Study on Curing Kinetics and Curing Mechanism of Epoxy Resin Based on Diglycidyl Ether of Bisphenol A and Melamine Phosphate

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ABSTRACT: The curing kinetics of the diglycidyl ether of bisphenol A/melamine phosphate (DGEBA/MP) was analyzed by the DSC technique. The Kissinger and Flynn–Wall–Ozawa methods were applied to determine the dynamic kinetics of the DGEBA/MP system. The activation energies obtained by these two methods were 83.9 and 85.6 kJ/mol, respectively. An autocatalytic equation was applied to determine the isothermal curing kinetics of the DGEBA/MP system. The DGEBA/MP system exhibits autocatalytic behavior in the isothermal curing procedure, whose kinetics fits well with the autocatalytic mechanism. The obtained isothermal curing activation energy of the DGEBA/MP system was 110.0 kJ/mol. The curing mechanism of DGEBA with melamine phosphate was investigated using FTIR, ^{13}C solid-state NMR, and ^{31}P solid-state NMR. It involved an epoxide–amine reaction, etherification of phosphoric acid and epoxy, dehydration, and thermal oxidation of the hydroxyl group of the DGEBA/MP system. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 892–900, 2004

Key words: epoxy resin; melamine phosphate; kinetics (polym.); FTIR; activation energy

INTRODUCTION

Epoxy resins have been widely used in coatings, adhesives, insulating materials, and composites because of their great versatility, low shrinkage, good chemical resistance, adhesion, and high-grade electrical insulation. Like most organic polymeric materials, the flammability of epoxy resins is rather high, thus limiting their applications in certain areas. Therefore, melamine phosphate is introduced herein as a curing agent and a flame retardant to improve the flame retardation of epoxy resins.

An optimal curing process depends on understanding the curing kinetics, the curing mechanism, and accurate modeling of the curing process. This modeling includes determination of the mechanism, or appropriate kinetic equation for the analyzed system, measurement of the reaction orders, and activation energies of the reaction. An accurate model not only helps to predict curing behavior for process design and control, but also can be used to predict aging and degradation of thermosetting polymer systems. It can further be used to compare the curing behavior of different systems or formulations using different matrices, catalysts, fillers, and additives.

The current understanding of the mechanism and kinetics of curing lags the rapid increase in formulations and the industrial applications of epoxy-based resins and composite systems. The mechanism and kinetics of curing are not yet comprehensively understood, and an accurate model of an optimal curing process has yet to be clearly established.[1] To date, no study has been reported on modeling the curing of the diglycidyl ether of bisphenol A/melamine phosphate (DGEBA/MP) system.

An appropriate method must be used to measure, accurately, the cure kinetics parameters: the degree of conversion (α), conversion rate ($d\alpha/dt$), and the activation energy (E).

The rate of conversion can therefore be defined as follows:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{\text{Rxn}}} \tag{1}$$

where ΔH_{Rxn} is the heat of reaction. DSC techniques use two basic approaches: isothermal curing is carried out at a single cure temperature and at a given cure cycle, and dynamic curing is carried out at a constant heating rate.

Dynamic kinetics

Kinetic analyses were performed using two kinetic models, the Kissinger and the Flynn–Wall–Ozawa[4–6] models. These two methods were used in this study, instead of other nonisothermal methods, because they

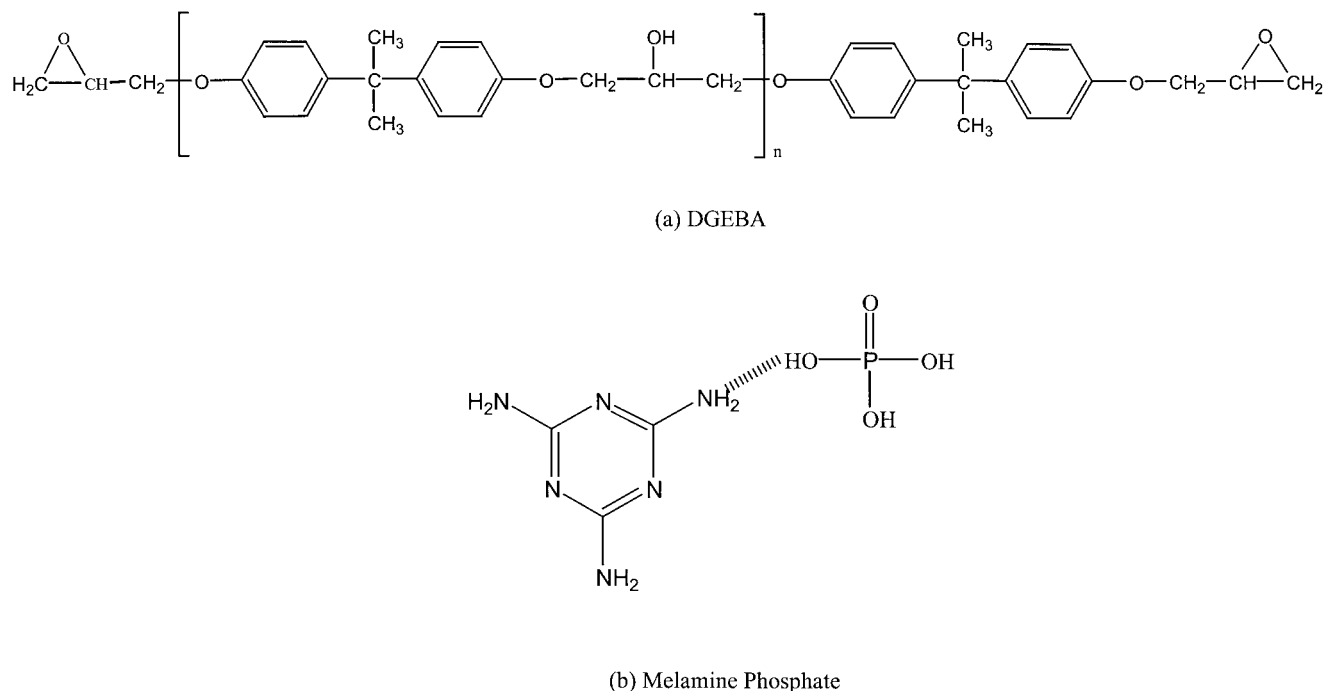*Correspondence to:* F.-C. Chang (Changfc@mail.nctu.edu.tw).

