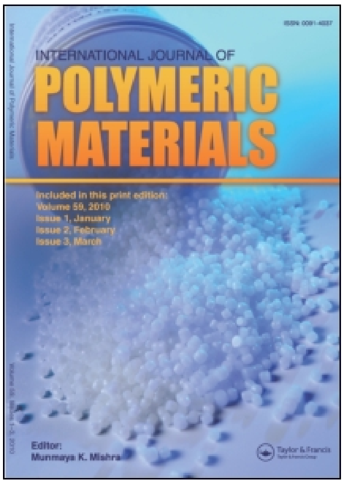
This article was downloaded by:
On: *18 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Curing Kinetics and Thermal Properties Characterization of o-Cresol-formaldehyde Epoxy Resin and MeTHPA System

Jungang Gao[a]; Min Zhao[a]; Yanfang Li[a]
[a] College of Chemistry and Environmental Science, Hebei University, Hebei, Baoding, P.R. China

**To cite this Article** Gao, Jungang , Zhao, Min and Li, Yanfang(2006) 'Curing Kinetics and Thermal Properties Characterization of o-Cresol-formaldehyde Epoxy Resin and MeTHPA System', International Journal of Polymeric Materials, 55: 12, 1009 — 1025

**To link to this Article: DOI:** 10.1080/00914030600620498

**URL:** http://dx.doi.org/10.1080/00914030600620498

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*International Journal of Polymeric Materials*, 55:1009–1025, 2006

ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600620498

# Curing Kinetics and Thermal Properties Characterization of o-Cresol-Formaldehyde Epoxy Resin and MeTHPA System

**Jungang Gao**
**Min Zhao**
**Yanfang Li**
College of Chemistry and Environmental Science, Hebei University,
Hebei, Baoding, P.R. China

*The kinetics of the cure reaction for a system of o-cresol-formaldehyde epoxy resin (o-CFER) with 3-methyl-tetrahydrophthalic anhydride (MeTHPA) as a curing agent and N,N-dimethyl-benzylamine as an accelerator was investigated by means of differential scanning calorimetry (DSC). Analysis of DSC data indicated that an autocatalytic behavior showed in the first stages of the cure for the system, which could be well described by the model proposed by Kamal, which includes two rate constants,* $k_1$ *and* $k_2$*, and two reaction orders, m and n. The activation energy* $E_1$ *and* $E_2$ *are 195.84 and 116.54 kJmol*$^{-1}$*, respectively. In the later stages, the reaction is mainly controlled by diffusion, and a diffusion, factor,* $f(\alpha)$*, was introduced into Kamal's equation. In this way, the curing kinetics were predicted well over the entire range of conversion. Molecular mechanism for the curing reaction was discussed. The glass transition temperature* $T_g$ *was determined by means of torsional braid analysis (TBA). The results showed that* $T_g$*s increased with curing temperature and conversion up to a constant value about 367.1 K. The thermal degradation kinetics of the system was investigated by thermogravimetric analysis (TGA), which revealed two decomposition steps.*

**Keywords:** epoxy resin, 3-methyl-tetrahydrophthalic anhydride, kinetics, glass transition temperature

## INTRODUCTION

Epoxy resins are widely used in the polymer industry as coatings, structural adhesives, insulating materials, polymer matrices for

Received 10 January 2006; in final form 16 January 2006.

Address correspondence to Jungang Gao, College of Chemistry and Environmental Science, Hebei University, Hebei, Baoding 071002, P.R. China. E-mail: gaojg@mail.hbu.edu.cn

composite materials, and so on. The widespread use of epoxy resins, however, is limited in many high performance applications because of their thermal properties. The factors that most influence the thermal properties of epoxy resin are the crosslink density and the structure of the molecular chain. With the introduction of o-cresol groups into the backbone of epoxy resins, the improved resins are considered worthy of further study in terms of their good thermal stability, chemical resistance, mechanical properties, and modification.

Studies of the applications and physical properties of o-cresol-formaldehyde epoxy resin (o-CFER) have been reported in recent years [1–2]. The cure kinetics of bisphenol epoxy resin had been investigated [3–4]. However, the descriptions of the cure kinetics and degradation kinetics of o-CFER with 3-methyl-tetrahydrophthalic anhydride (MeTHPA) system have been lacking until now.

In order to provide a basis for a curing process theory for the applications of o-CFER, it is necessary to conduct research into the curing kinetics of the o-CFER/MeTHPA system. Kamal's model [5], arising from an autocatalytic reaction mechanism, has been applied to isothermal DSC data [6–8]. In general, a good fit of experimental data was obtained in the early stages of the cure, but deviations have been observed in the later stages, particularly near vitrification when the reaction is primarily diffusion controlled. To take into account the diffusion effect, the Kamal model has been extended by the introduction of a diffusion factor $f(\alpha)$.

In this article, the DSC technique was used to study the curing kinetics of o-CFER/MeTHPA. Because the glass transition temperature ($T_g$) can be used effectively to monitor the curing reaction [9], the torsional braid analysis (TBA) was used to determine the $T_g$ of the o-CFER/MeTHPA system. The glass transition temperatures were measured for o-CFER/MeTHPA samples cured isothermally at different temperatures for various periods. Structure changes during the curing process were investigated by Fourier transform infrared analysis (FTIR). Molecular mechanism for the curing reaction was discussion. The mechanism of thermal degradation was studied by means of thermogravimetric analysis (TGA) [10–11].

