Kinetic Analysis of Curing Behavior of Diglycidyl Ether of Bisphenol A with Imidazoles Using Differential Scanning Calorimetry Techniques

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ABSTRACT: The curing kinetics and mechanisms of diglycidyl ether of bisphenol A (DGEBA) using imidazole (H-NI) and 1-methyl imidazole (1-MI) as curing agents are studied with differential scanning calorimetry (DSC) under isothermal (90–120°C) and dynamic conditions (50–250°C). The isothermal DSC thermograms of curing DGEBA with H-NI and 1-MI curing agents show two exothermic peaks. These peaks are assigned to the processes of adduct formation and etherification. These results indicate that there is no difference in the initiation mechanism of 1-unsubstituted (H-NI) and 1-substituted (1-MI) imidazoles in the curing reaction with epoxy resin. A kinetic analysis is performed using different kinetic models. The activation energies obtained from DSC scanning runs using the Ozawa and Kissinger methods are similar and in the range of 75–79 and 76–82 kJ/mol for DGEBA/H-NI and DGEBA/1-MI systems, respectively. These values compare well with the activation energies obtained from isothermal DSC experiments using the autocatalytic method (74–77 kJ/mol). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2634–2641, 2006

Key words: resins; kinetics; differential scanning calorimetry; polymer curing

INTRODUCTION

Imidazole-cured epoxy resins have superior physical properties compared to those cured with tertiary amines,[1] and they are widely used in the electronics industry as molding and sealing compounds. Imidazoles are also added to epoxy–anhydride systems to initiate the esterification reaction and to epoxy–phenol systems to catalyze the homopolymerization of epoxide groups. Most of the previous works[1–7] on epoxy–imidazole systems have focused on the reaction between phenyl glycidyl ether (PGE) and various imidazoles to form adducts. In a study of polymerization of PGE with 1-unsubstituted imidazole,[1] a two-step initiation mechanism was proposed in which pyrrole-type nitrogen (—NH—) reacts with the epoxy functional group to form a 1:1 adduct, and this adduct reacts with the second epoxy group through the pyridine-type nitrogen (—N=) to form a 1:2 adduct. These adducts were proposed[1] to act as initiators to polymerize PGE by an etherification reaction. An alternative mechanism was proposed[2] for the polymerization of PGE with 1-unsubstituted imidazole in which a 1:1 adduct is formed through the attack on the epoxy group by the more basic pyridine-type nitrogen (Scheme 1). The 1:2 adduct is formed by the reaction of the second epoxy group with the newly formed pyridine-type nitrogen.

In an early study, Dearlove[3] also used the first step of the mechanism (Scheme 1) to show the formation of a 1:1 adduct between PGE and 1-substituted imidazole through the attack on the epoxy group by the more basic pyridine-type nitrogen (Scheme 2). In a more extensive work, Ricciardi et al.[6] suggested that different products can be formed from the reaction between PGE and 1-substituted imidazoles; these products can initiate several mechanisms during the curing reaction, and therefore the imidazole becomes permanently incorporated into the epoxy network.

Another complicated matter in the cure of epoxy resins with imidazoles is a unique behavior in the regeneration of starting imidazole[4,6,7] during the curing reaction through two main pathways: N-dealkylation of the nitrogen substitutents at the 3-position and a Hofmann reaction involving β elimination of a hydrogen atom. The regenerated products may then initiate further polymerization.

Despite the considerable research conducted on the adduct reactions between PGE and stoichiometric amounts of imidazoles, the etherification reaction that crosslinks the resin and determines the final properties of the network has not been extensively explored.

In the present study, the curing behavior and properties of neat diglycidyl ether of bisphenol A (DGEBA)

