrometer and remote sensing fiber-optic probes. Details of the method used are described elsewhere.[13]

RESULTS AND DISCUSSION

Kinetics analysis

Several models have been used to describe the curing reaction of epoxy-amine systems. The reaction rate may be given by the following general expression:[2]

$$r = \frac{d\alpha}{dt} = k\,f(\alpha) = A\,\exp(-E/RT)\,f(\alpha) \qquad (1)$$

where r is the reaction rate, α is the conversion, t is time, k is the rate constant described by the Arrhenius expression $k = A\,\exp(-E/RT)$, A is the preexponential factor, E is the activation energy, R is the gas constant, and T is the temperature.

The most frequently used models are the nth order kinetics model[2] and a combination of the nth order and autocatalytic model[14] described by the following equations:

$$r = \frac{d\alpha}{dt} = k(1-\alpha)^n \text{ (nth order model)} \qquad (2)$$

$$r = \frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \text{ (autocatalytic model)} \qquad (3)$$

where k, k_1, and k_2 are the rate constants and m and n are the reaction orders.

Kissinger's method[15] uses an nth order equation for the reaction rate:

$$r = \frac{d\alpha}{dt} = q\frac{d\alpha}{dT} = A\,\exp(-E/RT)(1-\alpha)^n) \qquad (4)$$

where q is the heating rate. Since the maximum rate occurs when $dr/dt = 0$, differentiating eq. (4) with respect to time and equating the resulting expression with zero gives

$$q\frac{E}{RT_p^2} = An(1-\alpha_p)^{n-1}\exp(-E/RT_p) \qquad (5)$$

where T_p and α_p are the peak temperature and conversion at peak temperature, respectively. Rearranging eq. (5) and writing it in natural logarithm form gives

$$-\ln(q/T_p^2) = \ln(E/RAn) - (n-1)\ln(1-\alpha_p) + E/RT_p \qquad (6)$$

Hence in dynamic curing, a plot of $-\ln(q/T_p^2)$ against $1/T_p$ will be a straight line with a slope of E/R.

According to Ozawa's method,[16] the following relationship exists between the heating rate and the exothermic peak temperature in dynamic curing:

$$\log q = (1/2.303)\ln q = -0.4567(E/RT_p)$$
$$+ [\log(AE/R) - \log f(\alpha) - 2.315] \qquad (7)$$

TABLE I
Enthalpy of Cure and Residual Cures for Isothermally Cured RTM6

Cure temperature (°C)	Enthalpy of cure (J g^{-1})		Residual cure (J g^{-1})	
	DSC	Microwave	DSC	Microwave
160	421	—	40	38
170	423	—	33	31
180	423	—	17	21
190	441	—	13	19

Hence, a plot of $\ln q$ against $1/T_p$ should be a straight line with a slope of $-(2.303 \times 0.4567)E/R$.

The conversions and reaction rates for this work were calculated from the DSC or microwave calorimeter measurements using the following equations:

$$\alpha = \frac{\Delta H_t}{\Delta H_{\text{Tot}}} \qquad (8)$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{\text{Tot}}}\frac{d\Delta H_t}{dt} \qquad (9)$$

where ΔH_t is the enthalpy of reaction at time t (between the lowest time or temperature at which heat evolution begins and time t) and ΔH_{Tot} is the total enthalpy of reaction measured as the area under the heat flow against time for DSC measurements and power against time for microwave measurements.

Isothermal curing

Table I shows the enthalpy of cure for DSC curing and residual cure for each isothermal temperature after curing using DSC or microwave calorimeter. The residual cures were analyzed using DSC. It was not possible to determine the enthalpy of cure for the microwave-cured samples because at present it is not possible to convert the microwave power to the absolute values of heat flow from sample during curing. As can be seen, the residual cures for both conventionally and microwave-cured samples were similar, showing similar final degree of cure at each temperature using both methods.

Figure 2 shows the plots of conversion and reaction rate for the isothermal curing of RTM6 cured using DSC. Figure 3 shows the same plots obtained using the microwave calorimeter. The conversions and reaction rates were obtained using the DSC curves and eqs. (8) and (9).

Figures 2 and 3 show that under both heating conditions, curing reactions were completed over the same period of time. Some differences, however, were observed in the maximum reaction rates between the two methods.
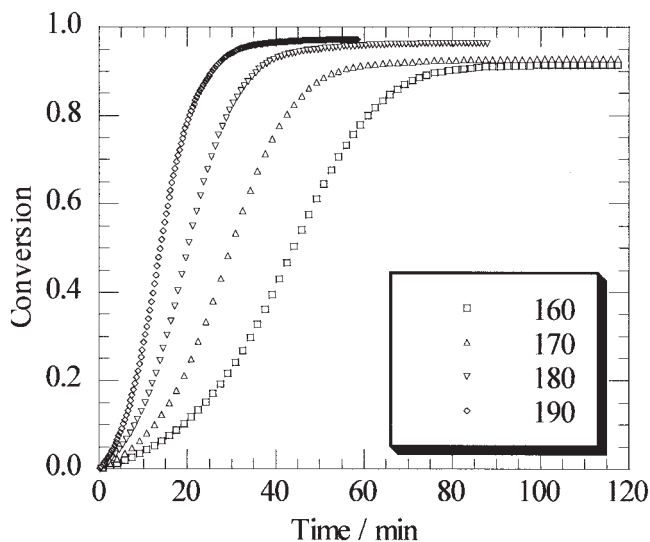
(a)
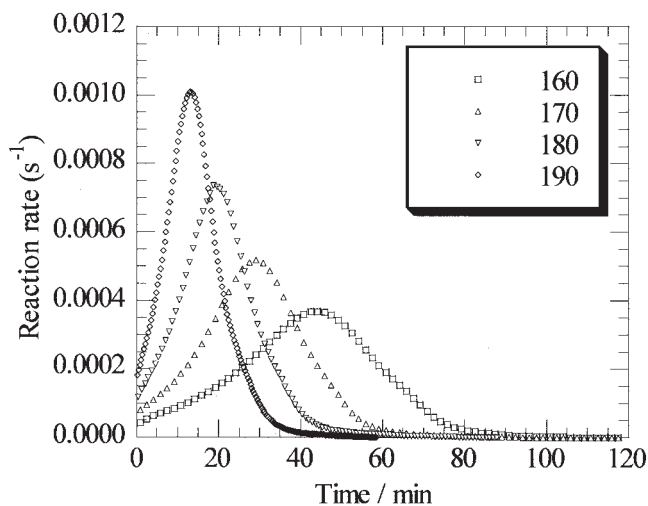
(b)