(a) DGEBA

(b) Melamine Phosphate

Figure 1   Chemical structures of this study.

do not require prior knowledge of the reaction mechanism to quantify kinetic parameters.

According to the method of Kissinger, the activation energy can be obtained from the maximum reaction rate, where $d(d\alpha/dt)/dt$ is zero at a constant-heating rate condition. The resulting relation can be expressed as

$$\frac{d[\ln(q/T_m^2)]}{d(1/T_m)} = -\frac{E}{R} \qquad (2)$$

where T_m is the temperature at which the rate is maximum and q is a constant heating rate. Therefore, a plot of $\ln(q/T_m^2)$ versus $1/T_m$ gives the activation energy without the need to make any assumption about the conversion-dependent function.

Based on Doyle's approximation,[7] Flynn–Wall–Ozawa developed an alternative method to calculate the activation energy:

$$\log(q) = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457E}{RT} \qquad (3)$$

Based on this equation, a more accurate value of the activation energy can be obtained by iteration or a least-squares technique to improve the linear approximation of the temperature integration term.

Isothermal kinetics

The conversion and the rate of conversion vary continuously throughout the process of reaction as the uncured resin is isothermally cured. Using DSC the conversion is measured as

$$\alpha_t = \frac{\Delta H_h}{\Delta H_{\text{Rxn}}} \qquad (4)$$

where the subscript t indicates the value at time t and ΔH_h is the heat of reaction at time t. An alternative method is to measure the heat evolved during the crosslinking of the partially cured sample. This latter method becomes necessary when the exothermic energy is too small to be detected by the former method. A distinct advantage of the latter method is that it allows T_g and the conversion to be measured simultaneously.[8,9] Using this method, the percentage of conversion is calculated as

$$\alpha_t = \frac{\Delta H_{\text{Rxn}} - \Delta H_r}{\Delta H_{\text{Rxn}}} \qquad (5)$$

where ΔH_r is residual heat of reaction. The analysis of autocatalyzed curing reactions assumes, in contrast, that at least one of the reaction products is also involved in the propagation reaction characterized by an accelerating isothermal conversion rate. The kinetics of autocatalyzed reactions is described as follows[8]:

$$\frac{d\alpha}{dt} = k'\alpha^m(1-\alpha)^n \qquad (6)$$

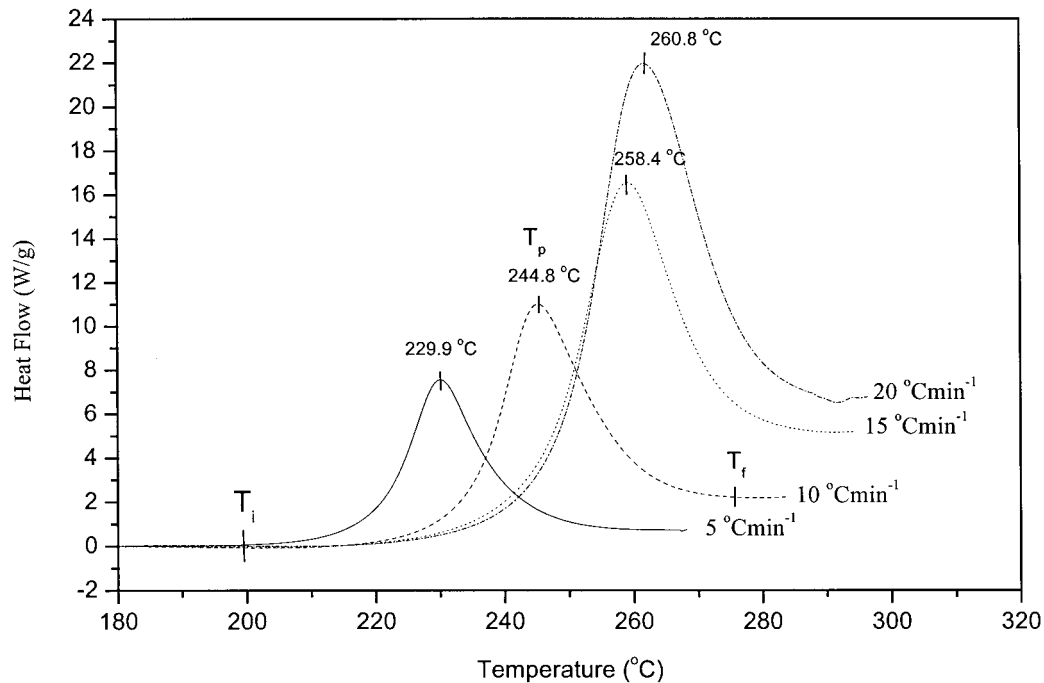where m and n are the reaction orders and $k'(T)$ is the specific rate constant.