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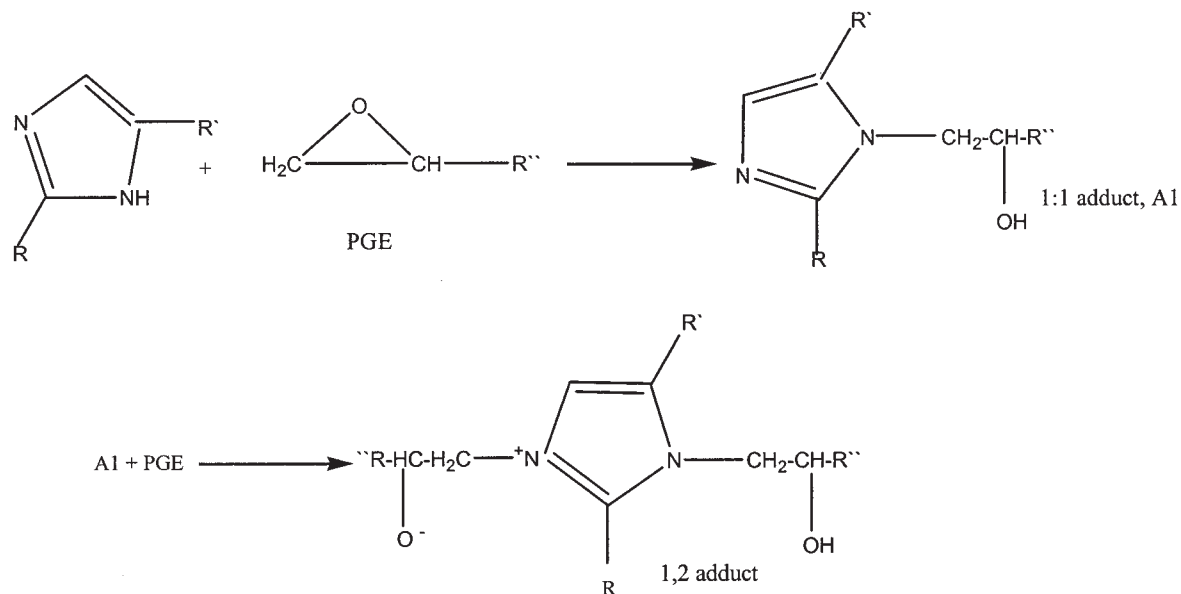
Scheme 1 The proposed mechanism of adduct formation for the cure of PGE with 1-unsubstituted imidazole.

using imidazole and 1-substituted imidazole as curing agents were investigated by scanning and isothermal differential scanning calorimetry (DSC). The kinetic parameters were compared to further elucidate the polymerization mechanism and the factors controlling the imidazole curing characteristics of DGEBA. The properties of cured epoxy resin will appear in the next article in this series.

EXPERIMENTAL

The materials used in present study are DGEBA (Epon 828) with an average molecular weight of 380 g/mol from Shell Co., 1-methyl imidazole (1-MI), and imidazole (H-NI) with a purity of 99% from Fluka (Fig. 1). All chemicals were used as received.

The DSC studies of the curing behavior were performed with a PerkinElmer DSC-4. All samples (~10 mg) of completely mixed resin and the curing agents were contained within sealed aluminum DSC pans. High purity indium was used to calibrate the calorim-

eter. The heating rates for the scanning runs were 5, 10, and 15°C/min. Scanning DSC studies of the cure of DGEBA was performed from 30 to 250°C using curing agents at concentrations of 5, 10, 15, and 20 wt %. Isothermal DSC studies of the cure of DGEBA at 90, 110, and 120°C were performed with various concentrations of imidazoles (5, 10, 15, and 20 wt %) at a heating rate of 10°C/min. The degree of thermal cure was followed by monitoring the DSC heat flow as a result of the curing reactions. The heat of the reaction (ΔH) was obtained by integrating the DSC exotherm peak area of the heat flow curve. In the DSC studies the ΔH that was obtained was assumed to represent the total heat of the reaction due to full cure.