Figure 2 (a) Plots of conversion against time and (b) plots of reaction rate against time for RTM6 obtained using DSC.
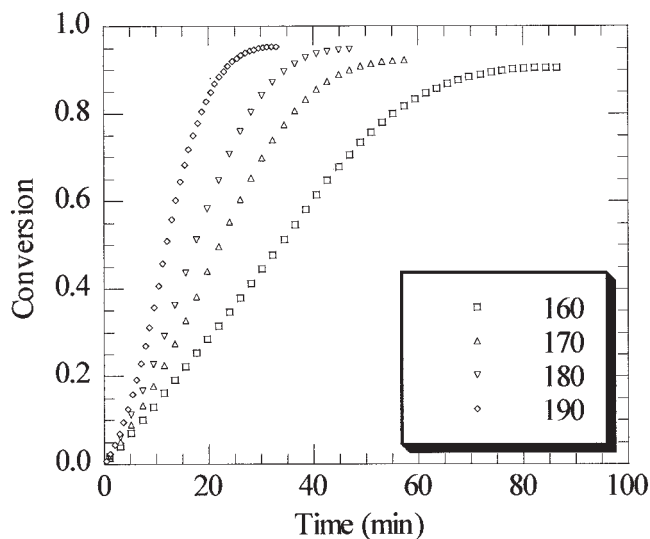
The curves of reaction rate against time were fitted to the kinetics eq. (3). The equation was modified to account for the diffusion effect, which occurs when the resin is transformed from the rubbery to glassy state. In this modified equation, α_{max}, the maximum conversion obtained at each curing temperature was used in the right hand side of the equation instead of a value of 1. α_{max} was calculated from enthalpy of reactions and residual cures measured using DSC. The DSC plots were also fitted using the equation described by Karkanas and Partridge.[17,18]

$$\frac{d\alpha}{dt} = k_1(1-\alpha)^{n_1} + k_2\alpha^m(1-\alpha)^{n_2} \qquad (10)$$

Again, 1 was replaced by α_{max} in eq. (10) to account for diffusion controlled reaction. Figure 4 shows the result

of fitting the DSC results to eqs. (3) and (10). As can be seen, both models produce a very good fit to the experimental data.

Table II summarizes the parameters obtained from fitting the experimental data to the eqs. (3) and (10). Values of preexponential factor and activation energy were calculated from the temperature dependence of k_1 and k_2 using the Arrhenius equation. Values of E_1 and E_2 for the conventionally cured samples are in agreement with those obtained by Karkanas and Partridge.[18] The values of A_1 and A_2 were, however, much smaller than the values obtained by them. As in their analysis they did not correct the kinetics models for diffusion control, the fits to the experimental data were not as good as in this work, and this might

(a)
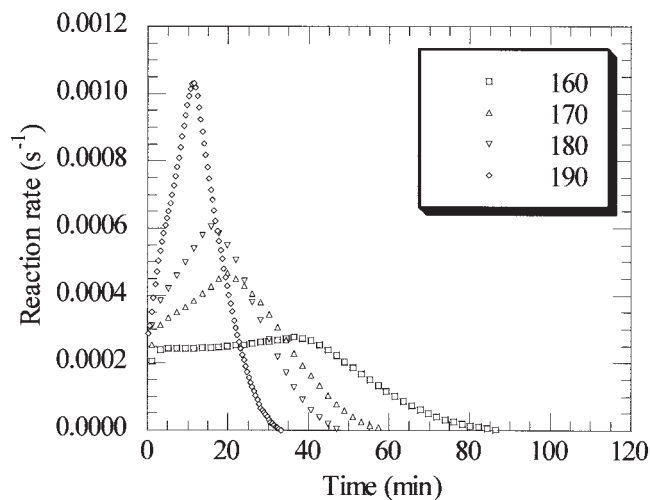
(b)

Figure 3 (a) Plots of conversion against time and (b) plots of reaction rate against time for RTM6 obtained using the microwave calorimeter.
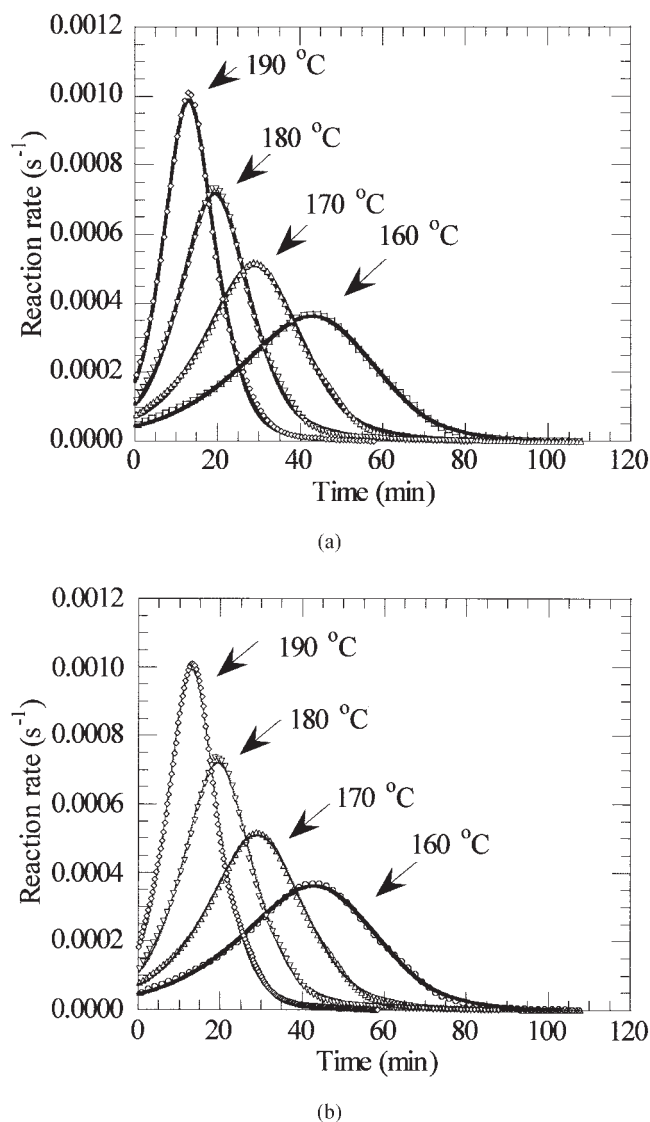
(a)

(b)

Figure 4 Plots of reaction rate against time for isothermal conventional curing showing the fit of data to (a) eq. (3) and (b) eq. (10). Symbols show the experimental results and the solid lines indicate the fits.

explain the observed differences in preexponential factors.

