

Comparison of the Curing Kinetics of a DGEBA/Acid Anhydride Epoxy Resin System Using Differential Scanning Calorimetry and a Microwave-Heated Calorimeter

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ABSTRACT: The cure of an epoxy resin system, based upon a diglycidyl ether of bisphenol-A (DGEBA) with HY917 (an acid anhydride hardener) and DY073 (an amine-phenol complex that acted as an accelerator), was investigated using a conventional differential scanning calorimeter and a microwave-heated power-compensated calorimeter. Dynamic cure of the epoxy resin using four different heating rates and isothermal cure using four different temperatures were carried out and the degree of cure and reaction rates were compared. The cure kinetics were analyzed using several kinetics

models. The results showed different activation energies for conventional and microwave curing and suggested different reaction mechanisms were responsible for curing using the two heating methods. Resins cured using conventional heating showed higher glass transition temperatures than did those cured using microwave heating. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2054–2063, 2007

Key words: epoxy; curing; microwave; dielectric properties; thermal analysis; calorimetry

INTRODUCTION

Epoxy resins are widely used in industry for preparing composites. 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 and the properties of the final product. Many studies have been reported in the literature that compare conventional and microwave curing of epoxy resins.^{1–11} Most of these studies focus on epoxy/amine systems and there is controversy about the effect of microwave heating on the curing of epoxy resins. Mijović and Wijaya¹ compared the two heating methods through studying the increase in glass transition temperature of an epoxy/amine system during curing and concluded that the curing of epoxy using conventional heating proceeded slightly faster than using microwave heating. In another study using high-performance liquid chromatography and Fourier transform infrared (FTIR) spectroscopy, Mijović et al.²

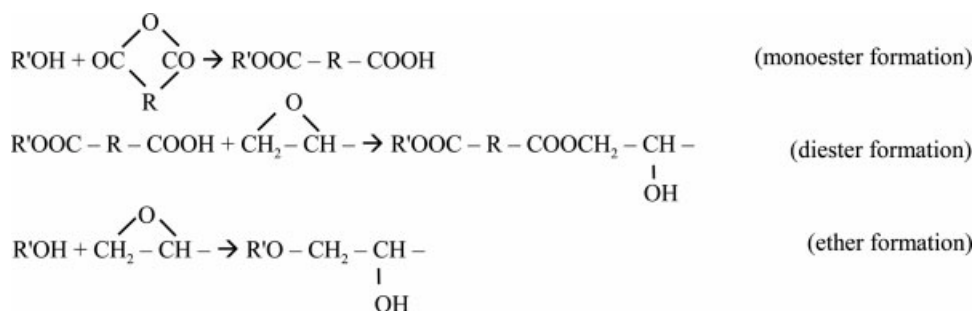
concluded that the kinetics of reaction was the same in conventional and microwave curing. Hedreul et al.³ and Hill et al.^{4,5} also reported that the two curing methods showed the same reaction kinetics. Wei et al.^{6,7} studied the curing using FTIR and glass transition temperature measurements and concluded that microwave curing proceeded faster than conventional curing. Boey and Rath⁸ also reported faster reaction rates using microwave heating than when using conventional heating. Marand et al.⁹ report an initial acceleration in the reaction rate, followed by a lower conversion using microwave heating. Studies have also been carried out on the mechanical properties of epoxy resins cured. Tanrattanakul and SaeTiaw¹⁰ and Zhou et al.¹¹ have compared the mechanical properties of conventionally- and microwave-cured epoxy resins and observed that microwave-cured resin showed equivalent or better mechanical properties than did conventionally cured resin.

This article presents the results of calorimetric studies of the cure of an epoxy-anhydride system (DGEBA/HY917/DY073) using conventional and microwave heating.

Kinetics analysis

The reactions taking place in an uncatalyzed acid anhydride-cured epoxy system include monoester, diester, and ether formation, as seen in Scheme 1.¹²

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Scheme 1 Reactions taking place during the cure of an epoxy acid-anhydride system.

Basic and acidic catalysts and/or tertiary amines are often added to accelerate the cure process.

Several models have been used to describe the curing reaction of epoxy-amine systems. The reaction rate may be given by the following general expression¹²:

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

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 n th order kinetics model¹² and the autocatalytic model¹³ described by the following equations:

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

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

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

*Kissinger's method*¹⁴: This method uses an n th order equation for the reaction rate:

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

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

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

Rearranging eq. (5) and writing it in natural logarithm form gives

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

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 .