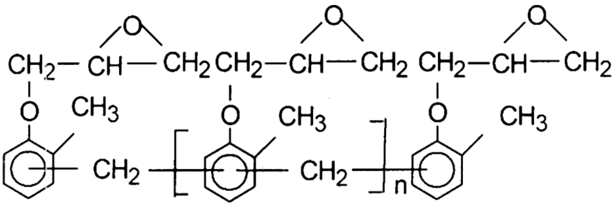
## EXPERIMENTAL

### Materials

Epichlorohydrin, o-cresol, formaldehyde, NaOH, KOH, acetone, ethyl alcohol, hydrochloric acid, 3-methyl-tetrahydrophthalic anhydride; N,N-dimethyl-benzylamine were all analytically pure grade and were supplied by Beijing Chemical Reagent Co. (Beijing, China).

## Synthesis of o-CFER

An epoxy resin based on o-cresol-formaldehyde (o-CFER) was synthesized according to Ren [12]. The molecular structure of this epoxy resin is approximate as:



where n is 1∼3. The epoxy value was determined according to Jay' method [13] to be 0.312 mol/100 g.

## IR Measurements

The o-CFER/MeTHPA samples were prepared with a stoichiometric ratio of one epoxy group to one carboxyl group. During isothermal curing, an FTS-40 IR spectrophotometer (FTIR, BIO-RAD Co., USA) was used for the investigation of the structural changes of the curing system [14]. The sample was dissolved in acetone and then coated as a thin film on a potassium bromide plate. Acetone was completely evaporated in vacuum. The non-cured sample was placed in a heated oven at a fixed temperature of 433 K. After the curing reaction at this temperature, both the non-cured sample and cured sample were analysed in a FTS-40 IR spectrophotometer separately.

## DSC Method

Curing studies were carried out on a DT-41 differential scanning calorimeter (Shimadzu Co. Ltd., Japan). The DSC instrument was calibrated with high-purity indium, $\alpha$-$Al_2O_3$ was used as the reference material. Isothermal and dynamic-heating experiments were carried out according to the method of Opalicki et al. [6] under a nitrogen flow of 40 mL $min^{-1}$.

o-CFER and the hardener MeTHPA were mixed homogeneously in a 1:1 molar ratio of carboxyl groups to epoxy groups, and N,N-dimethyl-benzylamine was used as a accelerator. The samples (ca. 10 mg) of the mixture were weighed accurately into an aluminum DSC sample pan, which was sealed with an aluminum lid. The entire operation was carried out in a dry chamber. Samples were placed in thermostatic baths at curing temperatures ($T_c$s) of 388, 393, 398, and 403 K, respectively. The reaction was considered complete when the rate curve leveled off to the baseline. The total area under the exothermal curve, based on the extrapolated baseline at the end of reaction, was used to calculate the isothermal heat of cure ($\Delta H_i$) at a given temperature. After each isothermal run, the sample was quenched to 283 K and then reheated at 10 K min$^{-1}$ to 573 K to determine the residual heat of reaction ($\Delta H_r$). The total heat evolved during the curing reaction was $\Delta H_0 = \Delta H_i + \Delta H_r$.

## Torsional Braid Analysis (TBA)

The specimens were prepared by dipping heat-cleaned glass fiber braid into an acetone solution of o-CFER/MeTHPA and accelerator, and then the acetone was completely evaporated *in vacuo*. The air oven was first heated up to the desired curing temperature $T_c$, and kept for a certain period of time until the system reached the equilibrium state. Specimens were quickly set into the thermostatic baths at $T_c$s between 388, 393, 398, and 403 K for 15, 30, 60, 90, 120, 180, and 240 min, respectively. Then they were taken out and cooled to room temperature, and their $T_g$s were determined using TBA at a heating rate of 2 K min$^{-1}$.

## Thermogravimetric Analysis Measurement (TGA)

The sample was cured at 433 K for 4 h, the thermal analysis was carried out on a Shimadzu DT-40 thermogravimetric analyzer under a static air atmosphere. About 3 mg of a sample, which had been completely cured, was placed in a platinum cell and placed on the detector place, and then the furnace was heated to 923 K at a heating rate of 10 K min$^{-1}$.

# RESULTS AND DISCUSSION

## Isothermal Curing

FTIR spectra of the o-CFER/MeTHPA system are shown in Figure 1. The most significant feature is the epoxide group absorption at 914 cm$^{-1}$ (marked by an arrow). This absorption peak of o-CFER/MeTHPA cured for 600 min at 433 K becomes much lower than that of noncured o-CFER. In addition, the IR absorption in the carbonyl group practically did not change. It is seen that this reaction can be completed at 433 K at less than 600 min.

The mechanisms of the curing reaction of thermosetting resins have two general kinetic models: *n*th-order kinetics and autocatalytic