The curing data from the isothermal microwave cures were also fitted to eqs. (3) and (10). Figure 5 shows the results. Both models fit reasonably well to the experimental data. Table III summarizes the parameters obtained. As can be seen, the k_1 values do not follow the Arrhenius trend. This is not unexpected because in the isothermal reactions, it took longer for the temperature to stabilize in the microwave calorimeter than in DSC. This was due to a slower initial heating rate in the microwave calorimeter ($\sim 100°C$ min^{-1}) compared with that in the DSC ($300°C$ min^{-1}), which made initial reaction rate values inaccurate.

Comparison of the parameters obtained for conventionally cured resin and microwave-cured resin reveals that the reaction orders are similar in both methods, while the preexponential factor and activation energies are much higher for the microwave-cured RTM6. Higher values of preexponential factor for microwave heating may suggest a higher frequency of collision between reactive moieties caused by the alignment of dipoles in the microwave field. Higher activation energies for microwave-cured resin may suggest a larger barrier to reaction for aligned dipoles.

Dynamic curing

Figure 6 shows the curves obtained using the DSC and microwave calorimeter for the dynamic cure of the epoxy resin system. As expected, increasing the heating rate increases the onset temperature for the reaction, and at any given temperature, the degree of cure is higher at lower heating rates. This is due to a thermal lag in the sample response to heating, which is greater at higher heating rates.

Table IV shows the enthalpy of cure for the epoxy resin obtained using conventional DSC at different

TABLE II
Parameters Obtained from Fitting the Isothermal Curing Results Using DSC to Eqs. (3) and (10)
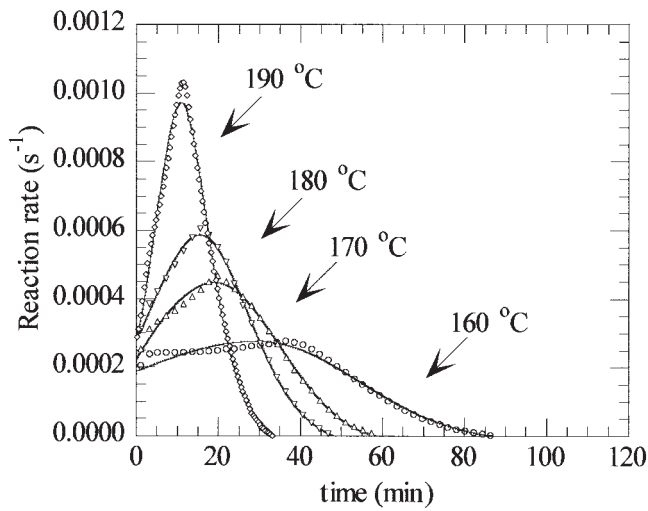
Cure temperature (°C)	k_1 (10^{-5} s^{-1})	k_2 (10^{-3} s^{-1})	m	n	n_1	n_2
Equation (3)[a]						
160	4.80	1.62	1.12	0.89		
170	7.71	2.53	1.15	1.02		
180	11.34	3.49	1.13	1.13		
190	18.03	4.61	1.10	1.16		
Equation (10)[b]						
160	4.63	1.57	1.10		0.73	0.88
170	7.47	2.45	1.15		0.60	1.02
180	11.36	3.41	1.12		1.16	1.10
190	17.70	4.88	1.14		0.51	1.26

[a] A_1, 27612 s^{-1}; E_1, 72.61 kJ mol^{-1}; A_2, 15369 s^{-1}; E_2, 57.70 kJ mol^{-1}.
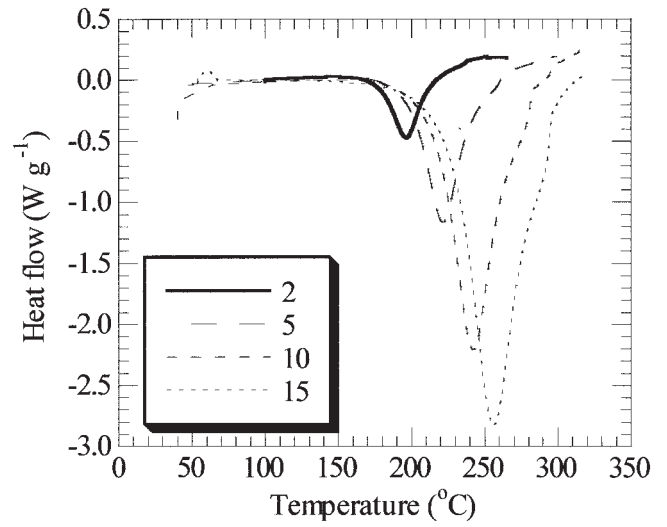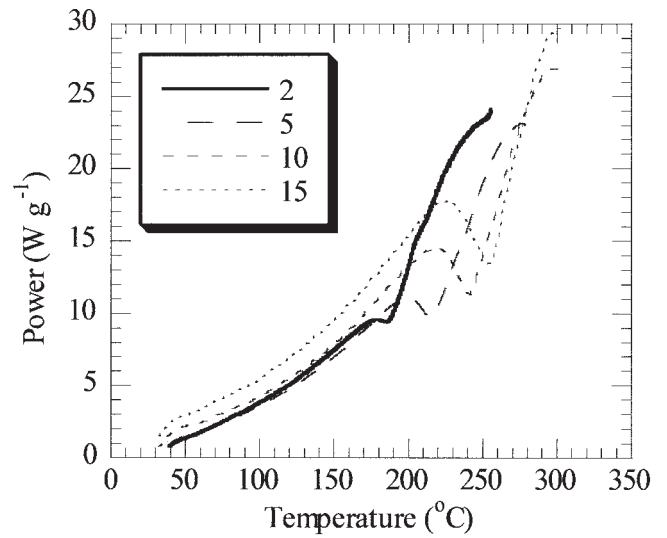[b] A_1, 39300 s^{-1}; E_1, 74.00 kJ mol^{-1}; A_2, 51534 s^{-1}; E_2, 62.23 kJ mol^{-1}.
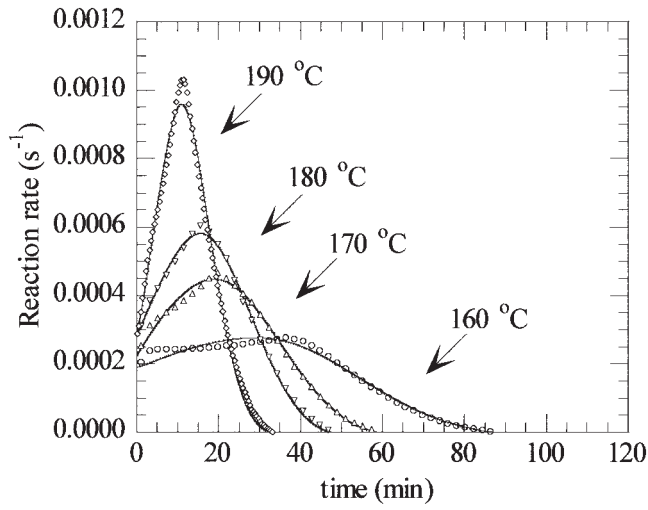
(a)