*Ozawa's method*¹⁵: According to this method, the following relationship exists between the heating rate

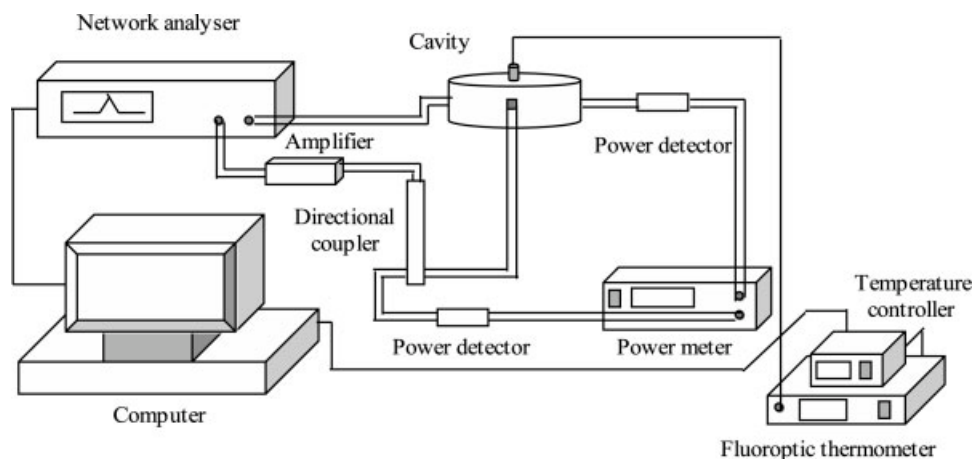


Figure 1 Schematic representation of the microwave-heated calorimeter.

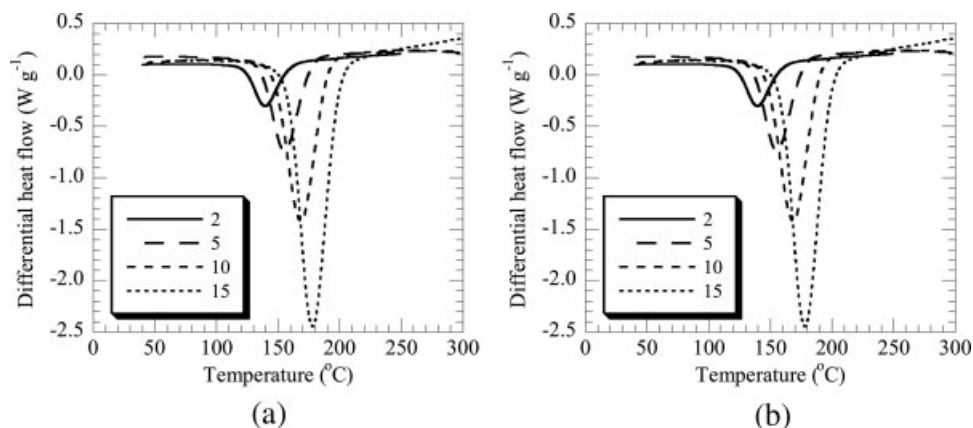


Figure 2 The curves obtained for the DGEBA/HY917/DY073 cure using (a) conventional DSC and (b) the microwave-heated calorimeter.

and the exothermic peak temperature in dynamic curing:

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

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

EXPERIMENTAL

Materials

The epoxy resin system used was a DGEBA with HY917/DY073. The epoxy resin was a liquid DGEBA with an average molecular weight of 384 g mol^{-1} and an epoxy value of 5.2 equiv. per kg. The HY917 (Vantico) was an acid anhydride hardener (4-cyclohexene-1,2-dicarboxylic anhydride). The accelerator DY073 (Vantico) was an amine-phenol complex, which consisted of dibutyl phthalate, tributylamine, and phenol. The resin was prepared by thoroughly mixing 100

parts DGEBA with 85 parts HY917 and 2 parts DY073 immediately before the analysis.

Curing procedure

Thermal curing was conducted using a PerkinElmer Pyris 1 DSC (differential scanning calorimeter). Curing of samples 5–10 mg in size was carried out under a nitrogen atmosphere at heating rates 2, 5, 10, and 15 K min^{-1} and also using isothermal temperatures 110, 120, 130, and 140°C . For each curing conditions, three measurements were carried out and averaged. All data were within 0.01 of the average.

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 TE_{111} 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 an amplifier (Microwave Amplifiers Ltd.). Transmitted and reflected powers were measured using an Anritsu ML4238A power meter. The power absorbed

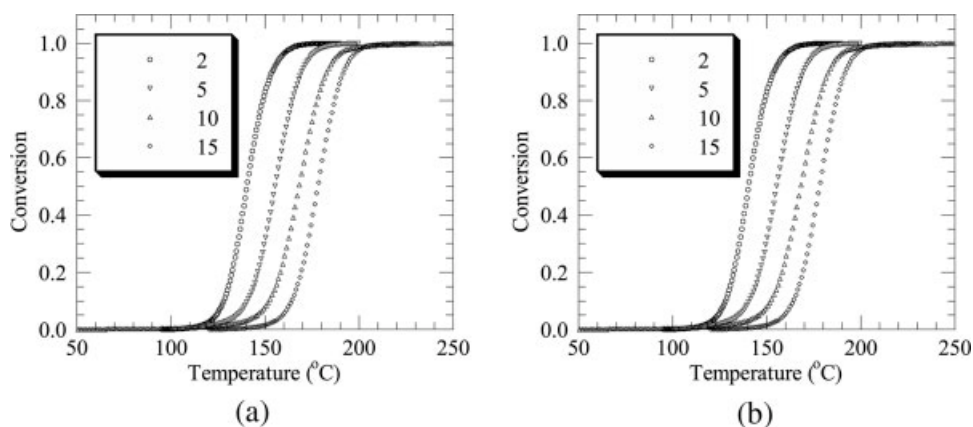


Figure 3 (a) Conversion and (b) reaction rates for the DGEBA/HY917/DY073 system obtained using conventional DSC.

