

Effect of the Crosslinking Degree on Curing Kinetics of an Epoxy–Anhydride System*

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SYNOPSIS

The cure kinetics of a diglycidyl ether of bisphenol A (DGEBA)-based epoxy resin with methyltetrahydrophthalic anhydride and an accelerator was studied by nonisothermal DSC data. The systems were uncured resin and partially cured with the following extents of cure measured by the residual heat method (α_{DSC}): 0.37, 0.63, 0.81, and 0.90. The activation energy calculated by the Kissinger method increases from 63 kJ/mol for the uncured epoxy to 77 kJ/mol for the partially cured with $\alpha_{\text{DSC}} = 0.90$. Additionally, the activation energy calculated by the isoconversional method shows a dependence on the conversion degree α . The activation energy tends to decrease initially with the conversion degree, possibly due to the autocatalytic effect; then, it passes through a minimum about $\alpha = 0.4$ and, finally, increases slightly due to the increase of crosslinks which reduce the mobility of the unreacted groups. A simple, consistent method of kinetic analysis was applied. This method enables one to select the most convenient model and the calculation of kinetic parameters. A two-parameter (m, n) autocatalytic model (Šesták–Berggren equation) was found to be the most convenient model to study the curing of epoxy systems. The results show a dependence of the kinetic parameters on the initial degree of crosslinking of the partially cured epoxy. The exponent m tends to decrease with the extent of cure, while the exponent n remains practically invariable. These results show a change of the kinetic when the initial extent of cure of the epoxy system increases. The $\ln A$ data, A being the preexponential factor in the Arrhenius dependence of the temperature on the rate of conversion, increase with the extent of cure, showing a correlation with the calculated activation energy values. The nonisothermal DSC curves theoretically calculated show a very good agreement with the experimental data. The two-parameter (m, n) autocatalytic model gives a good description of the curing kinetics of epoxy resins with different extents of cure. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The kinetics and mechanisms of the curing of epoxy resins by cyclic anhydrides have been extensively studied during the last 30 years. Such great attention derives from the multiple applications of these materials in the electrotechnical industry. Similarly, as happens with other thermosetting polymers, the

study of the cure kinetics contributes both to a better knowledge of the process development and to improving the quality of the final product.

At present, the uncatalyzed cure of epoxy–anhydride systems is quite well understood.^{1,2} It begins through the reaction of the anhydride group with hydroxyl groups which are present in oligomers or impurities of the resin, generating a monoester and a carboxylic group. The monoester reacts with the epoxide to form a diester to which carboxylic groups react with another anhydride. The concentration of hydroxyl groups increases and can produce an autocatalytic effect. In practice, a catalyst

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is used to accelerate the cure, but in this case, the mechanism is more complex. In the case when a tertiary amine is used as the catalyst, Matějka et al.³ proposed that the cure of a diepoxide occurs as an alternating copolymerization leading to a cross-linked polyester. Steinmann¹ observed that the curing of epoxides with hexahydrophthalic anhydride (HHPA) becomes complicated by side reactions such as chain anhydride formation and the isomerization of the anhydride, while the curing with phthalic anhydride (PA) prevents these reactions.⁴ Other curing mechanisms of such systems have been reviewed by Barton.⁵

The kinetics of the epoxy-anhydride system has been studied through phenomenological models: the n th-order reaction and autocatalytic model. Over the last 30 years, differential scanning calorimetry (DSC) has been a common analytical technique in the attempt to study the cure kinetics.⁶ The pioneering work of Fava⁷ showed calorimetric results of the catalyzed curing of the diglycidyl ether of bisphenol A (DGEBA)-HHPA system by both isothermal and residual heat of curing methods. Other authors⁸⁻¹⁰ studied the cure kinetics of such systems using various nonisothermal DSC scans which allow the calculation of the activation energy (Kissinger, Ozawa, and isoconversional methods). Woo and Seferis¹¹ studied the isothermal cure of DGBEA with trimellitic anhydride by DSC and Fourier transform infrared spectroscopy (FTIR). For the uncatalyzed system, the reaction was found to be second-order-limited by diffusion effects as the matrix gelling, while the catalyzed one was second order up to 0.3 of fractional conversion and first order thereafter. The effect on the anhydride structure was studied by Patel and Patel,¹² showing that HHPA presents a higher reactivity than does PA. The cure kinetics analyzed by the Freeman-Carroll method was found to have an order of reaction between 1 and 1.4 depending on the anhydride.