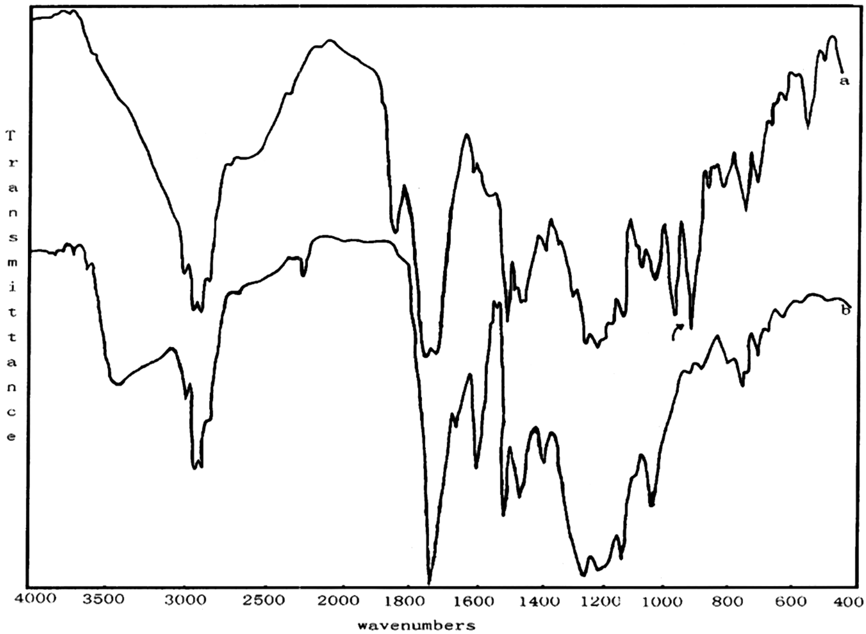


**FIGURE 1** FTIR spectra of o-CFER/MeTHPA after curing at 433 K for (a) noncured o-CFER and (b) o-CFER cured for 600 min.

kinetics [10]. The reaction rate of *n*th-order kinetics can be expressed as:

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

The reaction rate of autocatalytic kinetics can be defined as:

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

where $\alpha$ is the extent of reaction, given by $\alpha = \Delta H_t/\Delta H_0$, and $\Delta H_t$ is the partial area under a DSC trace up to time $t$; $m$ and $n$ are the reaction orders and $k'$ is the kinetic rate constant.

To take into account the autocatalytic reaction, where the initial reaction rate of the autocatalytic reaction is not zero, Kamal [5] proposed the following generalized expression.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \tag{3}$$

where $k_1$ and $k_2$ are the specific rate constants, which are functions of the temperature. According to the $n$th-order kinetic model, the maximum reaction rate will be observed at $t = 0$, and according to the autocatalytic model, the reaction rate is zero initially and attains the maximum value at some intermediate conversion.

During the curing reaction of thermosetting resins, the heat evolution recorded by DSC is proportional to the extent of consumption of the epoxide groups in the epoxy resins, or the reactive groups in the curing agent [15–16]; that is, the released heat is proportional to the extent of the reaction. Following this assumption, the curing kinetics was studied, and the kinetics data were determined. If the cure reaction is the only thermal event, then the reaction rate $d\alpha/dt$ is proportional to the heat flow [10], $dH/dt$, that is:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \tag{4}$$

The rate of cure can be determined by the curing exotherm.

Figure 2 shows plots of the curing reaction conversion $\alpha$ versus time $t$ at different isothermal temperatures, and the plots of $d\alpha/dt$ versus time $t$ are shown in Figure 3. As seen from Figures 2 and 3, the reaction rate at any temperature increases with time at the initial stage of cure and passes through a maximum. The peak of reaction rate becomes higher and shifts to shorter time with increasing curing temperature. But the conversion $\alpha$ reaches only about 80–90% in the

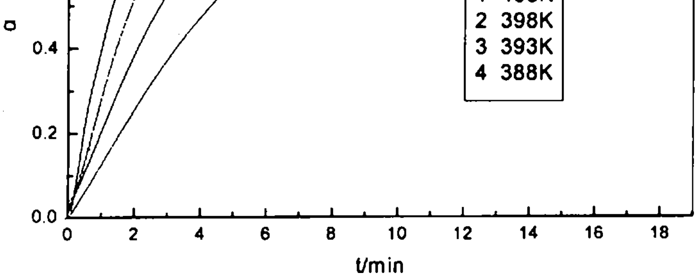


**FIGURE 2** Conversion, $\alpha$ versus time plots at different curing temperatures.

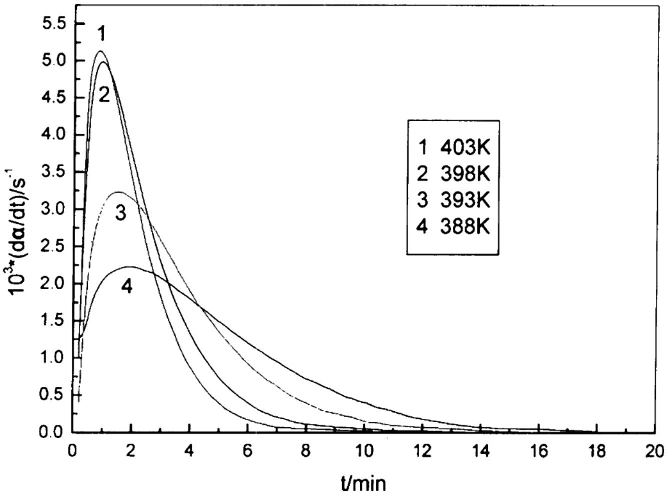


**FIGURE 3** Reaction rate, $d\alpha/dt$ versus time plots at different temperatures.

experiment time. The plots show a maximum reaction rate at time $t > 0$, thereby negating simple $n$th-order kinetics. To compute kinetic parameters in equation (3), several methods have been proposed [17–19]. In this study, $k_1$ was graphically calculated as the initial reaction rate at time $t = 0$, given by the intercept of Figure 3. Then, $k_2$, $m$ and $n$ were calculated through nonlinear regression according to Eq. 3. The resulting data are shown in Table 1.