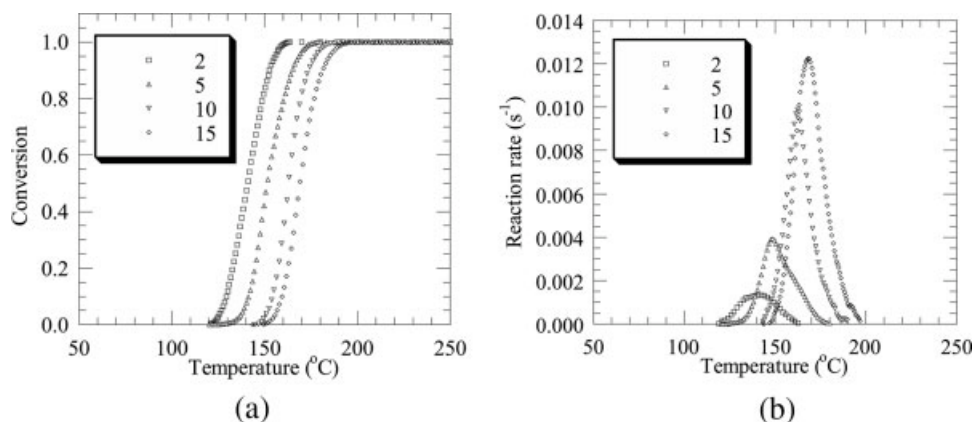


Figure 4 (a) Conversion and (b) reaction rates for the DGEBA/HY917/DY073 system obtained using the microwave-heated calorimeter.

by the sample was calculated as total power minus the transmitted and reflected powers and was used for the calorimetric analysis.

The epoxy resin samples (0.4–0.5 g) were cured in glass test tubes placed in the center of the cavity. The temperature of the sample was monitored using a fluoro-optic thermometer 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 give the desired heating rate. Dynamic curing was carried out at heating rates of 2, 5, 10, and 15 K min⁻¹ and isothermal curing was performed at 110, 120, 130, and 140°C. The dielectric properties were analyzed *in situ* during isothermal curing of the resin. Detailed description of the method can be found elsewhere.¹⁶

RESULTS AND DISCUSSION

Dynamic curing

Figure 2 shows the curves obtained using DSC and the microwave calorimeter for the cure of the epoxy resin system.

Figures 3 and 4 show the conversions and reaction rates for the DGEBA/HY917/DY073 obtained using conventional DSC and microwave-heated calorimeter, respectively. The conversions and reaction rates were obtained using the following equations:

$$\alpha = \frac{\Delta H_T}{\Delta H_{Tot}} \quad (8)$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_{Tot}} \frac{d\Delta H_T}{dt} \quad (9)$$

where α is conversion, ΔH_T is the enthalpy of reaction at temperature T and time t , ΔH_{Tot} is the total enthalpy of reaction, and $d\alpha/dt$ is the reaction rate. Enthalpies were measured by integrating the heat flow against time curves in the case of DSC measure-

ments and microwave power against time in the case of the microwave measurements. Sample background correction was carried out using Bandara's method¹⁷ prior to integration. Bandara's method takes into account the changes in specific heat during the curing reaction and is given by

$$F(t) = \frac{\int_0^t \{G(t) - F(t)\} dt}{\int_0^{t_{end}} \{G(t) - F(t)\} dt} \{P_2(t) - P_1(t)\} + P_1(t) \quad (10)$$

where $F(t)$ is the sample background, $G(t)$ is the total signal corrected for the instrument background, t_{end} 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 curve prior to the start of the curing reaction, and $P_2(t)$ is the DSC signal for the cure resin estimated by a rerun of the fully cured sample. In this work $P_2(t)$ was estimated through linear extrapolation of the portion of the curve after the end of the curing reaction.

As can be seen from Figures 3 and 4, in microwave curing, the curing reaction occurred over a smaller temperature range and, except in the case of curing at 2°C/min, the peak in reaction rate occurred at lower temperatures using microwave heating than in the case of conventional heating. The exothermic peak

TABLE I
Exothermic Peak Temperatures for DGEBA/HY917/DY073 System Cured Using Conventional and Microwave Heating

Heating rate (K min ⁻¹)	T_p (°C)	
	Conventional DSC	Microwave-heated calorimeter
2	140.0 ± 0.8	134.6 ± 1.2
5	155.5 ± 0.8	148.5 ± 0.9
10	168.5 ± 1.0	162.5 ± 2.1
15	178.0 ± 0.9	168.5 ± 1.0