Figure 2 Typical dynamic DSC thermogram of DGEBA/MP.

The curing of the epoxy resin, with amino curing agents, involves three principal reactions: epoxide–primary amine addition; epoxide–secondary amine reaction; and etherification of epoxide–hydroxyl, branching, and crosslinking, respectively.[10–15] These chemical reactions cause a complicated change in the physical state, from a viscous liquid to a gel, and eventually vitrify the material. FTIR and NMR were used to characterize chemical reactions of the epoxy resin.

The kinetics and mechanism of curing DGEBA with melamine phosphate have not yet been reported. This study reports that the melamine phosphate is able to function as a hardener and a flame retardant of the epoxy resin.

EXPERIMENTAL

Materials

The liquid epoxy resin used in this study was a diglycidyl ether of bisphenol A (BE-188) from Chang Chun Chemical Plastics of Taiwan with an equivalent
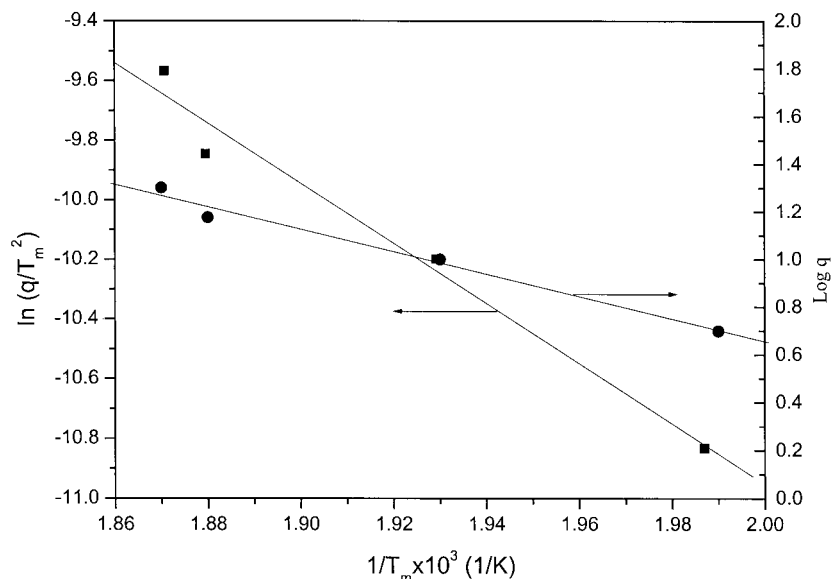

Figure 3 Activation energy of DGEBA/MP obtained by the Kissinger method and the Flynn–Wall–Ozawa method.
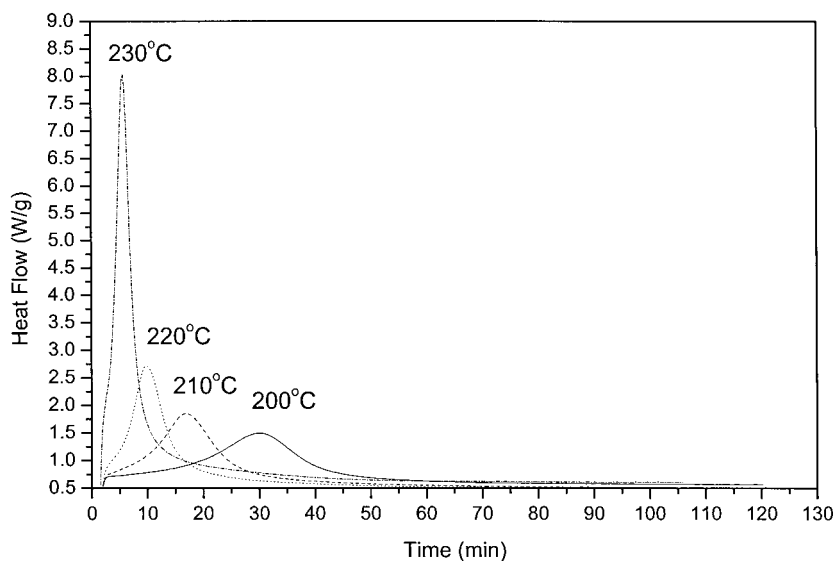
Figure 4 Typical isothermal DSC thermograms of DGEBA/MP at various curing temperatures.

epoxy molecular weight of 188 g/eq. The hardener used was melamine phosphate (MP, $C_3N_6H_3\cdot H_3PO_4$), also from Chung-Shan Institute of Science and Technology, Taiwan. Figure 1 presents the chemical structures of these compounds.

Dynamic-curing kinetics

A stoichiometric ratio of epoxy to amine was used in this DGEBA/MP system. The dynamic curing kinetics of the DGEBA/MP system was determined using a DuPont 2910 differential scanning calorimeter (Du-Pont, Boston, MA) operated in a nitrogen atmosphere. The sample weight of 6–7 mg was placed in a sealed aluminum sample pan. A dynamic curing reaction

scan was conducted from 30 to 350°C at a heating rate of 5, 10, 15, or 20°C/min and a nitrogen flow rate of 40 mL/min.