(b)

Figure 5 Plots of reaction rate against time for isothermal microwave curing showing the fit of data to (a) eq. (3) and (b) eq. (10). Symbols show the experimental results and the solid lines indicate the fits.

(a)

(b)

Figure 6 The curves obtained for the RTM6 cure using (a) conventional DSC and (b) the microwave-heated calorimeter.

TABLE III
The Fitting Parameters Obtained from Microwave Curing of RTM6

Cure temperature (°C)	k_1 (10^{-4} s^{-1})	k_2 (10^{-3} s^{-1})	m	n	n_1	n_2
Equation (3)[a]						
160	2.02	0.62	1.07	0.67		
170	2.35	1.09	0.88	0.73		
180	2.95	1.51	0.95	0.78		
190	2.86	3.11	0.94	0.90		
Equation (10)[b]						
160	2.04	0.63	1.06		0.74	0.66
170	2.38	1.11	0.88		0.87	0.71
180	2.89	1.64	1.02		0.44	0.96
190	2.84	3.62	1.03		0.35	1.01

[a] $A_2 = 1.6 \times 10^7$ s^{-1} and $E_2 = 86.37$ kJ mol^{-1}.
[b] $A_2 = 1.16 \times 10^8$ s^{-1}, and $E_2 = 93.51$ kJ mol^{-1}.

TABLE IV
Enthalpy of Cure for RTM6 Obtained Using DSC

Heating rate ($^\circ$C min^{-1})	Enthalpy (J g^{-1})
2	401
5	413
10	428
15	401

heating rates. The enthalpy of cure was calculated by integrating the curves of heat flow against time obtained from DSC. Sample background correction was carried out using Bandara's method[19] prior to integration. Bandara's method takes into account the changes

(a)

(b)

Figure 8 (a) Conversion and (b) reaction rates for the RTM6 obtained using the microwave-heated calorimeter.

in specific heat during the curing reaction and is given by

$$F(t) = \frac{\int_0^t \{G(t) - F(t)\}dt}{\int_0^{t_{end}} \{G(t) - F(t)\}dt} \{P_2(t) - P_1(t)\} + P_1(t) \quad (11)$$