In a previous article,¹³ the kinetics of an epoxy resin based on DGEBA cured by methyltetrahydrophthalic anhydride (MTHPA) with an accelerator under nonisothermal conditions was studied. A simple consistent method of kinetic analysis¹⁴ was applied, which showed that the most convenient phenomenological model for the description of curing was an autocatalytic kinetic model. The objective of this article was to study the cure kinetics of this epoxy-anhydride system at different degrees of crosslinking, under nonisothermal conditions. The degree of crosslinking of each sample was obtained by curing at different periods of time at 80°C. The extent of cure was calculated both by FTIR¹⁵ and

DSC.⁶ The activation energy corresponding to each curing process was calculated by methods using various nonisothermal DSC curves.

The value of the activation energy allows the selection of the kinetic model and the determination of the kinetic parameters.¹⁴ Results fit well to an autocatalytic model, and the parameters $\ln A$ and exponents m and n were calculated. The results show that increase of the crosslinking affects the kinetics of the residual curing, modifying not only the activation energy, but also the kinetic parameters: m , n , and $\ln A$.

THEORY

The basic rate equation in the analysis of DSC kinetics is

$$d\alpha/dt = Ae^{-x}f(\alpha) \quad (1)$$

where at a given time and temperature $d\alpha/dt$ is the rate of conversion; A , the preexponential factor; $x = E/RT$, the reduced activation energy (E is the activation energy), and $f(\alpha)$, the function representing the kinetic model. The empirical kinetic models mostly applied in curing reactions are the reaction order model:

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

and the two-parameter autocatalytic model (Šesták-Berggren equation):

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (3)$$

A basic assumption in the DSC technique is that the heat flow, ϕ , generated in the curing reaction is proportional to the rate conversion:

$$\phi = \frac{d\alpha}{dt} \Delta H \quad (4)$$

where ΔH is the total heat of curing. Combining eq. (4) with eq. (1), the heat flow measured in the DSC experiment may be described by the following equation:

$$\phi = Ae^{-x}\Delta Hf(\alpha) \quad (5)$$

The objective of the kinetic analysis of the DSC data is to find the most probable kinetic model which gives the best description of the curing reaction as

well as allowing the calculations of reliable parameters E and A .

For nonisothermal DSC curves, the change of the degree of conversion on temperature is

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \frac{d\alpha}{dt} = \frac{A}{\beta} e^{-x} f(\alpha) \quad (6)$$

where $\beta = dT/dt$ is the constant heating rate. Separating variables in eq. (6) and integrating and substituting eq. (5), the following integral kinetic equation is obtained:

$$\Delta H g(\alpha) f(\alpha) = \frac{E}{\beta R} \phi \left[\frac{\pi(x)}{x} \right] \quad (7)$$

where $\pi(x)$ is an approximation of the temperature integral which can be calculated by approximate expressions.^{14,16}

In the last 20 years, various methods have been described to evaluate all kinetic parameters from one nonisothermal DSC curve only. The main problem of kinetic analysis by these methods is the strong mutual correlation of the activation energy and preexponential factor in eqs. (5) and (7) as reported by Málek et al.^{14,17} It seems therefore not to be possible to calculate all kinetic parameters from one nonisothermal DSC curve only by conventional multiple linear regression or even nonlinear regression algorithms, unless there is *a priori* knowledge of the kinetic model or, at least, one kinetic parameter. This problem can, however, be solved if the activation energy is known.^{14,17}

The activation energy may be calculated from multiple-scan methods where measurements at several heating rates are needed. In the Kissinger method, E is calculated from the slope of $\ln(\beta/T_p^2)$ vs. $1/T_p$, where T_p is the peak temperature of the reaction. The error in the activation energy has proved not to exceed 5%.¹⁸ An alternative method of calculation of E is the so-called isoconversional method which follows from the logarithmic form of eq. (5):

$$\ln \Phi = \ln[\Delta H A f(\alpha)] - E/RT \quad (8)$$

This method allows one to calculate the E for a determined value of conversion degree α .