RESULTS AND DISCUSSION

Both dynamic and isothermal DSC studies were performed to determine the kinetics of the curing reaction of DGEBA with H-NI and 1-MI as curing agents.
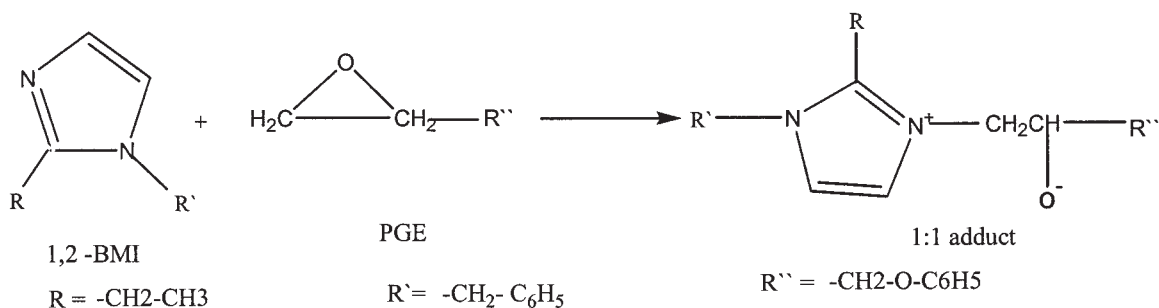
Scheme 2 The proposed mechanism of adduct formation for the cure of PGE with 1-substituted imidazole.
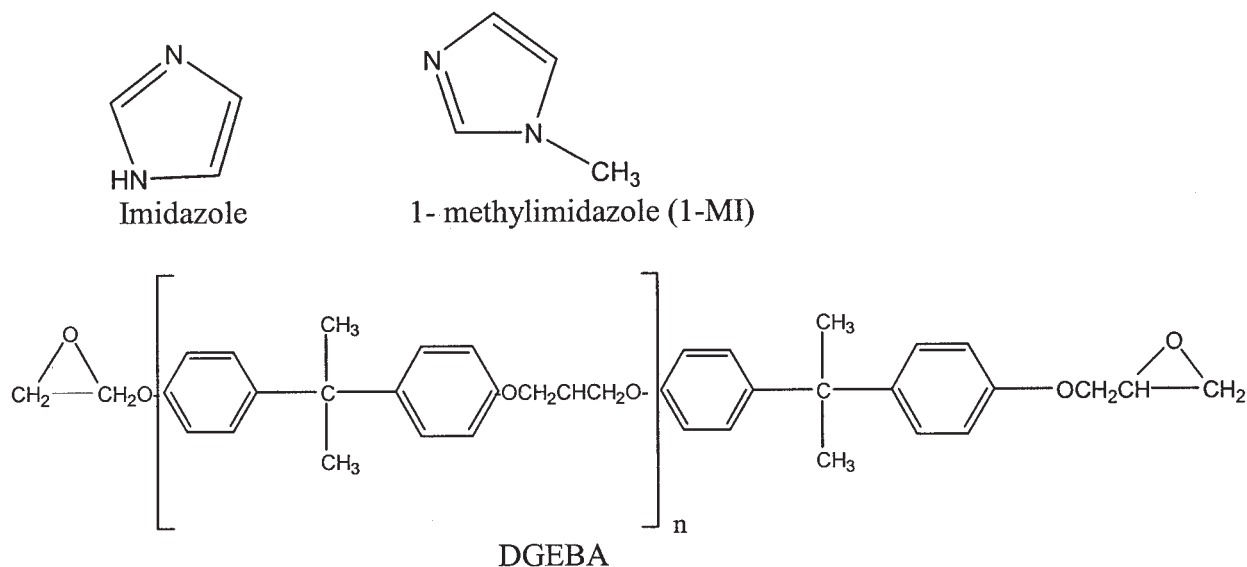
Figure 1 The structures of DGEBA and the curing agents.

Dynamic DSC analysis

Figures 2 and 3 show typical DSC thermograms for the dynamic cure of epoxy resin with 5, 10, 15, and 20 wt % H-NI and 1-MI, respectively. The total area under the thermograms was used to calculate the total heat of the reaction. Table I provides the data obtained from DSC dynamic thermograms of DGEBA cured with H-NI and 1-MI. An analysis of the heat evolved indicates that at all four concentrations complete or near complete cure were obtained with ΔH_{tot} being in the range of about 98–105 kJ/mol, which are comparable to values of 94–104 kJ/mol obtained by Vogt[8] for complete chain growth polymerization of DGEBA using various imidazole curing agents. The values obtained in this study for fully cured epoxy/imidazole systems are in agreement with many epoxy/amine condensation systems,[9] which are generally in the range of 100–118 kJ/mol. The general agreement between the ΔH_{tot} obtained from the cure of epoxy resins

using step growth and chain growth agents is expected as the heat evolved during the curing reaction involves largely the release of the strain energy located within the epoxy functional group. Based on mechanistic studies by Barton and Shepard[2] (Scheme 1), the pyrrole-type (H—N) nitrogen in the imidazole curing agents does not take part in the formation of the adducts (1:1 and 1:2). Therefore, the values of ΔH_{tot} must be attributed to the etherification reaction.

In order to determine the reaction kinetics by DSC analysis, the amount of heat evolved during a given time period is related to the number of reacting molecules. The dynamic multiple scan method, in which the variation of the peak exothermic temperature with the concentration of the curing agents and the heating rate is measured, can be used to analyze curing reactions. There is one distinct exothermic peak in Figures
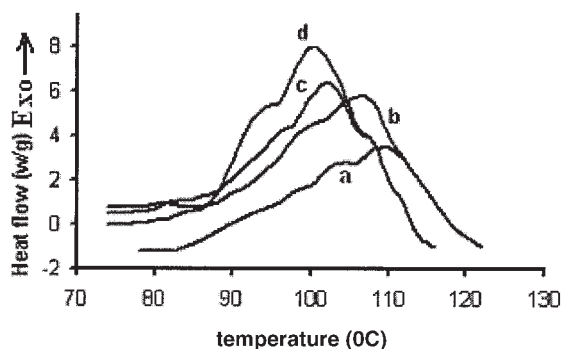

Figure 2 Typical DSC thermograms for dynamic scanning of DGEBA with 5 (curve a), 10 (curve b), 15 (curve c), and 20 wt % (curve d) H-NI; heating rate = 10°C/min.