Isothermal-curing kinetics

Isothermal curing was conducted at four different temperatures: 200, 210, 220 and 230°C.

FTIR

The sample was placed on a KBr pellet and FTIR spectrum was obtained at 220°C using a Nicolet Avatar 320 FTIR (Nicolet Analytical Instruments, Madi-
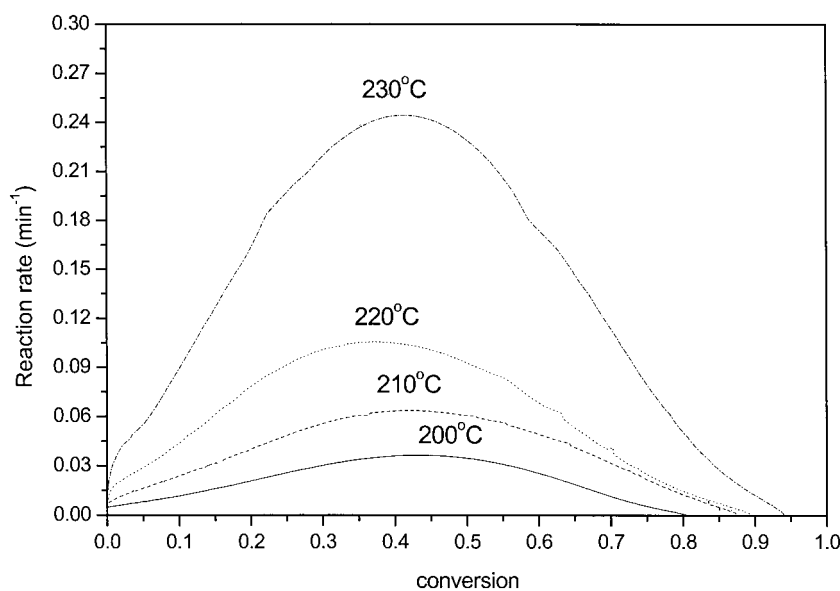

Figure 5 Reaction rate versus conversion of DGEBA/MP at various curing temperatures.

TABLE I
Data of Isothermal Curing of DGEBA/MP for Various Curing Temperatures

Curing temperature (°C)	Reaction rate constant (K, min^{-1})	m	n	$m + n$
200	0.13	0.97	0.87	1.84
210	0.31	1.05	1.48	2.53
220	0.84	1.19	1.99	3.18
230	3.66	1.48	3.20	4.68
Average reaction order		1.17	1.88	3.05
Activation energy (E_a, kJ mol^{-1})	110.0			

son, WI), to analyze the epoxide content of the system at a resolution of 2 cm^{-1}.

Solid-state NMR

High-resolution solid-state ^{13}C-NMR and ^{31}P-NMR experiments were carried out at room temperature using a Bruker DSX-400 spectrometer (Bruker Instruments, Billerica, MA) operated at resonance frequencies of 399.53–100.47 and 399.53–161.72 MHz for ^{13}C and ^{31}P, respectively. The ^{13}C and ^{31}P CP/MAS spectra were measured with a 3.9-μs 90° pulse, with 3-s pulse delay time, acquisition time of 30 ms, and 2048 scans. All NMR spectra were taken at 300 K using broadband proton decoupling and normal cross-polarization pulse sequencing. A magic angle sample spinning (MAS) rate of 5.4 kHz was used to eliminate resonance broadening attributed to the anisotropy of the chemical shift tensors.

RESULTS AND DISCUSSION

Dynamic kinetics

Both Kissinger and Flynn–Wall–Ozawa methods assume that the DSC peak exotherm is isoconversion and its value is independent of the heating rate. These two methods were applied to the data obtained in the dynamic heating experiments at different heating rates between 5 and 20°C/min used in this work. Figure 2 shows the heat flow measured by DSC cured under various heating rates. The temperature of maximum rate increases from 229.9 to 260.8°C with the increase of the heating rate.

By applying the Flynn–Wall–Ozawa and Kissinger methods of the maximum reaction rates (peaks of the DSC thermogram), activation energies can be determined by slopes of the lines shown in Figure 3. The obtained activation energies, based on the Kissinger and Flynn–Wall–Ozawa methods, are 83.9 and 85.6 kJ/mol, respectively. The activation energy, obtained by the Flynn–Wall–Ozawa method, is only slightly higher than that obtained by the Kissinger method, and the difference is insignificant.[16]