Once the activation energy has been determined, it is possible to select the kinetic model which best describes the DSC data. For this purpose, it is convenient to define the two following functions:

$$y(\alpha) = \phi e^x = \Delta H A f(\alpha) \quad (9)$$

$$z(\alpha) = \pi(x) \phi \frac{T}{\beta} = \Delta H g(\alpha) f(\alpha) \quad (10)$$

Both $y(\alpha)$ and $z(\alpha)$ functions can easily be calculated from eqs. (9) and (10) provided that the value of the activation energy is known. According to eq. (9), the function $y(\alpha)$ is proportional to the kinetic model. Thus, by plotting the $y(\alpha)$ dependence normalized within the $\langle 0, 1 \rangle$ interval, the shape of the function $f(\alpha)$ is obtained.¹⁴ Nevertheless, the shape of the $y(\alpha)$ function is strongly influenced by E . Hence, the precise activation energy value is vital for a reliable kinetic analysis. The maximum α_M of the $y(\alpha)$ function is a very important parameter to determine the most suitable model. If the $y(\alpha)$ function is decreasing monotonically, having a maximum at $\alpha_M = 0$ (practically $\alpha_M < 0.05$), then the reaction order model can be used to describe the curing process. If the maximum of the $y(\alpha)$ function is localized in the interval $0.05 < \alpha_M < \alpha_p$ (α_p is the conversion degree at the maximum of the DSC peak), then the two-parameter autocatalytic model (Šesták–Berggren equation) gives the best description of the experimental data.^{13,14}

It has been demonstrated (appendix of Ref. 14) that the function $z(\alpha)$ has a maximum at α_p^∞ for any kinetic model. The α_p^∞ corresponds to the maximum of a hypothetical DSC peak for $x_p \rightarrow \infty$. This parameter has a characteristic value for a given kinetic model and is practically independent of the activation energy value. The α_p^∞ parameter depends on the values of the kinetic exponents for both empirical models. Its value is very important for the kinetic model determination.¹⁴ Once the kinetic model has been determined, the kinetic exponents and preexponential factor can be calculated by methods described in Ref. 14.

EXPERIMENTAL

Materials and Cure Procedure

The epoxy resin was a diglycidyl ether of bisphenol A modified type (CIBA-GEIGY Araldite CY225) with an epoxy content of 4, 7 mol/kg. A hardener derived from methyltetrahydrophthalic anhydride with an accelerator (CIBA-GEIGY HY225) was used to cure the resin. Resin and hardener were mixed at a weight ratio of 10 : 8. The mixture was stirred at room temperature for 20 min and then degassed in a vacuum oven at room temperature for 15 min.

Samples were enclosed in aluminum DSC pans, introduced in Pyrex tubes under nitrogen atmosphere, and left in a thermostatic bath at the curing temperature 80°C for different periods of time (3, 6, 12, and 24 h), in order to obtain different extents of cure.

Differential Scanning Calorimetry

Calorimetric measurements were performed with a Mettler thermoanalyzer TA 4000 equipped with a low-temperature range DSC 30 differential scanning calorimetry module. The calorimeter was previously calibrated with an indium standard. The samples' weight were about 10 mg.

After the isothermal curing at 80°C, the sample was quenched from 80°C to room temperature, introduced in the DSC module, and then cooled to -10°C and immediately scanned at a heating rate of 10 K/min to 280°C under a nitrogen atmosphere. The DSC trace shows the glass transition region and the exothermal peak corresponding to the heat of curing. The degree of conversion, α_{DSC} , was calculated by the residual enthalpy of curing⁶:

$$\alpha_{\text{DSC}} = \frac{\Delta H_T - \Delta H_R}{\Delta H_T}$$

where ΔH_T is the total heat of curing obtained by a nonisothermal DSC scan of one fresh sample, and ΔH_R , the residual heat of curing of a sample isothermally cured at 80°C during a specified period of time. Both values were determined at four heating rates: 2.5, 5, 10, and 20 K/min. An average α_{DSC} was calculated for each partially cured epoxy resin.

A second scan obtained at the same heating rate of 10 K/min only shows the glass transition region without any other noticeable calorimetric event. The kinetic analysis of the DSC data and the calculations were performed with the TA-SYSTEM software package.¹⁴

Infrared Measurements

Infrared spectra were performed in a Nicolet 510 M Fourier transform infrared spectrometer. One hundred co-added spectra were scanned for each sample at 4 cm⁻¹ resolution. The resin samples were previously cured at 80°C for different periods of time to obtain an isothermal curve of the conversion degree against time. These samples were prepared for their infrared study by the KBr pellet technique,¹⁵ applying a pressure of 167 MPa for 5 min. The degree of conversion (α_{IR}) was obtained measuring the rel-

ative absorbance of the epoxy band (914 cm⁻¹) against the absorbance of the band associated with the benzene ring (1510 cm⁻¹) as a reference. These absorbances were calculated in the spectra processed by a base-line correction to obtain comparable results.