It can be seen from Table 1 that $k_1$ values are small compared with those obtained for $k_2$, which affects the reaction more. Furthermore, $k_1$ and $k_2$ values increase with the curing temperature. The reaction rate constants, $k_1$ and $k_2$, depend on the temperature and follow the Arrhenius relationship:

$$k_i = A_i \exp(-E_i/RT) \quad i = 1, 2 \tag{5}$$

where $A_i$ is the pre-exponential constant, $E_i$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. Rate constants

**TABLE 1** Kinetic Parameters for Isothermal Curing of o-CFER/MeTHPA

| $T$ (°C) | 115 | 120 | 125 | 130 |
|---|---|---|---|---|
| $k_1$ ($\times 10^{-4}$) | 2.06 | 6.06 | 12.3 | 21.4 |
| $k_2$ ($\times 10^{-3}$) | 4.77 | 7.31 | 12.2 | 19.0 |
| $m$ | 0.35 | 0.42 | 0.46 | 0.73 |
| $n$ | 1.19 | 1.27 | 1.47 | 1.92 |

$k_1$ and $k_2$ are shown as Arrhenius plot in Figure 4, the values of the associated activation energies $E_1$ and $E_2$ are 195.84 kJ/mol and 116.54 kJ/mol, respectively. The linear correlation coefficient is 0.9966 for $k_1$ values and 0.9952 for $k_2$.

Typical comparisons between the experimental DSC data for two different temperatures, 288 K and 293 K, and the autocatalytic model with Eq. 3 determined parameters, are shown in Figure 5. The kinetics behavior described by the kinetic model coincides with the experimental data in the early stage. As the reaction progresses, a deviation appears due to the onset of gelation and vitrification where the mobility of reactive groups is hindered, and the rate of conversion is controlled by diffusion rather than by kinetic factors [20]. Differences between model predictions and experimental data were observed. This can be interpreted in terms of crosslinking and free volume considerations. The free volume of materials decreases during curing and crosslinking reducing the rate of diffusion of reactive groups leading to decreased reaction rate.

To consider the diffusion effect more precisely, a semiempirical relationship, based on free volume considerations, was proposed by Chern and Poehlein [21]. In this relationship, a diffusion factor, $f(\alpha)$, is defined with two empirical parameters as follows:

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{6}$$

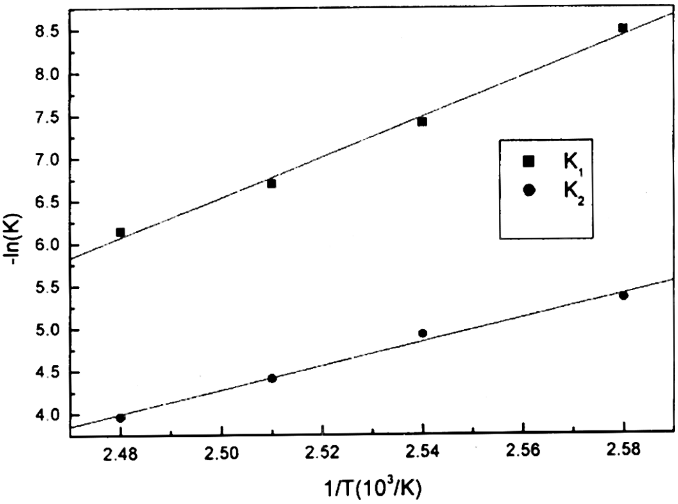


**FIGURE 4** Rate constants of curing reaction, $k_1$ and $k_2$ versus temperature.

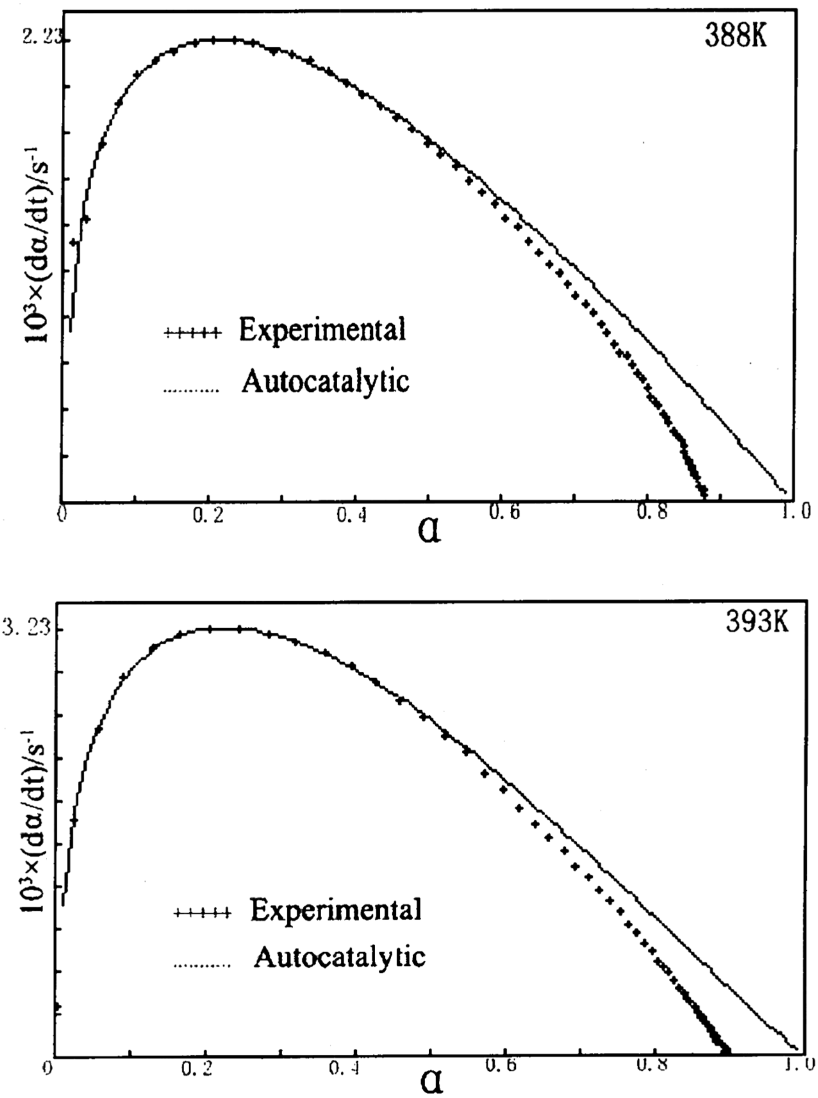


**FIGURE 5** Comparison of experimental data with theoretical values: plots of reaction rate $d\alpha/dt$ versus conversion $\alpha$ at 388 K at 393 K.