where $F(t)$ is the sample background, $G(t)$ is the total signal corrected for the instrument background, tend is the time of termination of the curing reaction, $P_1(t)$ is the DSC signal for the uncured sample estimated through linear extrapolation of the portion of the
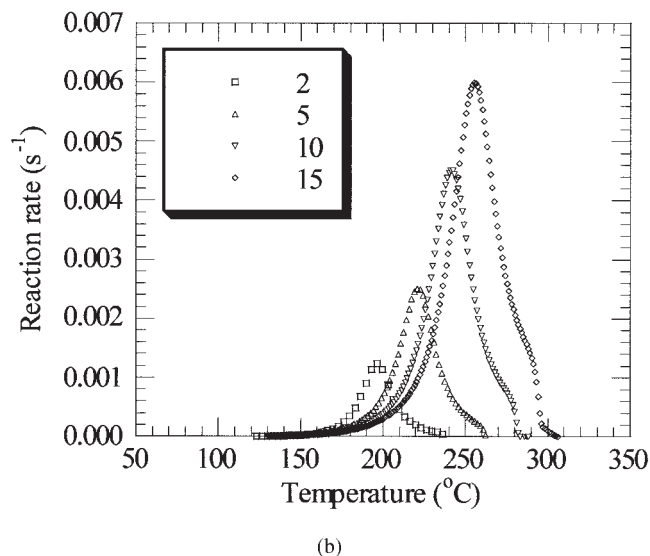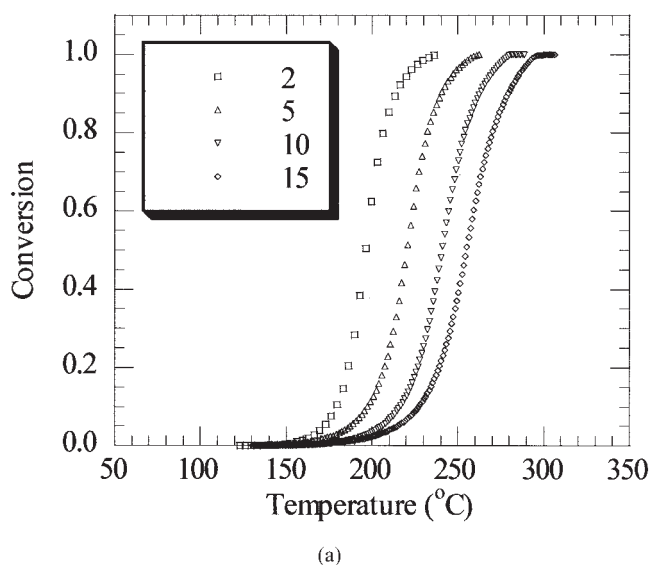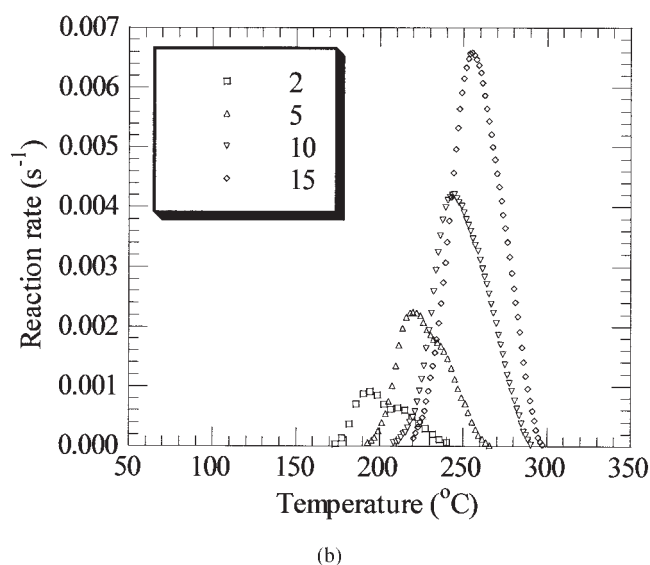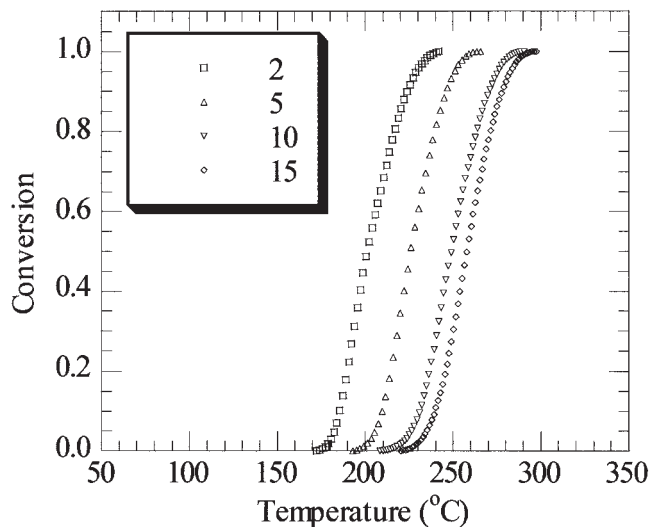

(a)

(b)

Figure 7 (a) Conversions against temperature and (b) reaction rates against temperature for the RTM6 obtained using conventional DSC.

TABLE V
Exothermic Peak Temperatures for RTM6 Cured Using Conventional and Microwave Heating

Heating rate ($^\circ$C min^{-1})	T_p ($^\circ$C)	
	DSC	Microwave
2	196.5	191.1
5	221.3	218.9
10	241.6	243.8
15	255.6	255.0

curve prior to the start of the curing reaction, and $P_2(t)$ is the DSC signal for the cured resin estimated by a rerun of the fully cured sample. In this work, $P_2(t)$ was
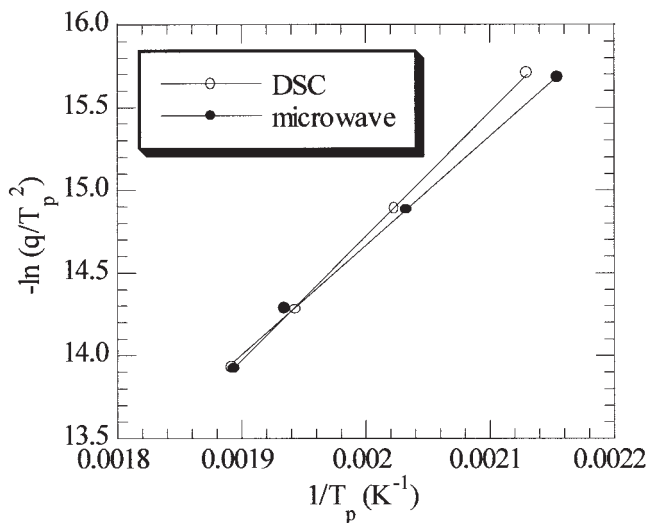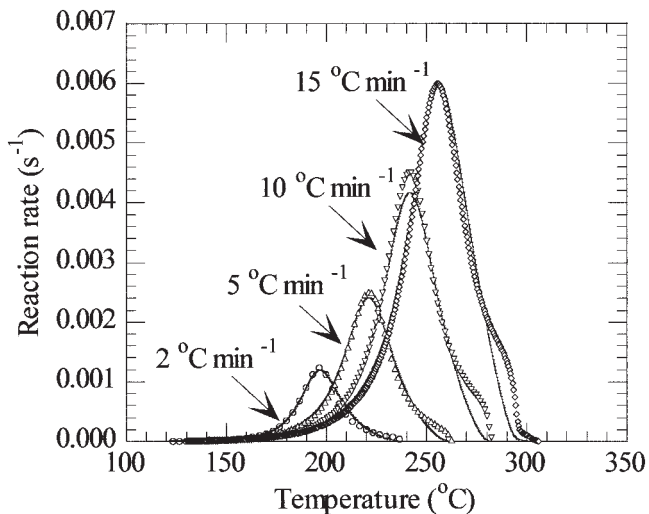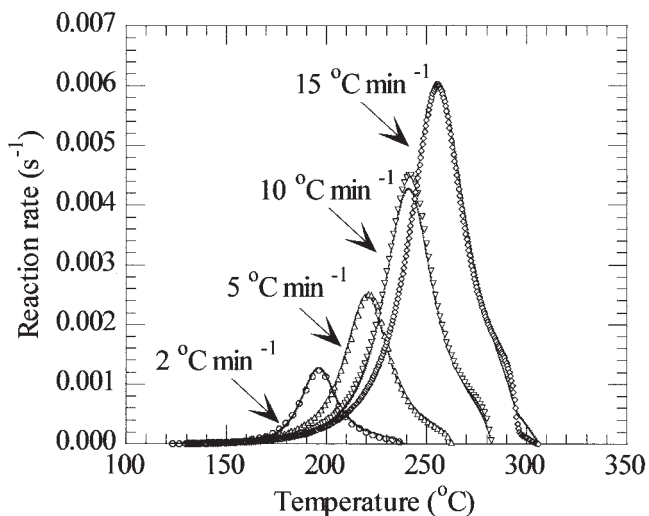