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves of the uncured epoxy resin and partially cured resins at a heating rate of 10 K/min. Additionally, Figure 2 shows the DSC curves of the uncured epoxy at different heating rates, β . These nonisothermal DSC curves were used for kinetic calculations. The extent of cure, α_{DSC} , of the epoxy partially cured at 80°C calculated by the residual heat method is indicated in Table I with the values obtained by the FTIR technique, α_{IR} . To analyze the differences between both methods in a larger interval of curing times, isothermal curing at 80°C was performed and conversion degrees were calculated by FTIR and DSC techniques (Fig. 3). Differences observed may be attributed to the limitations of the determination of the residual heat of curing.

The peak temperature, T_p , at four heating rates, allows the calculation of the activation energy by the Kissinger method (Table II). On considering the complex nature of cure reaction, this activation energy is an overall value including all the steps of the curing reaction. Table II shows that E increases with the previous extent of cure of the epoxy. As the crosslinking density of the resin is directly related to the extent of cure, the mobility of the reactive groups decreases with the extent of cure, which produces an increase of E on the overall reaction. The uncertainty of E tends to increase with the extent of cure because the residual heat of curing becomes gradually smaller and the peak becomes flatter, increasing the uncertainty of the T_p determination.

Figure 4 shows the apparent activation energy at each conversion degree, α , calculated by the isoconversional method. According to a previous work,¹³ E changes with the degree of conversion. This result has also been observed by Zukas¹⁰ in a catalyzed DGEBA-MTHPA system, which was assigned to an apparent change in the reaction mechanism with the extent of cure. Recently, Salla and Ramis¹⁹ reported a similar effect in the catalyzed curing of unsaturated polyesters.

For the uncured resin and the partially cured resins, the activation energy tends to decrease initially with the conversion degree possibly due to the au-

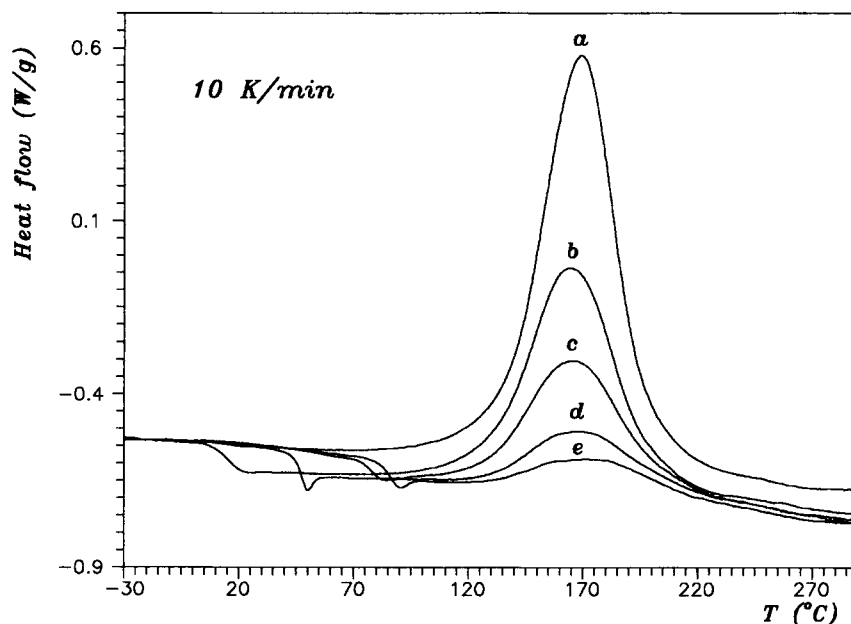


Figure 1 DSC curves of partially cured epoxy resin at 10 K/min for different curing times at 80°C: (a) $t_c = 0$; (b) $t_c = 3$ h; (c) $t_c = 6$ h; (d) $t_c = 12$ h; (e) $t_c = 24$ h.