Figure 3 Typical DSC thermograms for dynamic scanning of DGEBA with 5 (curve a), 10 (curve b), 15 (curve c), and 20 wt % (curve d) 1-MI; heating rate = 10°C/min.
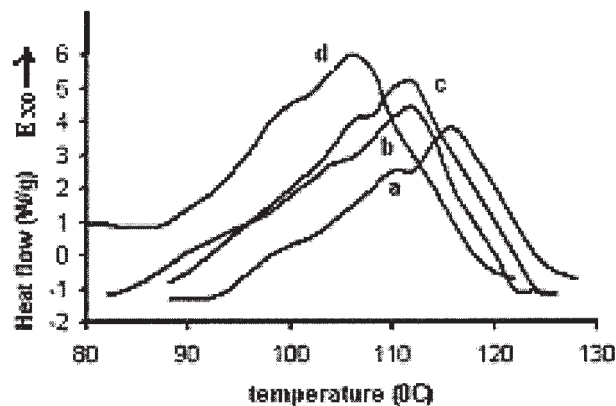
Composition	Max. peak (°C)	ΔH_{tot} (kJ/mol)	ln A (s^{-1})	E_{ao} (kJ/mol)	E_{ak} (kJ/mol)
DGEBA + 5 wt % H-NI	110	98.4	17	75	75.6
DGEBA + 10 wt % H-NI	108	100	17.1	76.5	75.3
DGEBA + 15 wt % H-NI	103	101.5	17.3	77.8	76
DGEBA + 20 wt % H-NI	99	104.3	17.8	79.2	78.6
DGEBA + 5 wt % 1-MI	115	101.8	17.7	76.4	77
DGEBA + 10 wt % 1-MI	112	102.8	19.6	79	79.8
DGEBA + 15 wt % 1-MI	110	104	19.8	81	80.3
DGEBA + 20 wt % 1-MI	107	105.2	20	82.7	81.5

E_{ao}, Ozawa method; E_{ak}, Kissinger method.

2 and 3, with a very small shoulder at lower temperature for each individual concentration and all heating rates. The adduct formation reactions appear as a low temperature shoulder on the large exothermic peak. The etherification reaction occurs as the largest exothermic peak and is characterized by a high heat flow corresponding to a rapid reaction rate. The reaction kinetics (activation energies and frequency factor) were evaluated for a single exothermic peak related to both adduct formation and etherification. The peak shift method developed by Ozawa[10,11] was used to calculate the activation energies (E_a) for DGEBA cured with concentrations of H-Ni and 1-MI ranging from 5 to 20 wt %.

The peak exothermic temperatures were measured for three different heating rates from 5 to 15°C/min. According to this method the relationship between the E_a, heating rate (ϕ), and peak exothermic temperature (T_p) can be described as

$$E_a = (R/1.025) \times \{\Delta\ln\phi/\Delta(1/T_p)\} \quad (1)$$

where R is the gas constant. By plotting $1/T_p$ versus ln ϕ at different heating rates, the values of E_a were obtained from the slope of the straight lines. The activation energies determined for the curing reaction of DGEBA with a range of H-Ni and 1-MI concentrations varied from 75 to 79 and 77 to 82 kJ/mol, respectively. According to method of Kissinger,[12] the E_a and frequency factor (A) can be determined using the following equations:

$$E_a = -\{d(\log \phi/T_p^2)\}/d(1/T_p)R \times 2.303 \quad (2)$$

$$\ln\phi = \ln(A_0R/E_a) + 2\ln T_p - E_a/RT_p \quad (3)$$

By plotting $1/T_p$ versus log ϕ/T_p^2 at different heating rates, values of E_a can be obtained from the slope of the straight lines. By plotting $2\ln T_p - E_a/RT_p$ versus ln ϕ using the resulting E_a and eq. (3), the values of the frequency factor can be obtained from the slope of the straight lines. The E_a values were 75–78 and 77–81

kJ/mol for the curing reactions of DGEBA/H-NI and DGEBA/1-MI systems, respectively. A summary of the kinetic results is given in Table I.