(a)
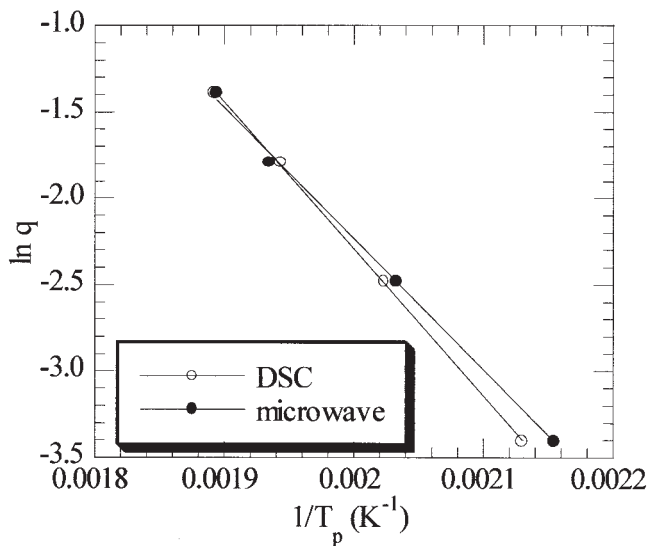
(b)

Figure 9 (a) Plots of $-\ln(q/T_p{}^2)$ against $1/T_p$, and (b) plots of $\ln q$ against $1/T_p$ for conventional and microwave curing of RTM6.

(a)

(b)

Figure 10 Plots of reaction rate against temperature for conventional dynamic curing as well as fits to (a) eq. (3) and (b) eq. (10).

estimated through linear extrapolation of the portion of the curve after the end of the curing reaction.

As can be seen from Table IV, the total heat of reaction is independent of the heating rate in the range analyzed, which may suggest similar reaction mechanism at different heating rates within the range analyzed.

Figures 7 and 8 show the conversions and reaction rates for the RTM6 obtained using conventional DSC and the microwave-heated calorimeter, respectively. The background correction for the microwave-cured samples was also carried out using Bandara's method. The presence of small shoulders was observed at a high degree of cure in plots of reaction rate against temperature for conventionally cured samples, which was more pronounced at high heating rates. A possi-
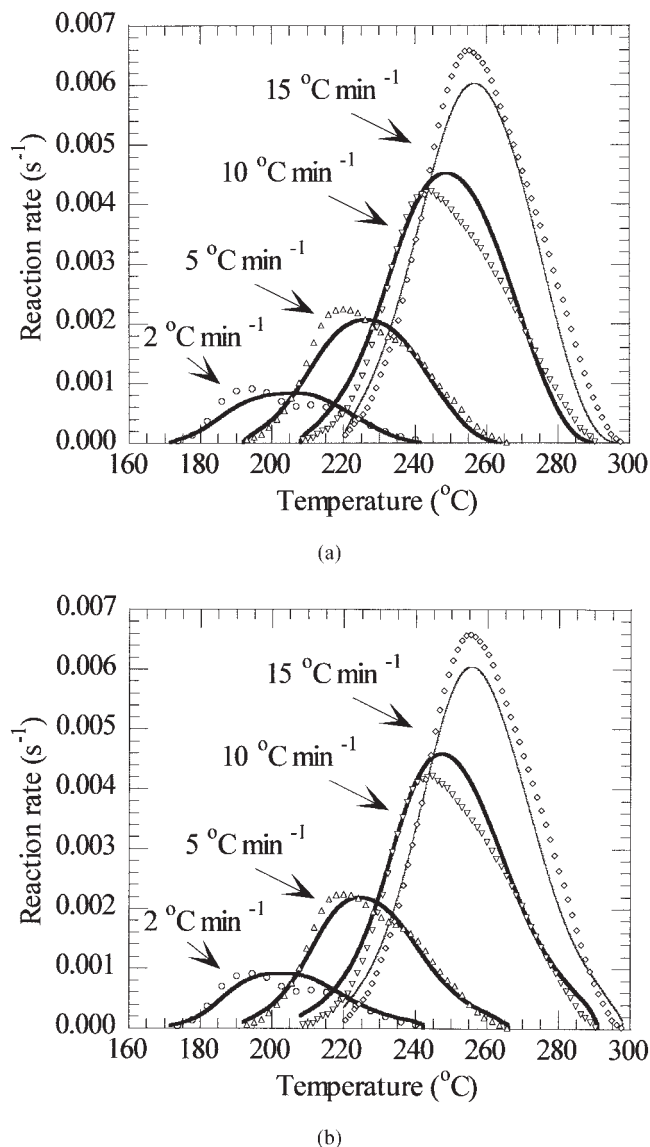
Figure 11 Plots of reaction rate against temperature for microwave dynamic curing as well as fits to (a) eq. (3) and (b) eq. (10).

ble explanation for these peaks is that competing reactions, i.e., epoxy-amine and epoxy-hydroxyl give rise to two overlapping peaks in plots of reaction rate against temperature. Shoulders were also observed in

the microwave-cured samples. They were, however, bigger and were more pronounced at lower heating rates. This may suggest different reaction mechanisms using conventional and microwave heating. The peak in the reaction rate, however, occurred at similar temperatures using microwave and conventional heating. The exothermic peak temperatures (Tp) for RTM6 cured using conventional DSC and the microwave-heated calorimeter are shown in Table V.