where $C$ is the diffusion coefficient and $\alpha_c$ is the critical conversion depending on the curing temperatures. The plots of $f(\alpha)$ versus conversion $\alpha$ at different curing temperatures are shown in Figure 6. For $\alpha \ll \alpha_c, f(\alpha)$ approximately equals unity and the effect of diffusion is

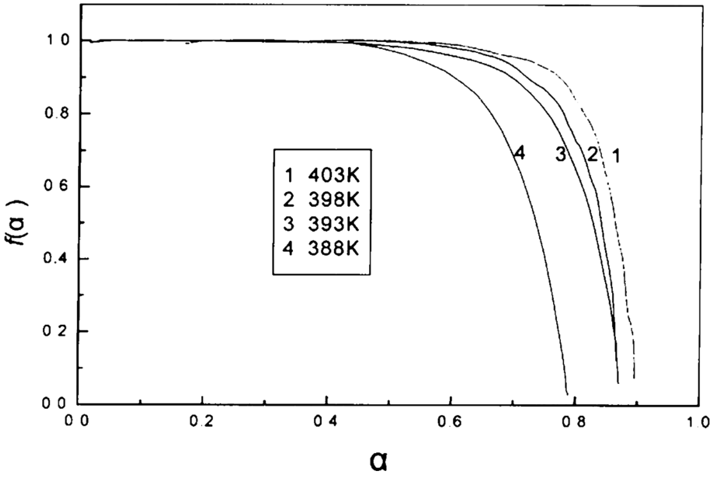


**FIGURE 6** Plots of diffusion factor $f(\alpha)$ versus conversion $\alpha$ at different curing temperature.

negligible, so that the reaction is kinetically controlled. As $\alpha$ approaches $\alpha_c$, $f(\alpha)$ begins to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$. Beyond that point, it continues to decrease and approaches zero, which means that the reaction becomes very slow and effectively stops.

Considering the diffusion effect, the kinetics equation of cure can be expressed in the following form to account for the effects of diffusion.

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \cdot \frac{1}{1+\exp[C(\alpha-\alpha_c)]} \tag{7}$$

Figure 7 shows the comparison between experimental values and those obtained from Eq. 7. The calculated values agree very well with experimental data at high temperatures. Therefore, the authors employ the proposed generalized kinetic model to predict and describe the advance of this epoxy resin system as a function of the curing temperature.

## $T_g$ Value and the Curing Process

$T_g$ has been used directly as a parameter for conversion in the analysis of reaction kinetic models [22–23], and there is a one-to-one relationship between the $T_g$ and the degree of cure. $T_g$ is particularly useful at high conversion and after vitrification because of the nonlinearity