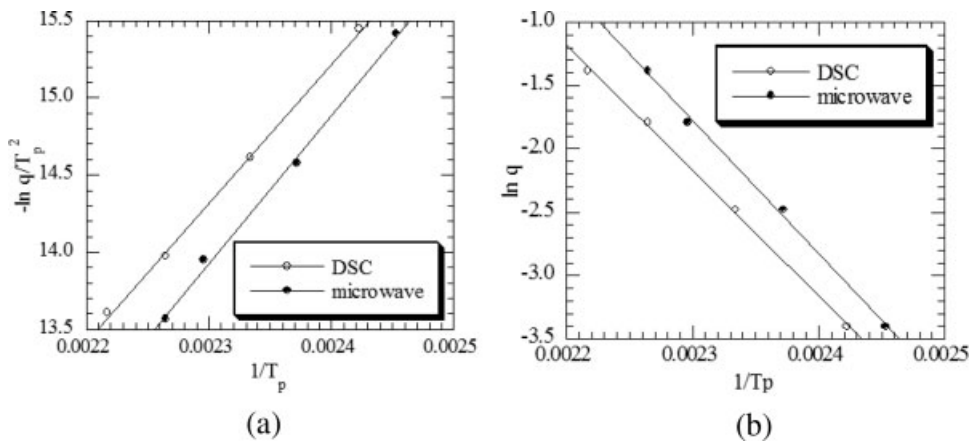


Figure 5 Plots of $-\ln(q/T_p^2)$ against $1/T_p$ for (a) conventional curing and (b) microwave curing of the DGEBA/HY917/DY073 system.

temperatures (T_p) for the DGEBA/HY917/DY073 system cured using conventional DSC and the microwave-heated calorimeter are shown in Table I.

Figure 5(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 was calculated using the Kissinger's method. The activation energies were 75.5 ± 0.2 and 80.0 ± 0.2 kJ mol $^{-1}$ for the conventional and microwave curing, respectively. Figure 5(b) shows the plots of $\ln q$ against $1/T_p$ to calculate the activation energies using Ozawa's method. The values obtained were 78.6 ± 0.2 and 82.8 ± 0.2 kJ mol $^{-1}$ for the conventional and microwave curing, respectively. As can be seen, although the values obtained for the activation energies were slightly different, both Kissinger's and Ozawa's methods gave a higher value of activation energy for the microwave curing of the epoxy resin system.

Equation (1) can be modified to give

$$\ln \frac{d\alpha}{dt} = \ln(Af(\alpha)) - \frac{E}{RT} \quad (11)$$

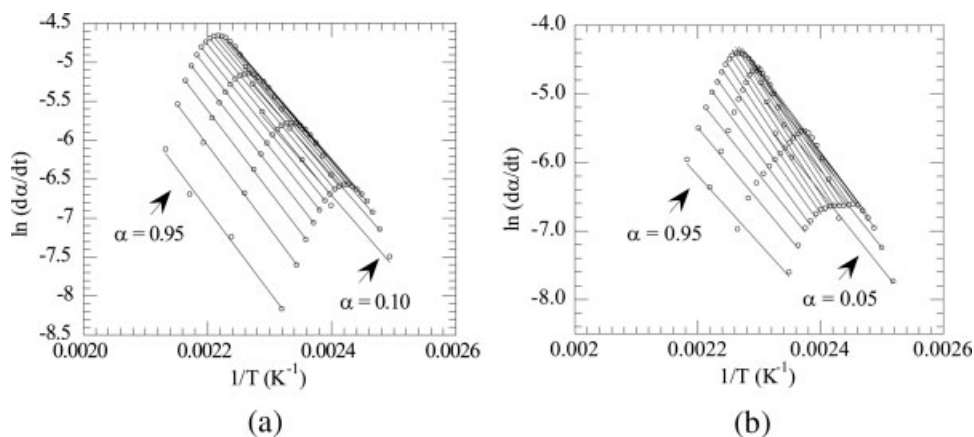


Figure 6 Plots of $\ln(d\alpha/dt)$ against $1/T$ for curing of the DGEBA/HY917/DY073 using (a) DSC and (b) microwave calorimeter.

Hence during the curing of an epoxy resin, the reaction rate is only a function of temperature at any given conversion and the plot of $\ln d\alpha/dt$ against $1/T$ should be a straight line with slope $-E/R$.¹⁸

Figure 6 shows such plots for the curing of the epoxy resin using DSC and the microwave calorimeter. Figure 7 shows the plots of activation energy against conversion for the resin obtained from the straight lines shown in Figure 6. As can be seen, in both cases, the activation energies were higher in the case of the microwave curing of the epoxy resin system. This is in agreement with the results obtained using the Kissinger's and Ozawa's kinetics methods. In conventional curing, the activation energy increased with conversion while in microwave curing a peak was observed in the activation energy against conversion. This suggests that different reaction mechanisms may exist using conventional and microwave heating of this epoxy resin system. This kinetics model, however, does not give an indication of the reaction orders and so a more detailed kinetics model is required to establish any differences in the cure mechanisms.