tocatalytic effect; then, it passes through a minimum about $\alpha = 0.4$ and, finally, increases slightly due to the increase of crosslinks which reduce the mobility of the unreacted groups. For the same reason, when the previous extent of the cure of the partially cured epoxy resin increases, the E values at different α are vertically shifted, reaching higher values. An average of the activation energies, E_{avg} , may be ob-

tained whose value also increases with the previous extent of cure of the epoxy resin (Table II). Similarly to the Kissinger method, the uncertainty of this E_{avg} increases with the extent of cure. The value of E_{avg} for the uncured resin is slightly lower than the value reported in another article (73 kJ/mol in Ref. 13). This difference is probably caused by the commercial materials being used without previous purification.

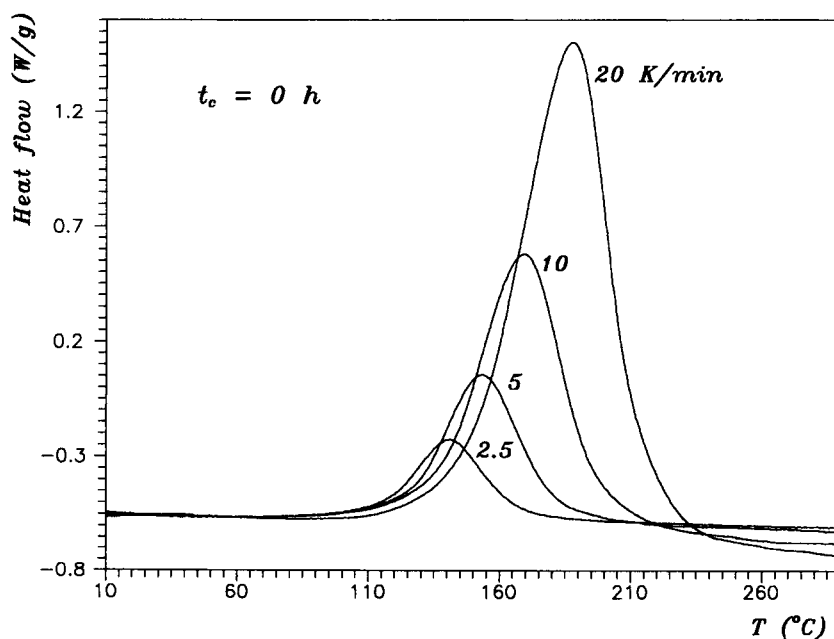


Figure 2 DSC curves of uncured epoxy resin ($t_c = 0$) at different heating rates (K/min).

Table I Extent of Cure of Partially Cured Epoxy Resin Calculated by the Residual Heat Method (α_{DSC}) and FTIR Spectroscopy (α_{IR})

t_c (h)	α_{DSC}	α_{IR}
3	0.37 ± 0.04	0.32 ± 0.02
6	0.63 ± 0.04	0.61 ± 0.02
12	0.81 ± 0.02	0.86 ± 0.01
24	0.90 ± 0.02	0.93 ± 0.01

It is not strange, then, that some differences in the reactivity of the resin of different batches may be observed.

The DSC data for the uncured and partially cured epoxy resin were converted to $y(\alpha)$ and $z(\alpha)$ functions according to eqs. (9) and (10). Figures 5 and 6 show that these functions normalized within the $\langle 0, 1 \rangle$ interval, respectively, for a heating rate of 10 K/min. For a better understanding, the functions for the other three heating rates are not included in these figures. The shape of $y(\alpha)$ suggests that the autocatalytic model is more adequate than is the reaction order model. The maximum of $y(\alpha)$ determines the exponents m and n of the $f(\alpha)$ in eq. (3), whose values are plotted in Figure 7(a) for the different epoxy resins. The preexponential factor values are plotted in Figure 7(b).