Isothermal DSC analysis

Typical DSC isothermal thermograms for DGEBA cured with different concentrations of imidazoles are shown in Figures 4 and 5. There are two distinct exothermic peaks for both H-NI and 1-MI curing systems. As the imidazole concentration is decreased, the area under the first peak decreases whereas the area under the second peak increases. Studies by others[8,13,14] using 1,3-unsubstituted imidazoles have also found a lower temperature shoulder that was attributed to the formation of adduct (Scheme 1 or 2). Therefore, the first peak in the present study should be attributed to the adduct reactions. The adduct formation is not a crosslinking process, and a network does not form appreciably during the first exothermic reaction. The initiation of the etherification reaction is marked by the appearance of the second exothermic peak during which ether crosslinks are formed. According to the mechanism shown in Schemes 1 and 2, there is no difference in the curing behavior between
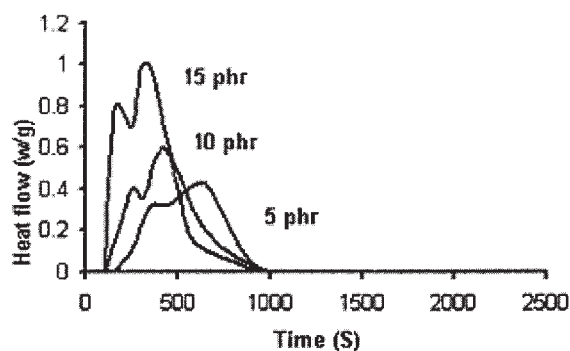

Figure 4 Typical DSC isothermal curing thermograms for DGEBA cured with different concentrations of H-NI at 110°C; heating rate = 10°C/min.
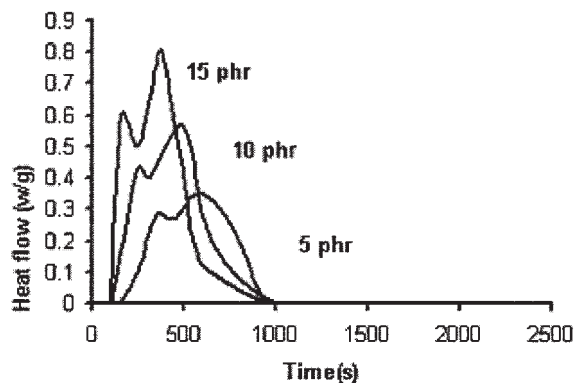
Figure 5 Typical DSC isothermal curing thermograms for DGEBA cured with different concentrations of 1-MI at 110°C; heating rate = 10°C/min.

1-unsubstituted and 1-substituted imidazoles in the formation of the 1:1 adduct. Because two imidazoles are considered to involve the same pyridine-type nitrogen during the formation of the 1:1 adduct, there should be no differences in their behavior.

One interesting curing behavior seen in Figures 4 and 5 is the rate of adduct formation (first peak), which increased with respect to the rate of etherification (second peak) as the imidazole concentration was raised. The only difference between these two types of imidazoles is that a 1:2 adduct is also generated for the 1-unsubstituted imidazole. Therefore, it is reasonable to conclude that the extra formation of the 1:2 adduct is responsible for the enhanced rate of etherification for the DGEBA/H-NI system. Other workers[8,13,14] have also distinguished a third high temperature exo-

thermic peak, particularly noticeable at higher imidazole concentration (>20 wt %). This exothermic peak was attributed to epoxy polymerization via HO etherification (originating from the 1:2 adduct) or to imidazole regeneration (Scheme 3), which can reinitiate polymerization. The proposed reaction mechanism for a diepoxide–imidazole system consists of both adduct and etherification reactions and is shown in Scheme 3. The results presented in Table II show that increasing the imidazole concentration generally increases the degree of isothermal cure. For both systems, a higher imidazole concentration yielded a higher total heat of reaction, which is in agreement with the scanning DSC results (Table I). The degree of cure depended on the curing conditions employed. Barton et al.[15] and Ricciardi et al.[6] have shown that the degree of cure and the final properties of the cured resin are mainly determined by the curing conditions. They have suggested that in a particular condition the process of imidazole regeneration occurs and this leads to formation of products that are not chemically bonded to the network. The regenerated products, which are significant only at high temperatures, plasticize the network and will decrease the glass-transition temperature and broaden the molecular weight distribution. The reaction kinetics were determined for DGEBA cured with 5, 10, 15, and 20 wt % H-NI and 1-MI at isothermal temperatures of 90, 110, and 120°C. The thermal conversion (α) or the extent of reaction at time t during the isothermal cure was determined from a single isothermal experiment in which the heat of the reaction is determined as a function of the cure time:

$$\alpha = \Delta H_t / \Delta H_{total} \qquad (4)$$
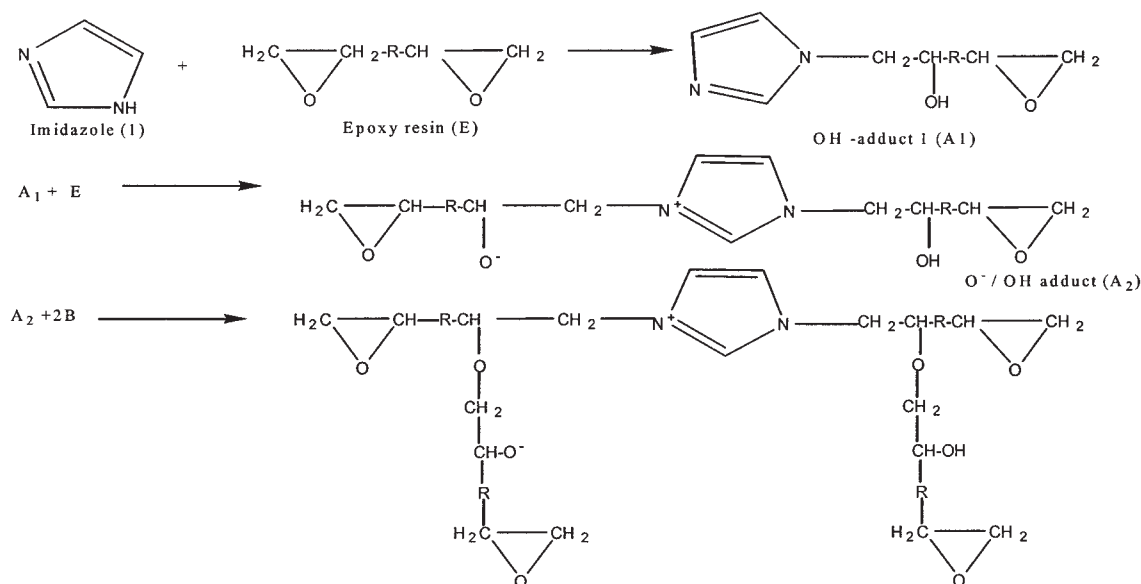
Scheme 3 The proposed mechanism for the curing reaction of a diepoxide with 1-unsubstituted imidazole.

TABLE II
Data Obtained from Isothermal DSC Experiments

Composition	ΔH (kJ/mol)	Temp. (°C)	Max. time (s)	k_1 (s^{-1})	n	m	k_2 (s^{-1})
DGEBA + 5 wt % H-NI	105	90	572	0.0038	0.42	0.33	0.002
DGEBA + 5 wt % H-NI	106.2	110	550	0.004	0.53	0.41	0.008
DGEBA + 5 wt % H-NI	107	120	538	0.0058	0.57	0.43	0.012
DGEBA + 10 wt % H-NI	118	90	448	0.003	0.5	0.4	0.0024
DGEBA + 10 wt % H-NI	118.3	110	430	0.0044	0.52	0.51	0.009
DGEBA + 10 wt % H-NI	121.4	120	411	0.005	0.58	0.6	0.014
DGEBA + 15 wt % H-NI	130.3	90	372	0.0028	0.41	0.3	0.003
DGEBA + 15 wt % H-NI	130.8	110	350	0.0036	0.47	0.36	0.009
DGEBA + 15 wt % H-NI	132	120	323	0.005	0.5	0.4	0.011
DGEBA + 20 wt % H-NI	142	90	210	0.0035	0.39	0.4	0.005
DGEBA + 20 wt % H-NI	143.2	110	194	0.0044	0.48	0.43	0.01
DGEBA + 20 wt % H-NI	143.8	120	175	0.0057	0.51	0.47	0.013
DGEBA + 5 wt % 1-MI	103.4	90	582	0.0031	0.37	0.34	0.0025
DGEBA + 5 wt % 1-MI	104.2	110	570	0.0043	0.41	0.38	0.0095
DGEBA + 5 wt % 1-MI	104.7	120	550	0.005	0.55	0.52	0.0016
DGEBA + 10 wt % 1-MI	112	90	528	0.0038	0.49	0.58	0.0018
DGEBA + 10 wt % 1-MI	112.6	110	500	0.0047	0.54	0.6	0.008
DGEBA + 10 wt % 1-MI	112.7	120	422	0.0066	0.6	0.69	0.011
DGEBA + 15 wt % 1-MI	128.3	90	397	0.0038	0.36	0.44	0.0065
DGEBA + 15 wt % 1-MI	128.77	110	381	0.0049	0.45	0.5	0.0085
DGEBA + 15 wt % 1-MI	129.5	120	365	0.0058	0.5	0.52	0.014
DGEBA + 20 wt % 1-MI	145.3	90	225	0.004	0.5	0.43	0.0078
DGEBA + 20 wt % 1-MI	146	110	202	0.0051	0.52	0.48	0.01
DGEBA + 20 wt % 1-MI	146.7	120	182	0.0058	0.55	0.51	0.015