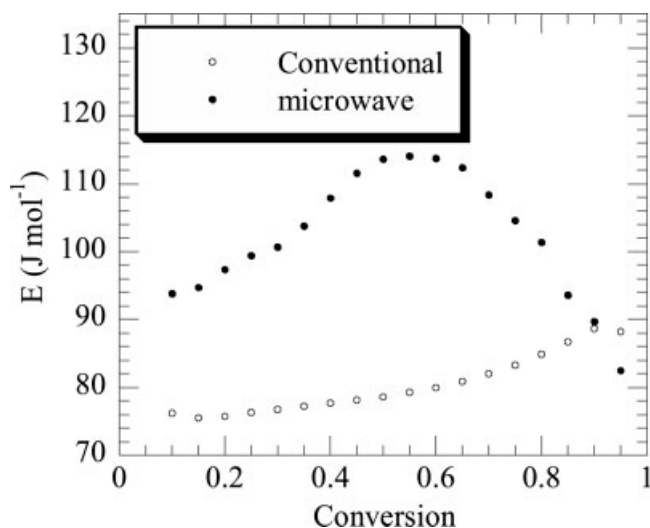


Figure 7 Activation energies for conventional and microwave curing as a function of conversion.

The acid-anhydride curing of epoxy resins generally follows an autocatalytic model as a result of an increase in the concentration of hydroxyl groups during diester formation (see Scheme 1). The autocatalytic model was used for the analysis of the curing behavior of the epoxy resin. This was achieved through direct fitting of the reaction rate data to the eq. (3) using Gnuplot which applies an implementation of the nonlinear least-squares Marquardt-Levenberg algorithm. It was found that the asymptotic errors in the obtained values for A_1 and E_1 were very high

(>100%) and the fit was not sensitive to the values of these parameters. Thus, only the autocatalytic part of equation, i.e., the following equation, was used for fitting the data.

$$r = A_2 \exp(-E_2/RT)\alpha^m(1-\alpha)^n \quad (12)$$

Figure 8 shows the curing data together with the fits for the DSC and microwave curing.

As can be seen from Figure 8, the DSC curves fitted very well to eq. (12). The fits obtained using the microwave results were not as good and the peak reaction rates predicted using the fits were lower than the experimental results. The fits were, however, adequate to describe the behavior of the resin cured using microwave heating. Table II shows the parameters obtained by fitting the curing results to eq. (12). Comparison of the fit parameters shows that the value of preexponential factor is much larger for microwave-cured samples, suggesting the possibility of more collisions between reactive groups during microwave curing. It is possible that this is a result of the heating process wherein the microwave energy couples with the dipoles in the materials and forces them to oscillate, thus forcing more collisions that would otherwise take place under conventional heating. The activation energy of the cure reaction was higher in microwave curing, suggesting a larger barrier to the curing reaction in this cure method. This is in agreement with the results obtained using the kinetics models described earlier, although the Kissinger's and Ozawa's methods assumed an n th order kinetic model and the

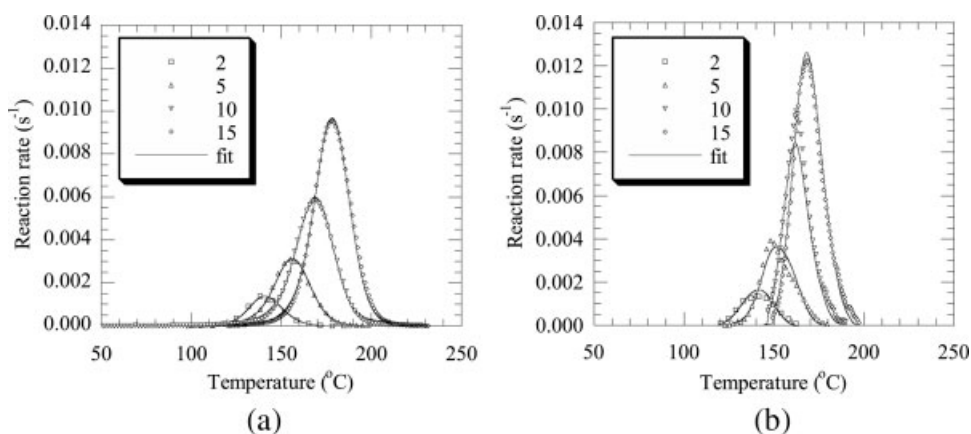


Figure 8 Reaction rate against temperature and the fitted curves for curing using (a) DSC and (b) microwave-heated calorimeter.

TABLE II
Parameters Obtained from Fitting of the Dynamic Cure Data to eq. (12)

	A_2 (s^{-1})	E_2 ($kJ\ mol^{-1}$)	M	N
DSC	6.39×10^7 ($\pm 6.43 \times 10^5$)	79.9 (± 0.04)	0.64 (± 0.01)	1.25 (± 0.01)
Microwave	3.49×10^{11} ($\pm 2.01 \times 10^9$)	109.0 (± 0.20)	0.49 (± 0.01)	1.35 (± 0.01)

TABLE III
 T_g 's of Products Obtained through Dynamic Curing
of DGEBA/HY917/DY073

Heating rate (K min ⁻¹)	Onset (°C)	Half C_p (°C)	End (°C)
DSC			
2	110	115	121
5	108	112	116
10	92	95	100
15	71	77	83
Microwave			
2	102	106	111
5	81	87	93
10	73	78	82
15	65	71	75

direct fitting assumed an autocatalytic reaction model. A similar effect has been observed during conventional and microwave heating of the RTM6 epoxy-amine system.¹⁹

To investigate the effect of the curing method on the glass transition temperatures of the cured resins, these were measured using DSC for both types of curing methods. Table III shows the glass transitions of the resulting products. The T_g values are average of three measurements and the results were within $\pm 2^\circ\text{C}$.