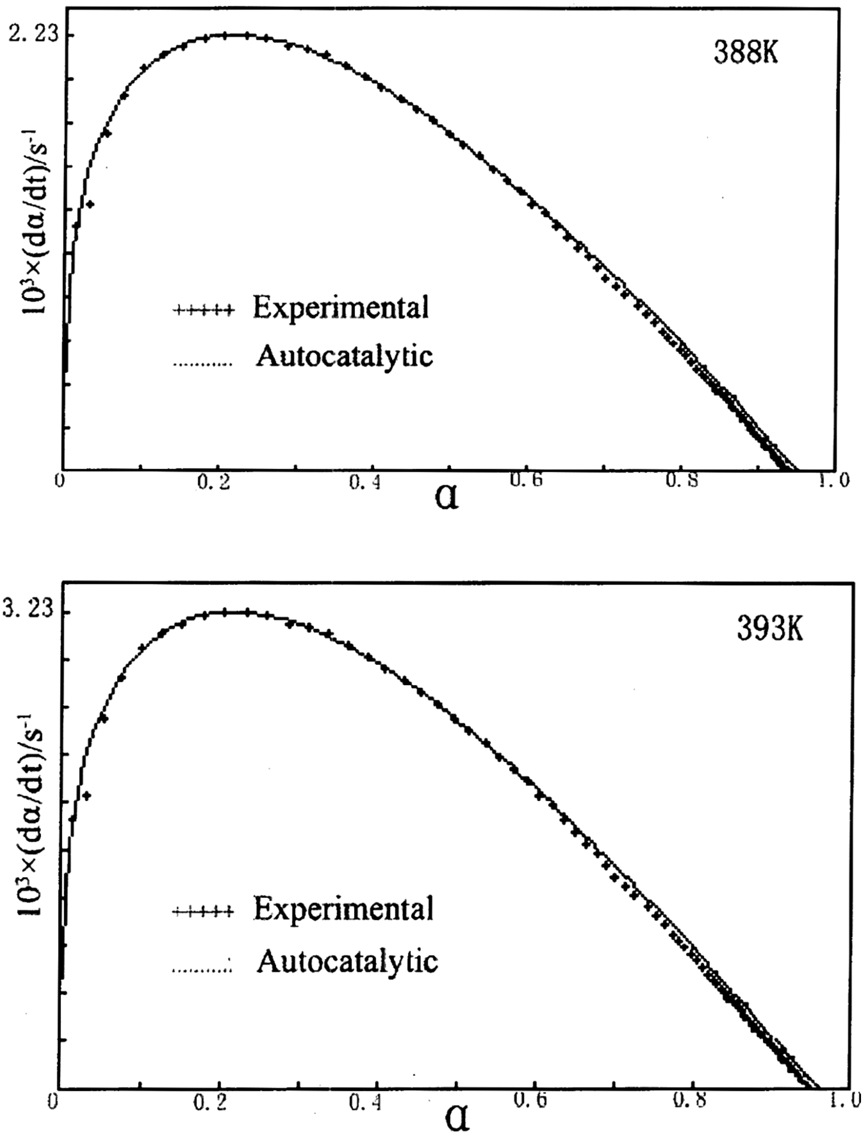


**FIGURE 7** Comparison of experimental data with theoretical values calculated from Eq. 7: reaction rate $d\alpha/dt$ versus conversion $\alpha$ at 388 K and 393 K.

of $T_g$ versus conversion reaction [24–25]. $T_g$ of o-CFER/MeTHPA specimen cured isothermally at different temperatures for various periods of time obtained from TBA measurements is plotted versus cure

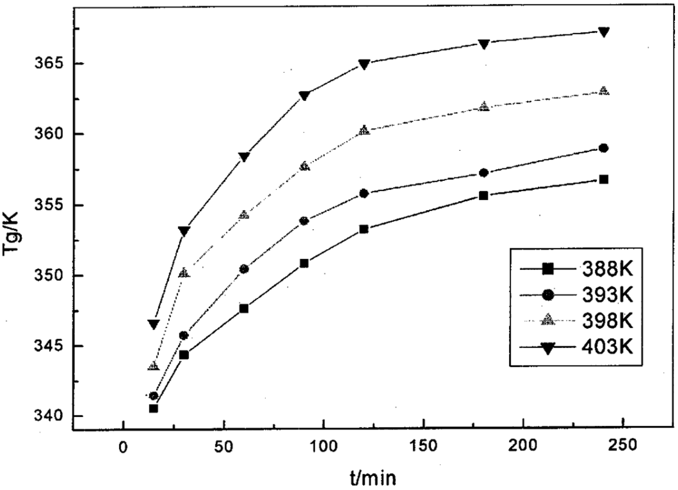


**FIGURE 8** $T_g$ values of o-CFER/MeTHPA cured isothermally at different temperatures for various periods.

time in Figure 8. As seen from Figure 8, different glass transition behaviors occurred for the samples with different degrees of cure, $T_g$ increased with curing time and temperature.

At low $T_c$s, $T_g$ increases during the early stages of cure, then levels off and remains a low $T_g$ value compared with higher $T_c$s. Even if the curing time is prolonged the under low $T_c$, the resin system does not reach high conversion. This result is different from the DSC experiment, because the curing time is much longer than in DSC. Because the process of vitrification usually drastically lowers the reaction rate, complete cure usually involves temperatures in the vicinity of the maximum of the glass transition temperature. This is indicative of autocatalytic kinetics in the first stages and diffusion-controlled reaction as the $T_g$ rises [20]. Similar results have been obtained in this study of the conversion, or reaction rate versus time at different isothermal cure temperatures.

At the beginning of the curing reaction process, the degree of cure is low, and the sample gives low $T_g$ value. At this stage, the process is characterized by a gradual increase in molecular weight, and this transition behavior reflects the movement of molecular chains in the system. Because only low molecular chains exist and have a lower viscosity at this stage, there are many chances for the molecules to collide and this results in a high reaction rate. With the weight-average molecular weight increasing, most of the reactive functional groups are attached to the gel, and their mobilities are very limited, so the curing reaction becomes diffusion-controlled. The crosslinking density further increases with rising reaction time, and the $T_g$ of the network is enhanced with a decrease in the distance between crosslink points. At this time, the sample is highly cured and the $T_g$ value becomes higher.

## Thermal Degradation

The process of the weight loss is shown in Figure 9. The weight loss fractions of resin were calculated, and the weight loss rates are shown as a function of temperature in Figure 10. The TGA trace of MeTHPA cured o-CFER revealed two degradation steps in an air atmosphere. The following kinetic equation was assumed to hold for the thermal degradation reaction [10–11]:

$$\ln(C/T^{1.92}) = \ln\frac{AE}{\phi R} + 3.77 - 1.92\ln E - \frac{E}{RT} \tag{8}$$

where $C = W/W_0$, $W$ is the remaining weight, $W_0$ is the total weight, $E$ is the degradation activation energy, $A$ is the frequency factor, $\phi$ is the heating rate, and $R$ is the ideal gas constant. The degradation activation energy of the different stages can be calculated from the plots of $\ln(C/T^{1.92})$ versus $1/T$. $E_1$ and $E_2$ were the degradation activation energy of the first and the second stage, respectively. The activation energy of thermal degradation for the system in the first step is