Isothermal kinetics

The kinetics of epoxy–amine reactions has been well established in the literature.[17–21] In the DSC curve of dynamic curing for the DGEBA/MP system, at a heating rate of 10°C/min as shown in Figure 2, T_i (199.2°C) is the initial temperature of the curing reaction, T_p (244.8°C) is the peak maximum temperature, and T_f (276.4°C) is the final temperature, respectively. Based on this result, this study used isothermal curing temperatures of 200, 210, 220, and 230°C.
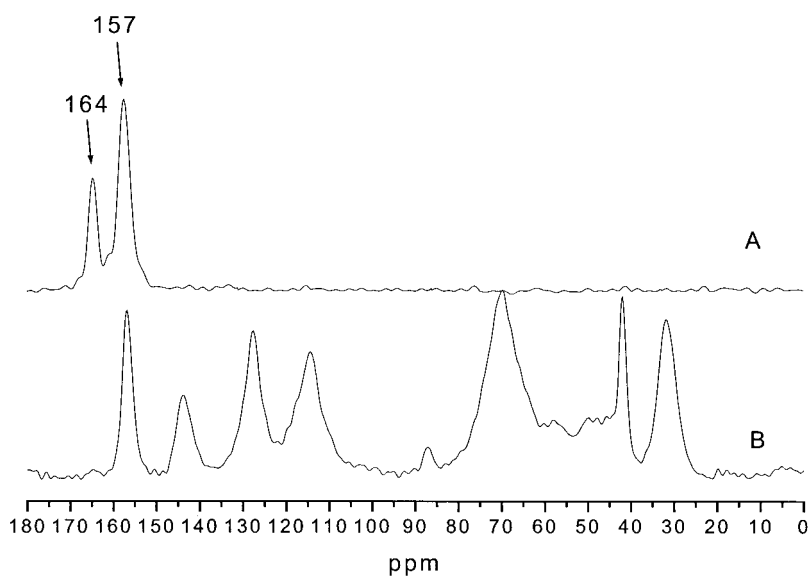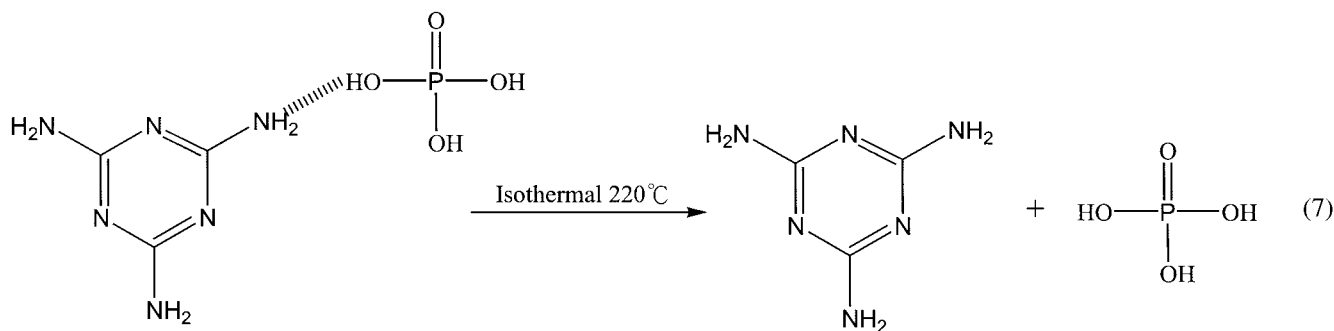

Figure 6 ^{13}C solid-state NMR of (A) melamine phosphate and (B) DGEBA cured with melamine phosphate.

Scheme 1 Decomposition of melamine phosphate.

Figure 4 shows the typical isothermal DSC thermograms of the DGEBA/MP system. The maximum times, for the reaction peaks at curing temperatures of 200, 210, 220, and 230°C, are 29.8, 16.9, 9.9, and 5.7 min, respectively. The reaction rate at any temperature increases with time and passes through a maximum. The maximum reaction peak becomes higher, and less time is needed, as the isothermal temperature is increased. Figure 5 plots the reaction rate versus conversion of the DGEBA/MP system. This result indicates that the curing reaction of the DGEBA/MP system is strongly autocatalytic in nature and thus eq. (6) is applicable. Table I shows kinetic parameters obtained for DGEBA cured with MP. The reaction orders ($n + m$) of isothermal curing at 200, 210, 220, and 230°C obtained from eq. (6) are 1.84, 2.53, 3.18, and 4.68, respectively. The R^2 coefficient of fitted data is 0.998. Many previous studies have assumed that the overall reaction order is 2 for the epoxy–amine reaction of the epoxy/amine system, at a relatively lower curing temperature, and that etherification and homopolymerization reactions could be neglected.[22–25] Other studies

have also reported that the reaction order ($n + m$) of the epoxy–amine reaction was near 2 under isothermal curing.[26,27] In this study, the overall order of the curing reaction of the DGEBA/MP system at 200°C is 1.84. Therefore, the DGEBA/MP system undergoes an epoxy–amine reaction at low curing temperature.