It is observed that the maximum α_M of the $y(\alpha)$ function shifts to lower values of the conversion degree when the extent of cure increases from the uncured resin to the partially cured for 3, 6, and 12 h at 80°C. This fact is related to the decrease of the exponent m with the extent of cure, while the ex-

Table II Activation Energy Values by the Kissinger Method and Average Activation Energy Values Obtained by the Isoconversional Method in kJ/mol

t_c (h)	$E_{(Kissinger)}$	E_{avg}
0 (uncured)	63 ± 3	69 ± 2
3	69 ± 4	73 ± 2
6	71 ± 3	79 ± 4
12	73 ± 5	92 ± 8
24	77 ± 7	—

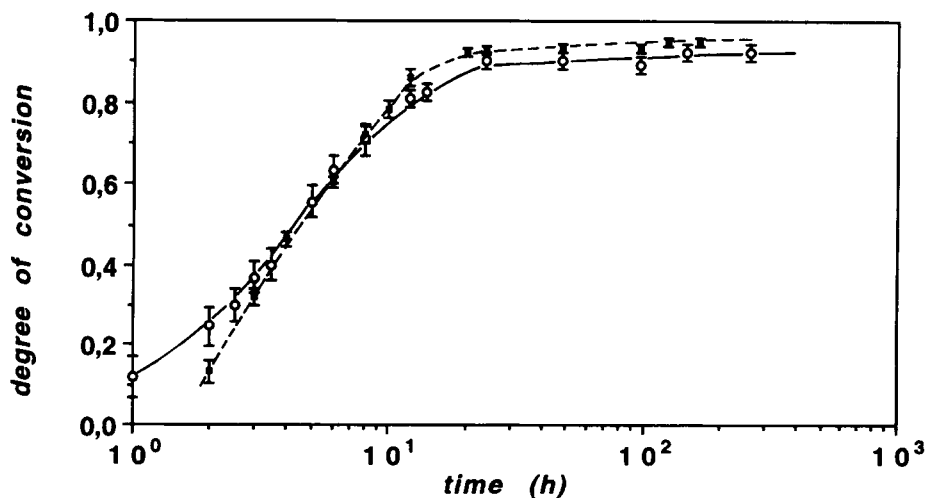
ponent n remains practically unchanged. These results show that the kinetics of the residual curing changes from the uncured resin to the partially cured.

This change of the kinetic parameters is probably due to the decrease of both the concentration and the mobility of the unreacted chemical groups of the partially cured epoxy, which, in turn, affect the initiation and propagation steps of the curing process.

The $z(\alpha)$ function shows a maximum value between 0.56 and 0.48, being less dependent on the crosslinking density than is the maximum of the $y(\alpha)$ function and practically independent of the activation energy (Table III).

The results of the activation energy calculated by the Kissinger method and the preexponential factor show a correlation expressed by the following equation:

$$\ln A = -1.036 + 0.226E$$

**Figure 3** Conversion degree of isothermal curing of an epoxy resin at 80°C against time by (■) FTIR and (○) DSC techniques. Lines are drawn as visual guides.

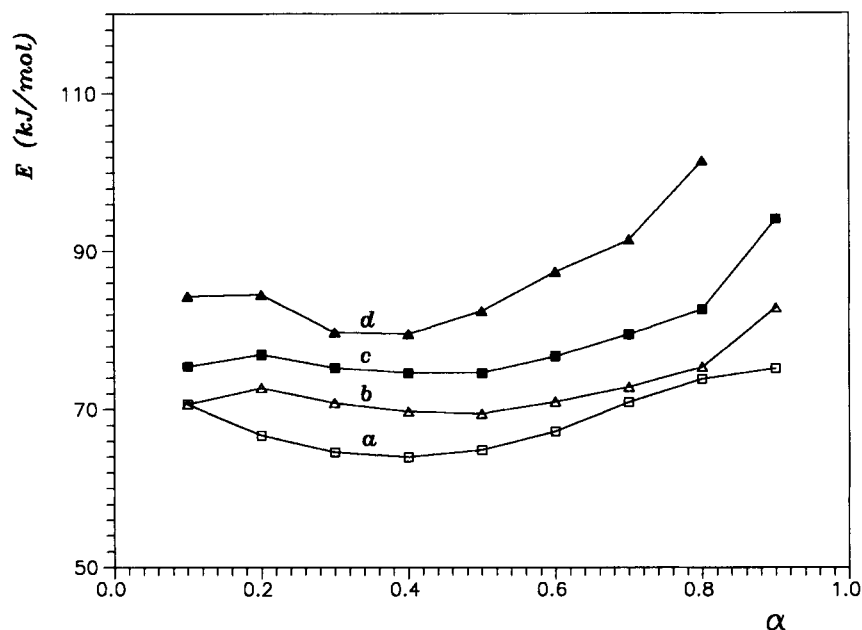


Figure 4 The values of the activation energy calculated by the isoconversional method at various values of conversion degree for different partially cured epoxies: (a) $t_c = 0$; (b) $t_c = 3$ h; (c) $t_c = 6$ h; (d) $t_c = 12$ h. Lines are drawn as visual guides.

with a correlation coefficient $r = 0.99$. Any change in the activation energy is, therefore, compensated by the change in $\ln A$. As indicated above, this correlation shows that the methods of kinetic analysis which try to determine all the kinetic parameters from only one experimental DSC curve are somewhat problematic.