where ΔH_t is the heat of the reaction from the start of the curing reaction to t, and ΔH_{tot} is the total heat of the reaction from the start of the curing reaction to t at the end of the isothermal cure (which is the area under the DSC trace up to t divided by the total area of the DSC trace). The rate of heat released during cure, measured as a function of time and temperature, was assumed to be directly proportional to the rate of the reaction[16,17]:

$$d\alpha/dt = (1/\Delta H_{total})(dH/dt) \qquad (5)$$

The reaction rate ($d\alpha/dt$), which is proportional to the rate of heat generation (dH/dt), accordingly increases with increasing isothermal temperature or concentration of the curing agent. This can be seen in Figure 6, which shows the dependence of the maximum reaction rate on the concentration of the curing agents.

The maximum heat generation or reaction rate is reached in a shorter time at a definite concentration with increasing isothermal temperature. Figure 7 provides typical plots of the $d\alpha/dt$ versus time at different isothermal temperatures and concentrations of imidazole. Figure 8 shows typical plots of the reaction rate versus conversion for the isothermal DSC thermograms presented in Figure 5. This behavior of the reaction rate is characteristic of chemical reactions in which products act as catalysts for the continuing reaction and are referred to as the autocatalytic reactions. The maximum rate for the present systems is

observed at conversions of around 30–40%, as expected for an autocatalytic reaction. The autocatalytic model is a phenomenological approach. In this model a general equation is assumed for the curing process of many amine-cured epoxy systems, as follows[18-20]:

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (6)$$

where m and n are the reaction orders and the introduction of the variable values usually makes it possible to obtain a good fit to experimental data, $m + n$ is the overall reaction order, and k_1 and k_2 are the reaction constants where k_1 can be calculated if the initial
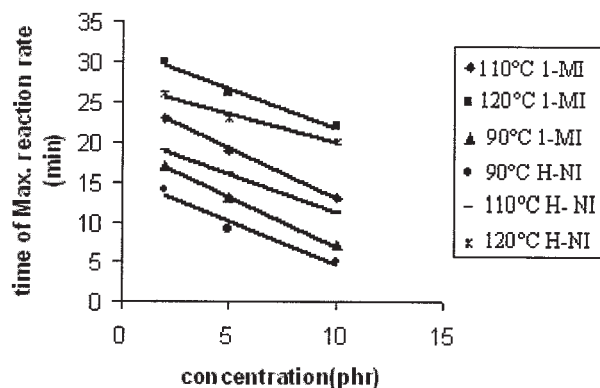

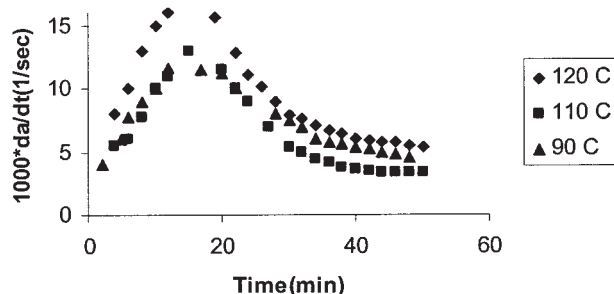**Figure 6** The time of the maximum reaction rate versus the concentration of curing agents.

Figure 7 The reaction rate ($d\alpha/dt$) versus time (t) curves at different isothermal temperatures for DGEBA + 10 wt % imidazole.

Figure 9 Arrhenius plots of ln k versus $1/T$ for DGEBA with 10 wt % curing agents.

reaction rate at $t = 0$ can be estimated. Both kinetic constants k_1 and k_2 depend on the temperature according to the Arrhenius law. For determination of the cure kinetics by means of an autocatalytic model, first the isothermal cure in DSC is realized at several temperatures, then the experimental rate equation (α, $d\alpha/dt$) is determined for the complete course of the reaction, and finally the experimental results are adjusted with the kinetic equation. Thus, the reaction orders and the rate constants are obtained for each temperature. Finally, using the Arrhenius equation for the dependence of the rate constants on the temperature, the activation energies and the frequency factors are determined. To compute the parameters in eq. (6) from experimental data, several methods have been proposed.[21] In the present study, the kinetic parameters (m, n, k_1, and k_2) were determined using the same procedure given elsewhere.[22] The summary of the kinetic results is given in Table II.