Figure 2 shows that the initial curing temperature (T_i) of the DGEBA/MP system was 199.2°C. Therefore, it is similar to that of isothermal curing at 200°C for the DGEBA/MP system. At 210 and 220°C, the overall curing reaction orders of the DGEBA/MP system are 2.53 and 3.18, respectively. The etherification of an epoxide ring and a hydroxyl group forms an ether linkage, which becomes significant at high curing temperature in certain epoxy resin/amine systems. The importance of this reaction, in terms of its effect on the network, was previously reported.[28,29] Many studies have assumed that the overall reaction order was 3 for etherification of the epoxy/amine system at later stages of curing and at a high curing temperature.[30–32] The literature indeed demonstrated that the reaction order of etherification is near 3.[31] The obtained overall
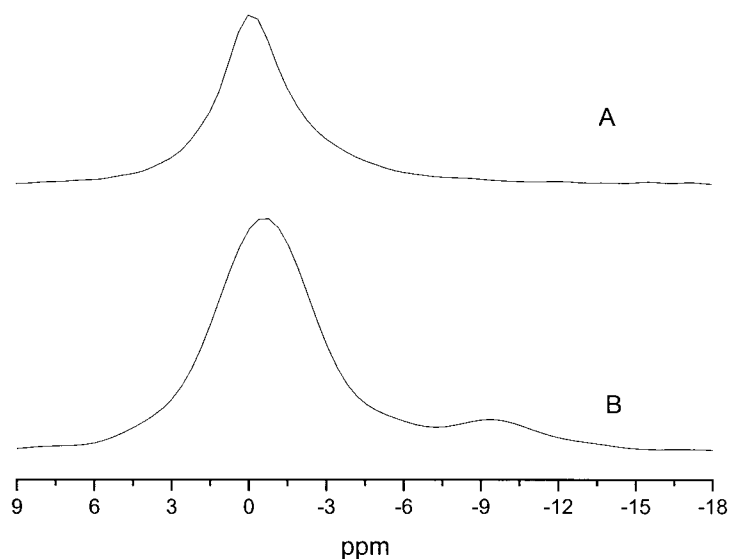

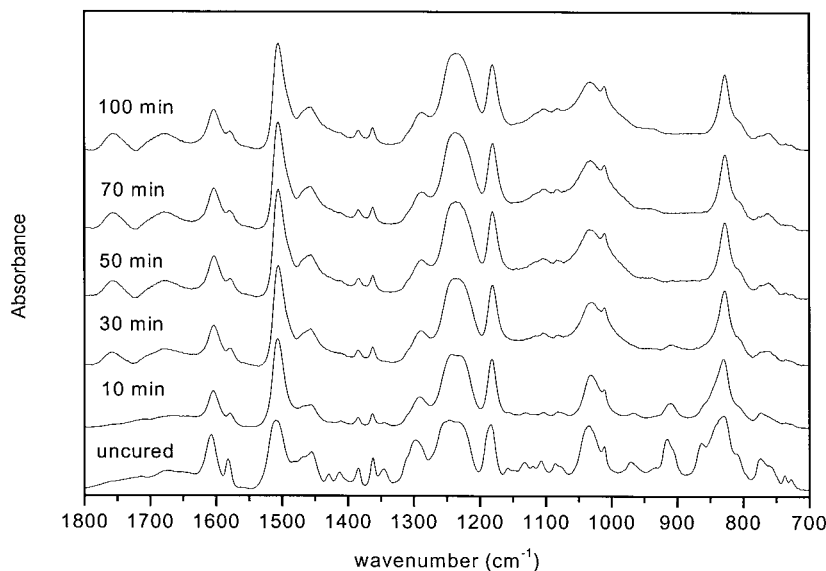**Figure 7** ^{31}P solid-state NMR of (A) melamine phosphate and (B) DGEBA cured with melamine phosphate.

**Figure 8** FTIR spectra, at various times, of DGEBA/MP at 220°C.

curing reaction order of the DGEBA/MP system was 3.18, close to 3, at 220°C. Therefore, at a high curing temperature of 220°C, the DGEBA/MP system exhibited etherification between the epoxide ring and the hydroxyl group. At 230°C, the overall curing reaction order of the DGEBA/MP system was 4.68.

The reaction rate constants at isothermal-cure temperatures of 200, 210, 220, and 230°C were 0.13, 0.31, 0.84, and 3.66 min^{-1}, respectively. The reaction rate constant increased with increasing isothermal temper-

ature and the activation energy of isothermal curing was 110.0 kJ/mol.