Experimental DSC data (points) and curves (full lines) calculated using the kinetic parameters for each epoxy sample are compared in Figure 8. The two-parameter (m, n) autocatalytic model gives a good description of the curing process and allows one to interpret the propagation step of the curing reaction when the crosslinking density of the sample is changed.

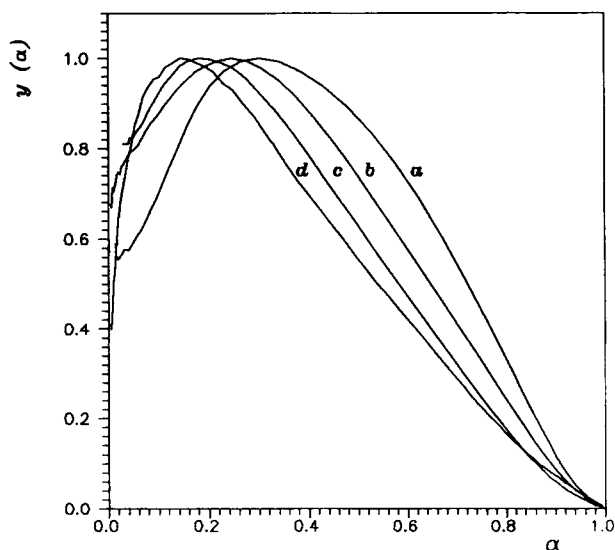


Figure 5 The $y(\alpha)$ functions of partially cured epoxy resin for different curing times: (a) $t_c = 0$; (b) $t_c = 3$ h; (c) $t_c = 6$ h; (d) $t_c = 12$ h.

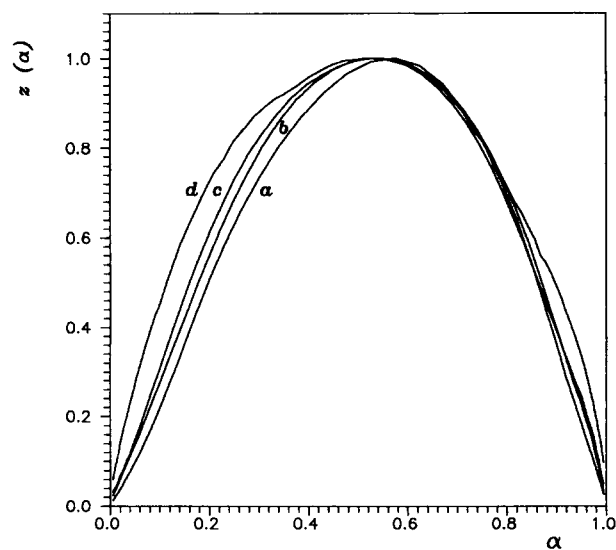


Figure 6 The $z(\alpha)$ functions of partially cured epoxy resin for different curing times: (a) $t_c = 0$; (b) $t_c = 3$ h; (c) $t_c = 6$ h; (d) $t_c = 12$ h.