Figure 9(a) shows the plots of $-\ln(q/T_p^2)$ against $1/T_p$ for the epoxy resin system cured using conventional DSC and microwave calorimeter from which the activation energies were calculated using the Kissinger's method. The activation energies were 62.41 and 54.91 kJ mol^{-1} for the conventional and microwave curing, respectively. Figure 9(b) shows the plots of ln q against $1/T_p$ to calculate the activation energies using Ozawa's method. The values obtained were 70.68 and 63.13 kJ mol^{-1} for the conventional and microwave curing, respectively.

The dynamic cure data were fitted to eqs. (3) and (10) by restricting the values of A_1 and E_1 to the values obtained from the isothermal data. Figure 10 shows the experimental data as well as the fits. As can be seen, the fits to eq. (10) provide better results at high degree of cure. This is due to the presence of small shoulders in plots of reaction rate against temperature at high degree of cure, possibly suggesting the presence of a second reaction. It is, therefore, not unexpected that eq. (10) describes the curing process more successfully. This effect was also observed by Karkanas and Partridge.[17,18]

The data obtained from microwave cures were also fitted to eqs. (3) and (10). Figure 11 shows the experimental data together with the calculated fits. The fits to the microwave curing data were not as good as those obtained for thermal curing. The hypersurface for the curve fit to the thermal cure showed a well-defined minimum, but the corresponding minimum in the hypersurface for the microwave cure was poorly defined and displayed multiple shallow local minima, so that the individual kinetics parameters for the microwave process were subject to great error. The difference between the fitted curve and experimental data may be due to the greater precision in the data for

TABLE VI
Kinetics Parameters for Dynamic Curing of RTM6

	A_1 (s^{-1})	E_1 (kJ mol^{-1})	A_2 (s^{-1})	E_2 (kJ mol^{-1})	m	n	n_1	n_2
Conventionally cured RTM6								
Eq. (3)	27612	72.61	7401	54.49	1.14	1.38	—	—
Eq. (10)	39300	74.00	5216	50.75	1.48	—	0.46	1.92
Microwave-cured RTM6								
Eq. (3)	—	—	2.74×10^5	73.3	0.40	1.08	—	—
Eq. (10)	6.8×10^4	78.5	8.6×10^4	67.4	0.58	—	0.33	1.43

(a)

(b)
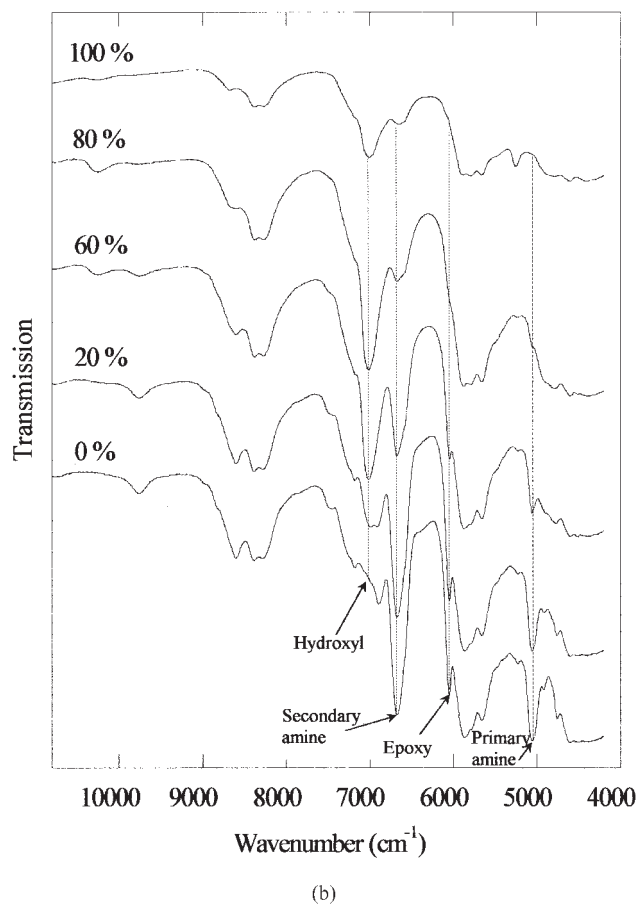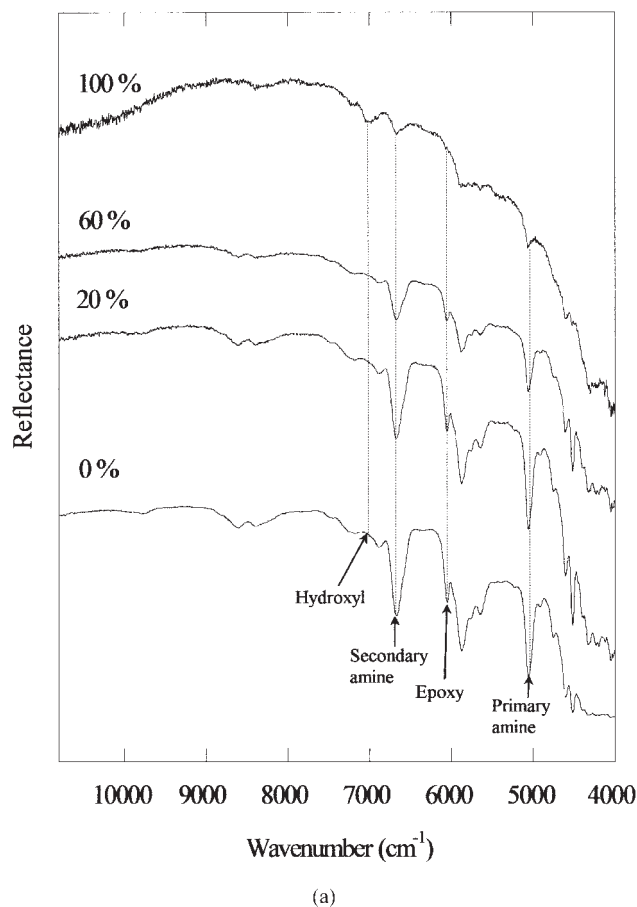
thermal curing process. The heating rate of the microwave-cured samples was not perfectly linear and slight deviations (±2%) were observed in the heating rate during the curing of the epoxy resin. This may account for the less accurate data for microwave-cured samples.