For all formulations, the values of m and n appear to increase somewhat with increasing isothermal temperature and it can be concluded that the $m + n$ is one (Table II).

Considering that k_2 is the rate constant for the cure reaction, the E_a and A can be calculated using Arrhenius-type behavior:
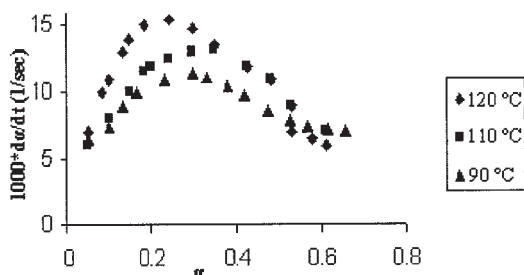
$$K_2 = A\exp(-E/RT) \qquad (7)$$

Integration of eq. (7) yields

$$lnk_2 = \ln A - E_a/RT \qquad (8)$$

Plotting ln k_2 versus $1/T$ gives straight lines of slope $-E_a/R$ and an intercept of ln A. These plots are given in Figure 9. Table III provides the values of E_a and frequency factors obtained from isothermal DSC experiments for DGEBA/1-MI and DGEBA/H-NI systems, which are quite comparable with the E_a obtained from the scanning DSC runs using the Ozawa and Kissinger methods (Table I). These values compare well with the values of E_a obtained by Ooi et al.[14] and Berger and Lohse.[23]

CONCLUSION

The cure reactions of DGEBA/H-NI and DGEBA/1-MI systems were studied using the basic assumption that the heat evolution recorded by DSC is proportional to the extent of consumption of the epoxide group in the epoxy resin.

All isothermal DSC curves for both systems showed a low temperature exothermic peak. The area under the low temperature shoulder (first peak) became more distinct and pronounced as the imidazole concentration was raised. The first peak was attributed to the forma-

Figure 8 The reaction rate ($d\alpha/dt$) versus thermal conversion (α) curves for DGEBA + 10 wt % 1-MI at different isothermal temperatures.
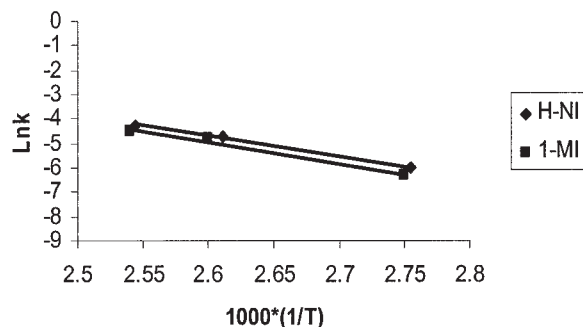
TABLE III
Values of E_a and Frequency Factor of Curing DGEBA with H-NI and 1-MI Using Isothermal DSC Data

Composition	ln A (sc^{-1})	E_a (kJ/mol)
DGEBA + 5 wt % H-NI	16.9	72
DGEBA + 10 wt % H-NI	17.2	74.5
DGEBA + 15 wt % H-NI	17.4	75.3
DGEBA + 20 wt % H-NI	17.85	77.2
DGEBA + 5 wt % 1-MI	17.8	76
DGEBA + 10 wt % 1-MI	19.7	78
DGEBA + 15 wt % 1-MI	19.9	79.5
DGEBA + 20 wt % 1-MI	20.3	80

tion of adducts (1:1 and 1:2) and the second exothermic peak was attributed to the etherification reaction. Because two imidazoles were considered to contain the same pyridine-type nitrogen involved in the formation of adducts, there should be no differences in their behavior in the curing reaction with epoxy resin. The results showed that the rate of the reaction was proportional to the heat flow, and a higher isothermal temperature led to an increase in the reaction rate. The extent of the reaction at the highest (peak) value of the reaction rate was dependent on the isothermal temperature and hardener concentration. The isothermal DSC curves showed the maximum rate of heat evolution at around 30–40% conversion. A four-parameter semiempirical equation for autocatalytic systems, which contained two rate constants (k_1 and k_2) and two reaction rate orders (m and n), was applied as a kinetic model for the polymerization reaction of DGEBA resin cured with H-NI and 1-MI. The activation energy and frequency factor were obtained from the Arrhenius equation.

The activation energy of the dynamic DSC curing reaction of DGEBA with H-NI and 1-MI was determined by the Ozawa and Kissinger methods. The E_a values were in the range of 76–79 and 74–76 kJ/mol for DGEBA/1-MI and DGEBA/H-NI, respectively, which were comparable with the E_a values (77 and 74 kJ/mol) obtained for the above systems using an isothermal DSC curing reaction.

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