Table III shows that for both conventional and microwave curing, the T_g of the cured epoxy resin decreased with increasing the heating rate used for its cure. It also shows that at each heating rate, the T_g of the conventionally cured epoxy resin was higher than that of the resin cured using microwave heating.

Isothermal curing

Figure 9 shows the plots of conversion and reaction rate for the isothermal curing of the epoxy resin cured using DSC. Figure 10 shows the same plots obtained

using the microwave calorimeter. Isothermally cured samples were analyzed for their final conversion using DSC. Each cured sample was heated in DSC at a heating rate of 10 K min⁻¹ to 250°C and the enthalpy of the residual cure was analyzed. The final conversion for the isothermally cured sample was calculated as $1 - ([\text{the residual enthalpy of reaction for the isothermally cured sample}]/[\text{the enthalpy of reaction for uncured resin}])$. The residual enthalpy of reaction was 0 for all isothermally cured samples except for samples cured using conventional heating at 110 and 120°C.

As can be seen from Figures 9 and 10, the reaction rate at the start of the reaction ($\alpha = 0$) is not maximum, indicating that n th order kinetics model does not apply to the isothermal cure of the DGEBA/HY917/DY073 epoxy resin system.

Equation (11) was used to obtain the activation energy values during isothermal cure of the epoxy resin system. Figure 11 shows the plot of activation energy against conversion for the two heating methods.

For isothermal cure of the DGEBA/HY917/DY073 system, the activation energy of the cure reaction was smaller in microwave heating than in conventional heating. This is the opposite of the results obtained using the dynamic cure of this epoxy resin (see Fig. 7). It is possible that since there are at least two different reactions involved in the curing of the epoxy resin system, they have different activation energies and preexponential factors, giving rise to different apparent overall values depending on the heating cycle used. The activation energy of the cure reaction for the microwave curing showed a maximum with conversion. This effect was also observed in the dynamic cure of this epoxy resin.

As in dynamic cure, the T_g 's of the samples isothermally cured using conventional and microwave heating were analyzed using DSC to study the effect of the type of heating used for curing the epoxy resin. Table

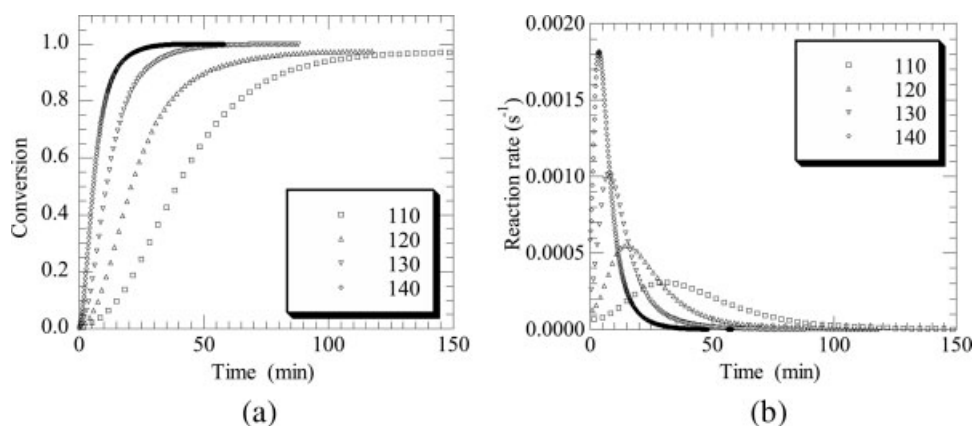


Figure 9 (a) Plots of conversion against time and (b) plots of reaction rate against time for the DGEBA/HY917/DY073 obtained using DSC.

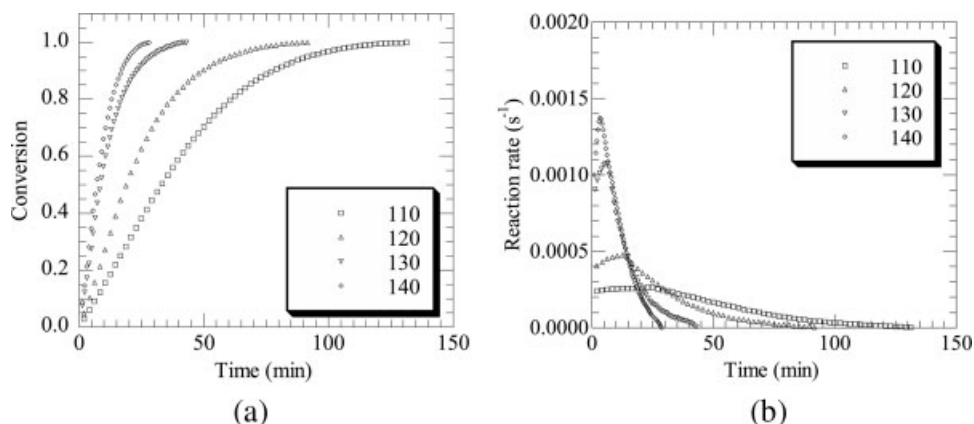


Figure 10 (a) Plots of conversion against time and (b) plots of reaction rate against time for the DGEBA/HY917/DY073 obtained using the microwave calorimeter.