Curing mechanism

The curing mechanism of the epoxy/amine system was characterized by NMR and FTIR. Figure 6 shows the ^{13}C solid-state NMR spectrum of the melamine phosphate. The absorption peaks of the $-N\!\!=\!\!C-N-$ group, and its hydrogen bonding with
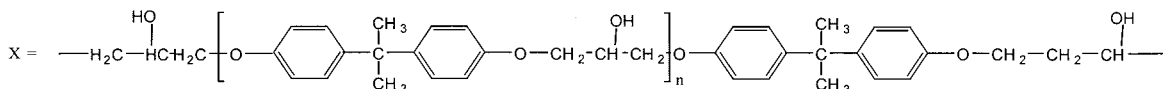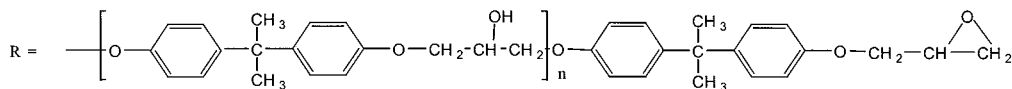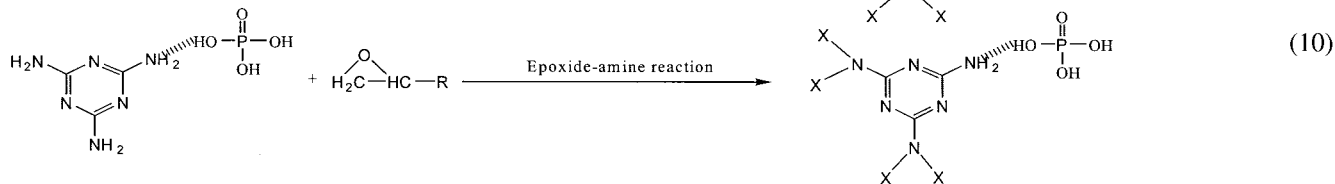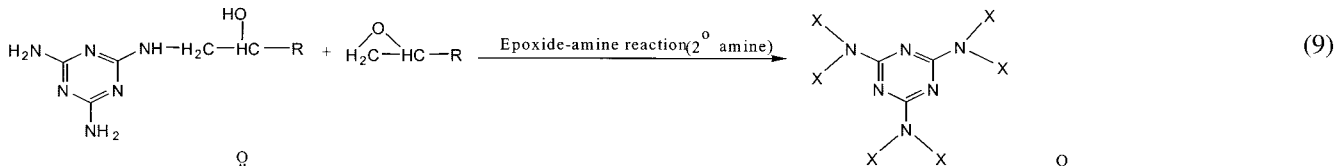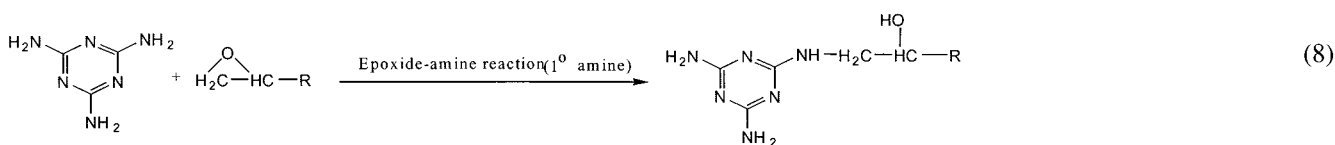
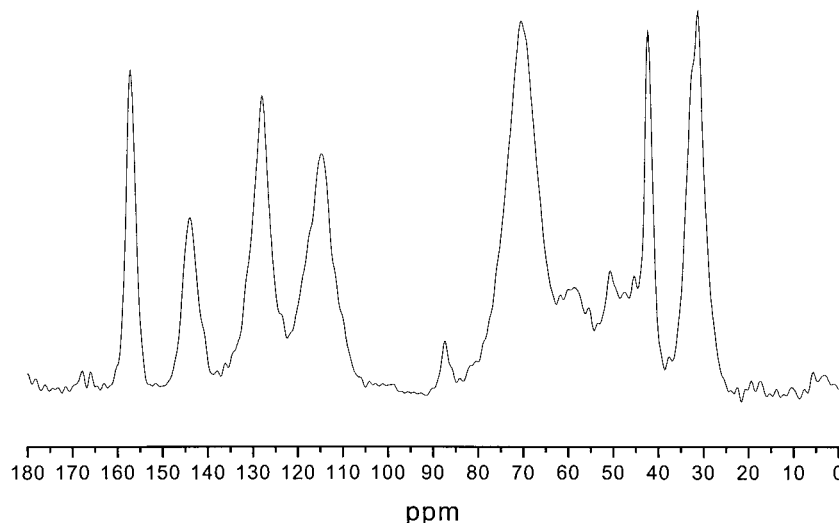**Scheme 2** Epoxide–amine reaction of DGEBA/MP and DGEBA/melamine.

**Figure 9** ^{13}C solid-state NMR of DGEBA cured with melamine.

hydroxyl, are at 157 and 164 ppm, respectively. Figure 6 shows the ^{13}C solid-state NMR spectrum of DGEBA cured with melamine phosphate, at 220°C for 100 min, where the peak at 164 ppm almost disappears, implying that most melamine phosphate is decomposed into melamine and phosphoric acid as shown in Scheme 1. Figure 7(A) shows the ^{31}P solid-state NMR spectrum of the melamine phosphate and the DGEBA cured with melamine phosphate where the absorption peak of phosphoric acid is at 0 ppm.

For the amine–epoxide reaction, Figure 8 shows the IR absorption spectra of the initial (uncured) and after heat treatments at 220°C for various time periods. A comparison of these spectra, for curing at 220°C, reveals that the stretching vibration band of the epoxy ring at 915 cm^{-1} decreases and shifts downward. At the same time, the absorption peak of the NH$_2$ group at 774 cm^{-1} also decreases. These results are related to the epoxide–amine reaction for the epoxy/amine system. Scheme 2 presents the mechanism of the epoxide–amine reaction. Figure 9 shows the ^{13}C solid-state NMR spectrum of DGEBA cured with melamine at 220°C for 100 min, which is essentially the same as the DGEBA cured with melamine phosphate. Therefore, the epoxide–amine reaction of the DGEBA/MP

system indeed occurs between melamine and the epoxy.

Figure 8 shows that the absorption peak of the –P—O—C– group at 1016 cm^{-1} increases with curing time, implying that the DGEBA/MP system undergoes etherification during curing. Figure 7(B) shows the ^{31}P solid-state NMR spectrum of DGBEA cured with melamine phosphate at 220°C, with major and minor peaks at 0 and −9 ppm, respectively. The major peak corresponds to the phosphoric content, whereas the minor peak is attributed to P(=O)(OC) groups. Scheme 3 shows the mechanism of the etherification of the DGEBA/MP system.