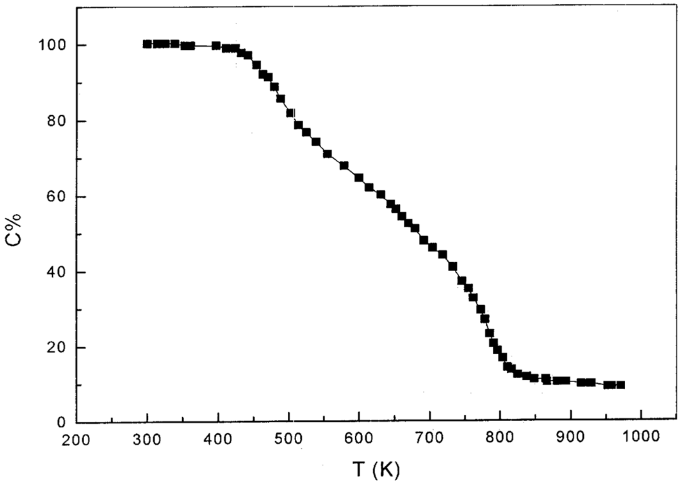
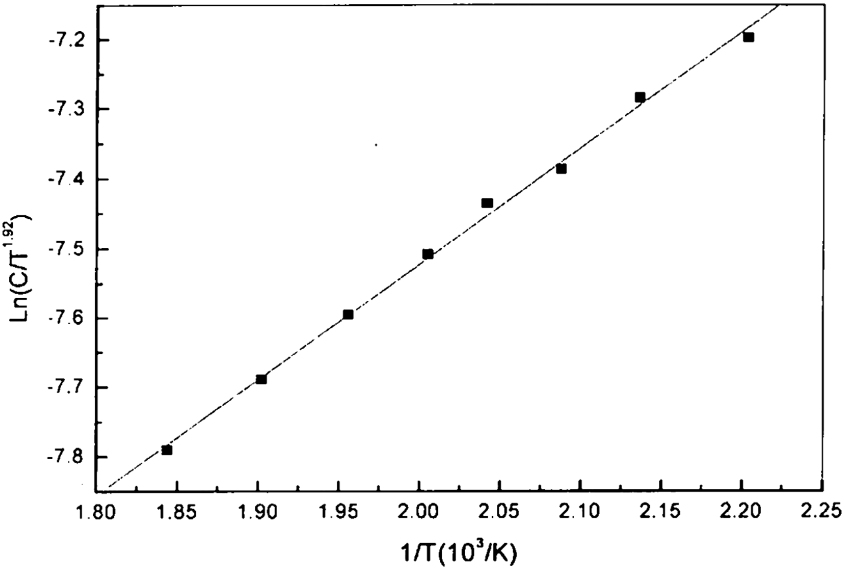


**FIGURE 9** The two steps of the thermal degradation of o-CFER/MeTHPA system.



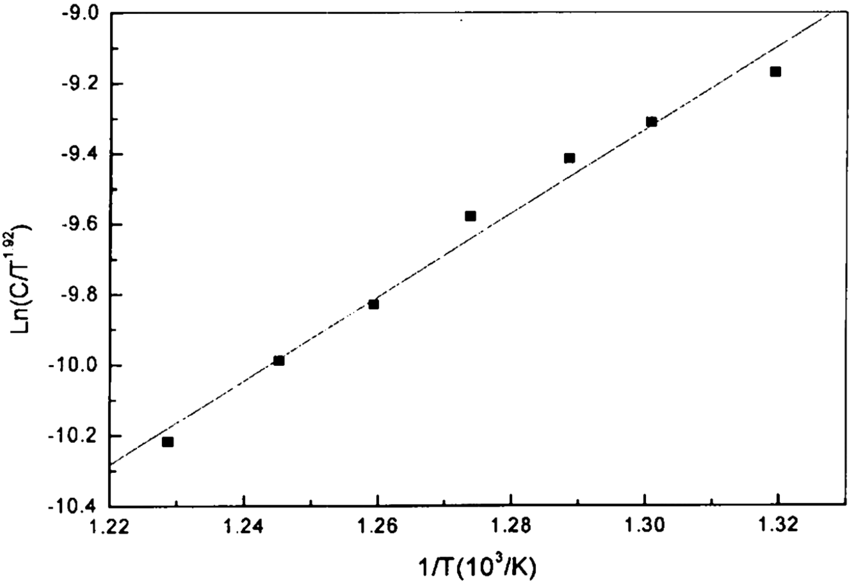
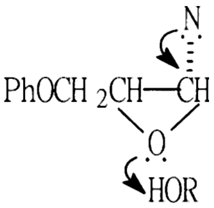


**FIGURE 10** Weight loss function $\ln(C/T^{1.92})$, versus reaction temperature $T$ for thermal degradation in the first and second steps.

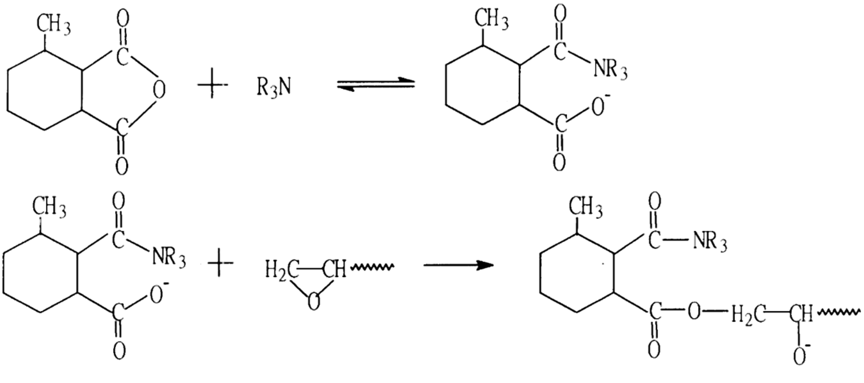
13.88 kJ $mol^{-1}$, and the linear correlation coefficient is 0.9985. The second step is 98.97 kJ $mol^{-1}$ with the linear correlation coefficient is 0.9924. The degradation activation energy in the second stage is much higher than that in the first stage, illustrating that the breaking of strong bonds takes place in the second stage, while weak bonds, for example: $-CH_2-CH_2-$, $-CH_2-O-CO-$, and so on were broken in the first stage.