IV shows the T_g 's of the isothermally cured samples. The T_g values are average of three measurements and the results were within $\pm 2^\circ\text{C}$. For both conventional and microwave curing, the glass transition temperature of the cured resin showed a peak with the cure temperature. The cure temperature that generated the highest glass transition temperature was, however, different using conventional and microwave heating. As in the dynamic curing, the samples cured using conventional heating had higher T_g values than did the microwave-cured ones. Glass transition temperature is known to depend on the extent of crosslinking in epoxy resins.^{1,20} The lower T_g 's observed for the microwave-cured samples may suggest a lower crosslink density in those samples when compared with conventionally cured samples. This may have been caused by the faster curing during microwave heating, which resulted in a more rapid increase in viscosity and hence lower mobility in the resin molecules, making some of the reactive groups inaccessible. This could in turn have resulted in a lower conversion in

the microwave-cured samples. Similar results have been observed by Marand et al. for a DGEBA/DDS epoxy system.⁹ When the microwave-cured samples were analyzed using DSC by heating to 300°C at 10 K min^{-1} no residual cure was observed. The difficulties in the measurement of residual cures at conversions beyond 90% have been reported in the literature.²¹ It is, therefore, likely that the residual cure in the microwave-cured samples was too small to be measured using DSC.

Dielectric properties

Figure 12 shows the dielectric properties of the resin during curing using microwave-heated oven against curing time and conversion. The experimental data for the dielectric loss factor showed a significant scatter ($\sim 10\%$); however, the expected trends in the dielectric properties were observed. The dielectric constant and loss factor decreased with the extent of cure, because of decreased molecular mobility (caused by the increased resin viscosity), and depletion of the functional polar groups during the cure reaction.²²⁻²⁴

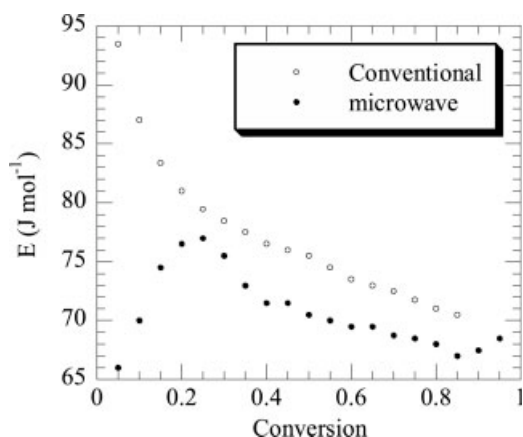


Figure 11 Activation energies for conventional and microwave isothermal cure as a function of conversion.

TABLE IV
 T_g 's of Products Obtained through Isothermal Curing of DGEBA/HY917/DY073

Temperature ($^\circ\text{C}$)	Onset ($^\circ\text{C}$)	Half C_p ($^\circ\text{C}$)	End ($^\circ\text{C}$)
Conventional			
110	103	107	111
120	109	112	117
130	114	117	121
140	110	114	118
Microwave			
110	85	88	94
120	108	112	120
130	102	108	116
140	100	106	112