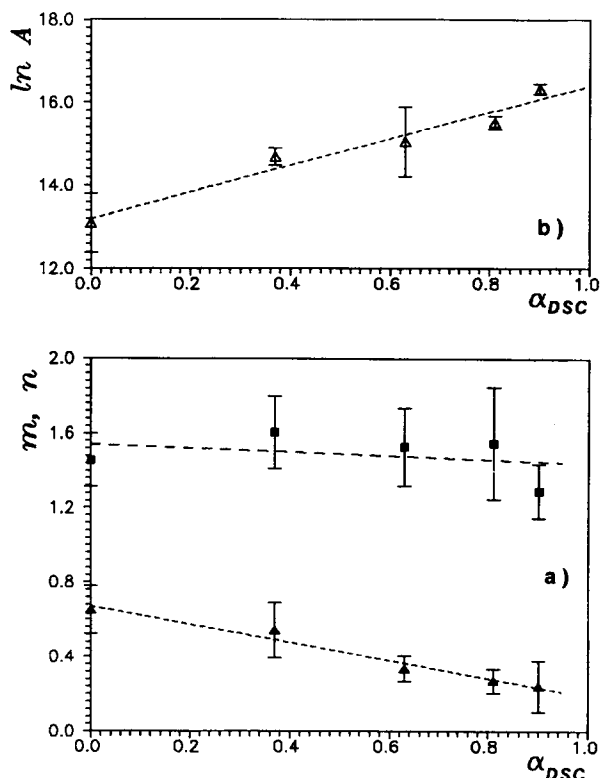


Figure 7 The variation of kinetic parameters with the initial extent of cure of partially cured epoxy resins. Error bars correspond to the standard deviation: (a) exponents (\blacktriangle) m and (\blacksquare) n . (b) (\triangle) Preexponential factor $\ln A$. The lines correspond to a linear regression.

CONCLUSIONS

The cure kinetics of partially cured epoxy resin was studied by nonisothermal DSC data. Measurements at different heating rates provide a determination of the activation energy by the Kissinger method. This E value gradually increases with the extent of cure of the partially cured epoxy resin, which may be due to the decrease of the mobility of the reactive groups. In addition, the activation energy calculated by the isoconversional method at different degrees

Table III Average Values of the Maximum of $y(\alpha)$ Function (α_M) and $z(\alpha)$ Function (α_p^∞) for the Different Partially Cured Epoxy

t_c (h)	α_M	α_p^∞
0 (uncured)	0.31 ± 0.02	0.56 ± 0.04
3	0.25 ± 0.03	0.53 ± 0.02
6	0.17 ± 0.03	0.53 ± 0.02
12	0.14 ± 0.02	0.48 ± 0.06

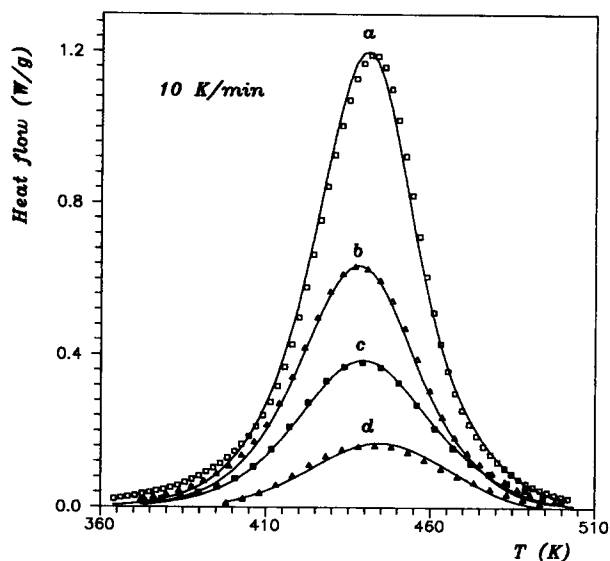


Figure 8 Comparison of (points) experimental and (full lines) calculated DSC curves for partially cured epoxy resin: (a) $t_c = 0$; (b) $t_c = 3$ h; (c) $t_c = 6$ h; (d) $t_c = 12$ h.

shows a dependence on the conversion degree. The activation energy tends to decrease initially with the conversion degree, possibly due to the autocatalytic effect; then, it passes through a minimum about $\alpha = 0.4$ and, finally, increases slightly due to the increase of crosslinks which reduces the mobility of the unreacted groups.

A simple, reliable method of kinetic analysis¹⁴ enables one to select the most convenient model for the catalyzed cure of the DGEBA-based epoxy with MTHPA: A two-parameter autocatalytic model (Šesták-Berggren equation) is the more adequate. Results show a dependence of the kinetic parameters on the initial degree of crosslinking of the partially cured epoxy. The exponent m tends to decrease with the extent of cure, while the exponent n remains practically invariable. These results show a change of the kinetics when the initial extent of cure of the epoxy system increases. The $\ln A$ data increase with the extent of cure, showing a correlation with the calculated activation energy values.

The kinetic parameters obtained allow one to calculate theoretical nonisothermal DSC curves showing a very good agreement with the experimental data. The two-parameter (m, n) autocatalytic model provides a good description of the curing kinetics of epoxy resins with different extents of cure.

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