For dehydration and thermal oxidation, Figure 8 shows that the absorption peak, of the –C=C– group at 1670 cm^{-1}, increases with curing time because of dehydration of the DGEBA/MP system occurring during later stages of curing,[33] as shown in Scheme 4. The absorption peak, at 1757 cm^{-1} as shown in Figure 8, is the ketone group resulting from the thermal oxidation of the hydroxyl group in the DGEBA/MP system occurring in the later stages of curing, as shown in Scheme 5. The area of this ketone peak increases with curing time, as shown in Figure 8. The IR spectra are able to demonstrate that dehydration and thermal oxidation of the hydroxyl group of the DGEBA/MP

$$\tag{11}$$
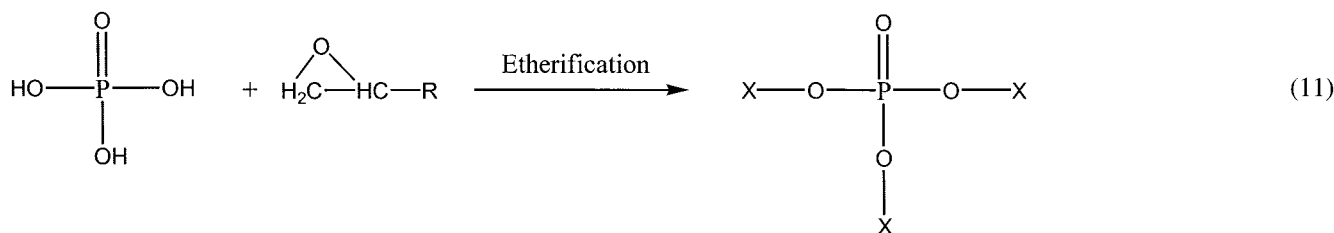
Scheme 3 Etherification of DGEBA/H$_3$PO$_4$.

(12)
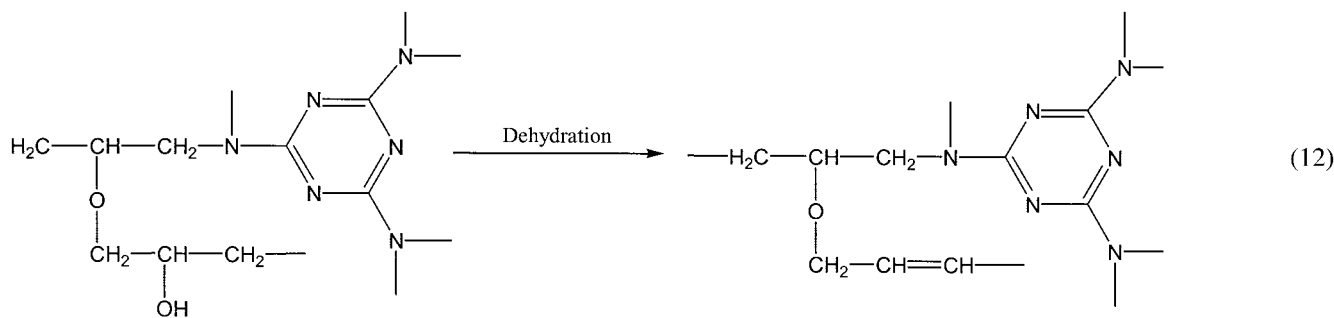
Scheme 4   Dehydration of DGEBA/MP.

(13)
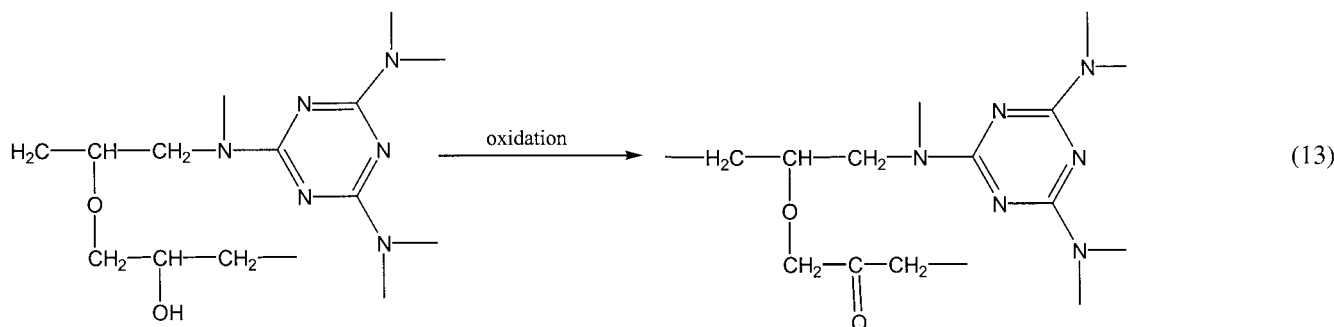
Scheme 5   Thermal oxidation of DGEBA/MP.

system occur simultaneously in the later stage of curing.

CONCLUSIONS

The Kissinger and Flynn–Wall–Ozawa methods were applied in defining dynamic kinetics of the DGEBA/MP system. The activation energies, obtained by these two methods, are 83.9 and 85.6 kJ/mol, respectively. For isothermal-curing kinetics, the DGEBA/MP system has an autocatalytic behavior and the isothermal-cure activation energy is 110.0 kJ/mol. The curing mechanism of the DGEBA/MP system involves the epoxide–amine reaction, etherification of phosphoric between phosphoric acid and epoxy, dehydration, and thermal oxidation of the hydroxyl group of the DGEBA/MP system.

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