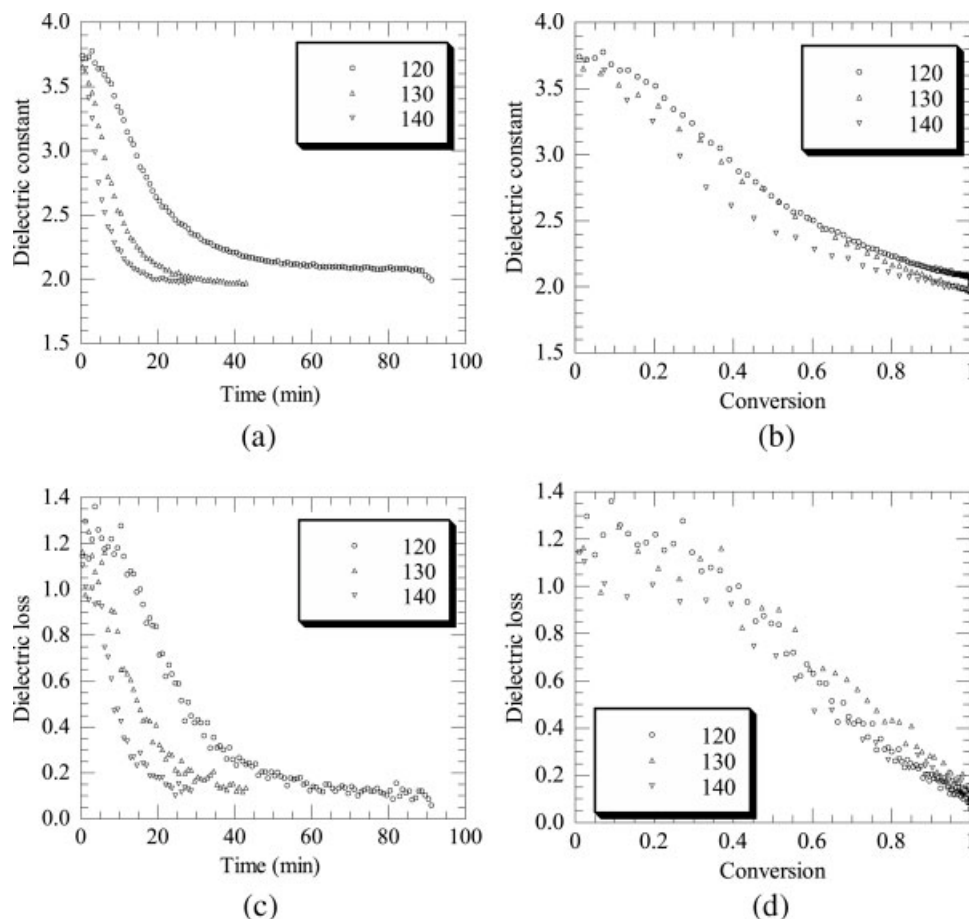


Figure 12 Dielectric properties of the DGEBA/HY917/DY073 during microwave cure: (a) dielectric constant against time, (b) dielectric constant against conversion, (c) dielectric loss against time, and (d) dielectric loss against conversion.

CONCLUSIONS

A detailed calorimetric study was carried out to compare the kinetics of cure in an epoxy–acid system (DGEBA/HY917/DY073) using conventional and microwave heating methods. Both dynamic and isothermal curing were carried out. Several kinetics models were used to describe the curing processes. Resin cured dynamically showed shorter cure times and higher reaction rates using microwave heating. The values of the activation energy and preexponential factor were higher in microwave curing than in conventional curing. The reaction orders were, however, similar using the two heating methods. Resins cured using conventional heating had higher glass transition temperatures than those cured using microwave heating at each heating rate used for curing the resin.

In the case of isothermal cure, microwave curing resulted in lower activation energy than conventional curing. Again, the glass transition temperature of the microwave-cured resin was lower than that of the conventionally cured resin. It seems probable that there are several reactions taking place in each case,

but that different reaction paths are relatively more dominant depending upon the heating method.

References

- Mijović, J.; Wijaya, J. *Macromolecules* 1990, 23, 3671.
- Mijović, J.; Fishbain, A.; Wijaya, J. *Macromolecules* 1992, 25, 986.
- Hedreul, C.; Galy, J.; Dupuy, J.; Delmotte, M.; More, C. *J Appl Polym Sci* 1998, 68, 543.
- Hill, D. J. T.; George, G. A.; Rogers, D. G. *Polym Adv Technol* 2001, 12, 169.
- Hill, D. J. T.; George, G. A.; Rogers, D. G. *Polym Adv Technol* 2002, 13, 353.
- Wei, J.; Hawley, M. C.; DeMeuse, M. T. *Polym Mater Sci Technol* 1992, 66, 478.
- Wei, J.; Hawley, M. C. *Polym Eng Sci* 1995, 35, 461.
- Boey, F. Y. C.; Rath, S. K. *Adv Polym Technol* 2000, 19, 194.
- Marand, E.; Baker, K. R.; Graybeal, J. D. *Macromolecules* 1992, 25, 2243.
- Tanrattanakul, V.; SaeTiaw, K., *J Appl Polym Sci* 2005, 97, 1442.
- Zhou, J.; Si, C.; Mei, B.; Yuan, R.; Fu, Z., *J Mater Process Technol* 2003, 137, 156.
- Barton, J. M. In *Advances in Polymer Science*, Vol. 72: Epoxy Resins and Composites I; Dušek, K., Ed.; Springer-Verlag: Berlin, 1985; p 111.

13. Kamal, M. R. *Polym Eng Sci* 1974, 14, 231.
14. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
15. Ozawa, T. *J Ther Anal* 1970, 2, 301.
16. Nesbitt, A.; Navabpour, P.; Degamber, B.; Nightingale, C.; Mann, T.; Fernando, G.; Day, R. J. *Meas Sci Technol* 2004, 15, 2313.
17. Bandara, U. *J Therm Anal* 1986, 31, 1063.
18. Lü, C.; Cui, Z.; Yang, B.; Su, X.; Huo, C.; Shen, J. *J Appl Polym Sci* 2002, 86, 589.
19. Navabpour, P.; Nesbitt, A.; Degamber, B.; Fernando, G.; Mann, T.; Day, R. *J Appl Polym Sci* 2006, 99, 3658.
20. DiBenedetto, A. T. *J Polym Sci Part B: Polym Phys* 1987, 25, 1949.
21. Boey, F. Y. C.; Yap, B. H. *Polym Test* 2001, 20, 837.
22. Delmotte, M.; Julien, H.; Ollivon, M. *Eur Polym Mater* 1991, 27, 371.
23. Jow, J.; Hawley, M. C.; Finzel, M.; Kern, T. *Polym Eng Sci* 1988, 28, 1450.
24. Finzel, M. C.; Hawley, M. C.; Jow, J. *Polym Eng Sci* 1991, 31, 1240.