## Molecular Mechanism for Curing Reaction

It is known that the addition of hydroxyl-containing compounds (water, alcohols, phenols, etc.) considerably promotes the interaction of epoxy compounds with anhydrides, amines, and other nucleophilic species. The reaction proceeds through a trimolecular transition state initially suggested by Smith [26] for the reaction of epoxy compounds with amines:



As reported [27], the maximum curing reaction rate was observed at $t = 0$ in the presence of hydroxyl-containing solvent, and obeyed nth order kinetics. This is due to the participation of protons. As to the pure epoxy resin/anhydride system, the curing reaction is as follows:



where the oxygen negative ion reacts with epoxy group. Tertiary amine is not reformed in the reaction. Because of the participation of hydroxyl group in the macromolecular chain, the $k_1$ is not zero and is not also the typical catalysis mechanism. It is favorable for the $-$OH in the epoxy resin molecular chain to become a proton donor and participate in the reaction with the increasing curing temperature. The reaction mechanism ought to become trimolecular mechanism with the participation of the proton. This is the reason that the $m+n$ value increases with the temperature.

## CONCLUSIONS

1. The cure reaction for the system of o-CFER/MeTHPA system is shown to have autocatalytic kinetic behavior in the kinetically controlled stage and was well described with the model proposed by Kamal, which includes two rate constants, $k_1$ and $k_2$, and two reaction orders, $m$ and $n$. The curing reaction at the later stage was practically diffusion-controlled. To consider the diffusion effect more precisely, $f(\alpha)$ was introduced into Kamal's equation to make it possible to describe and predict the cure reaction of this epoxy resin. The theoretical values agree very well with the experimental data.
2. In order to achieve a higher conversion and a higher $T_g$, a long curing time and a higher temperature are necessary for the system of o-CFER/MeTHPA. The sample has a highest $T_g = 367.1\,\mathrm{K}$.
3. The TGA trace of this system revealed two decomposition stages and exhibits one order degradation reaction kinetics. The activation energies of thermal degradation in the first and second stages were 13.88 and $98.97\,\mathrm{kJ\,mol^{-1}}$, respectively.

## REFERENCES

[1] Akira, I., Takeaki, S., Yoshiji, M., Haruhiko, F., Hiroshu, U., *Jpn. Kokai Tokkyo Koho JP* 80727 (2002).
[2] Liu, S. and Liao, H., *Thermosetting Resin* **16**, 38 (2001).
[3] Gao J. G., Shen, S. G., and Li, D. L., *Inter. J. Polym. Mater.* **53** (4), 341 (2004).
[4] Gao, J. G. and Zhao, H. C., *Polym. Inter.* **51**, 1422 (2002).
[5] Kamal, M. R., *Polym. Eng. Sci.* **l4**, 231 (1974).
[6] Opalicki, M., Kenny, J. M., and Nicolais, L., *J. Appl. Polym. Sci.*, **61**, 1025 (1996).
[7] Khanna, U. and Chanda, M., *J. Appl. Polym. Sci.*, **49**, 319 (1993).
[8] Duswalt, A. A., *Thermochim Acta*, **8**, 57 (l974).
[9] Kenny, J. M. and Opalicki, M., *Makromol Chem., Macromol Symp.* **68**, 41 (1993).
[10] Liu, Z. H. (1991). *Introduction of Thermal Analysis*, Chemical Industry Publishing Co.: Beijing.
[11] Madhusudanan, P. M., Krishnan, K., and Ninan, K. N., *Thermochim Acta*, **97**, 189 (1986).
[12] Ren, L., *Thermosetting Resin* **l3**, 17 (1998).

[13] Jay, R. R., *Anal. Chem.* **36**, 665 (1964).
[14] Hong, S. G. and Wu, C. S., *J. Therm. Anal. Cal.* **59**, 711 (2000).
[15] Woo, E. M. and Seferis, J. C., *J. Appl. Polym. Sci.*, **40**, 1237 (1990).
[16] Ghaemy, M. and Riahy, M. H., *Eur. Polym. J.* **32**, 1207 (1996).
[17] Ryan, M. E. and Dutta, A., *Polymer*, **20**, 203 (1979).
[18] Moroni, A., Mijiovic, J., Pearce, E. M., and Foun, C. C., *J. Appl. Polym. Sci.* **32**, 3761 (1986).
[19] Kenny, J. M., *J. Appl. Polym. Sci.* **51**, 761 (1994).
[20] Cole, K. C., Hechler, J. J., and Noel, D. *Macromolecules* **24**, 3098 (1991).
[21] Chern, C. S. and Poehlein, G. W., *Polym. Eng. Sci.* **27**, 782 (1987).
[22] Simon, S. L. and Gillham, J. K., *J. Appl. Polym. Sci.* **47**, 461 (1993).
[23] Wisanrakkit, G. and Gillham, J. K., *J. Appl. Polym. Sci.* **41**, 2885 (1990).
[24] Venditti, R. A. and Gillham, J. K., *J. Appl. Polym. Sci.* **64**, 3 (1997).
[25] Wisanrakkit, G., Gillham, J. K., and Enns, J. B. *J. Appl. Polym. Sci.* **41**, 1895 (1990).
[26] Smith, I. T., *Polymer* **2**, 95 (1961).
[27] Liu, T. D., Wang, Q. C., and Xu, X. P., *Thermosetting Resin* **2**, 38 (1989).