The errors in A_1 and E_1 obtained by fitting to eq. (3) were very high, suggesting the inadequacy of this equation in describing the dynamic curing of RTM6 using microwave heating. Equation (10), therefore, was better for describing the kinetics in microwave-cured samples.

Table VI summarizes the parameters obtained by fitting the experimental data to the kinetics equations. Comparison of the kinetics parameters obtained using eq. (10) for samples cured using two different processes shows that as in the isothermally-cured samples, the activation energies were higher for the microwave-cured samples. This is not in agreement with the values obtained using Kissinger's and Ozawa's methods. This, however, is not unexpected, as those methods use a simple nth order reaction kinetics, which is inadequate for describing the curing of RTM6. The values of preexponential factors are also larger for microwave-cured samples, suggesting the possibility of more collisions between reactive groups during microwave curing. Unlike in the data from isothermal curing, reaction orders are not the same between two methods, suggesting that a different reaction mechanism may have been followed using these methods. This difference is in agreement with the results from previous work that suggested that in microwave curing of epoxy-amine systems, the epoxy-amine reaction proceeds more rapidly when compared with the epoxy-hydroxyl reaction. This was not the case during conventional cure.[20] Marand et al.[6] have also proposed selective activation of epoxy-amine reaction during microwave curing to explain their kinetic analysis. If we assume that the dynamic curing data show competing reactions occurring at different but overlapping temperature ranges, it is possible that the isothermal data are dominated by one of these reactions (i.e., the reaction at lower temperature). This could lead to the similar reaction orders obtained in conventional and microwave isothermal curings. The dynamic data, however, are influenced by both reactions. Hence the differences in the reaction orders for conventional and microwave curings may reflect the differences in the dominant reaction path for the two heating methods.

To further investigate the cure mechanism of the RTM6 resin system, near-infrared spectra were ob-

Figure 12 Near-infrared spectra showing the development of the curing during (a) conventional and (b) microwave curing at 2°C min^{-1}.

tained during dynamic curing of the resin ($2°C \ min^{-1}$) in both DSC and the microwave calorimeter. Figure 12(a) shows the near-infrared spectra for a conventionally cured sample at different conversions. As can be seen, the peaks at 5071 and $6675 \ cm^{-1}$, which are assigned to the primary and secondary amines, respectively, deplete as the reaction proceeds. Both peaks are, however, present at the end of the experiment. Furthermore, it can be seen that a peak corresponding to hydroxyl groups develops at $6970 \ cm^{-1}$. The area under the hydroxyl peak is similar to that of the secondary amine at complete conversion. Figure 12(b) shows near-infrared spectra for the microwave-cured resin. As in the conventional heating, the peaks corresponding to the primary and secondary amines are depleted as the cure reaction progresses. Unlike in the conventional heating, however, the primary amine reacts completely during the microwave curing of the RTM6. Furthermore, at the end of the reaction, the amount of the secondary amine left is much less than the hydroxyl groups present. Near-infrared results confirm the results obtained using DSC, which suggested different reaction paths between conventional and microwave curing of RTM6.

CONCLUSIONS

A detailed calorimetric study was carried out to compare the kinetics of cure in an epoxy-amine system (RTM6) using conventional and microwave heating methods. Both dynamic and isothermal curings were carried out. Several kinetics models were used to describe the curing processes. Resin cured isothermally showed similar cure times and final degree of cure using both conventional and microwave heating methods. Fitting the isothermal cure data to a combination of nth order and autocatalytic kinetics equation showed larger values of preexponential factor and activation energy under microwave heating. The reaction orders were, however, similar using both heating

methods, suggesting similar mechanisms of curing. The dynamic curing data showed not only higher preexponential factor and activation energy for microwave curing but also different reaction orders using the two heating methods. This may suggest different curing mechanisms using thermal and microwave heating. Near-infrared spectra obtained during dynamic curing of the epoxy resin confirmed the calorimetry results and revealed that amine groups reacted more rapidly in the microwave curing than in the conventional curing of the resin.

References

1. Sourour, S.; Kamal, M. R. Thermochim Acta 1976, 14, 41.
2. Barton, J. M. In Advances in Polymer Science, Vol. 72: Epoxy Resins and Composites I; Dušek, K., Ed.; Springer-Verlag: Berlin, 1985; p 111.
3. Dušek, K.; Bleha, M. J Polym Sci Polym Chem Ed 1977, 15, 2393.
4. Ryan, M. E.; Dutta, A. Polymer 1979, 20, 203.
5. Kenny, J. M.; Trivisano, A. Polym Eng Sci 1991, 31, 1426.
6. Marand, E.; Baker, K. R.; Graybeal, J. D. Macromolecules 1992, 25, 2243.
7. Wei, J.; Hawley, M. C.; DeMeuse M. T. Polym Mater Sci Technol 1992, 66, 478.
8. Wei, J.; Hawley, M. C.; DeMeuse M. T. Polym Eng Sci 1995, 35, 461.
9. Hedreul, C.; Galy, J.; Dupuy, J.; Delmotte, M.; More, C. J Appl Polym Sci 1998, 68, 543.
10. Hill, D. J. T.; George, G. A.; Rogers, D. G. Polym Adv Technol 2002, 13, 353.
11. Mijovic, J.; Wijaya, J. Macromolecules 1990, 23, 3671.
12. Nesbitt, A.; Navabpour, P.; Nightingale, C.; Mann, T.; Day, R. J. In Proceedings of the 9th International Conference on Microwave and RF Heating, Loughborough, September 2003.
13. Nesbitt, A.; Navabpour, P.; Nightingale, C.; Mann, T.; Degamber, B.; Fernando, G.; Day, R. J. Meas Sci Technol 2004, 15, 2313.
14. Kamal, M. R. Polym Eng Sci 1974, 14, 231.
15. Kissinger, H. E. Anal Chem 1957, 29, 1702.
16. Ozawa, T. J Therm Anal 1970, 2, 301.
17. Karkanas, P. I.; Partridge, I. K. Polym Int 1996, 41, 183.
18. Karkanas, P. I.; Partridge, I. K. J Appl Polym Sci 2000, 77, 1419.
19. Bandara, U. J Therm Anal 1986, 31, 1063.
20. Wallace, M.; Attwood, D.; Day, R. J.; Heatley, F. J Mater Sci, accepted.