Analysis of the Cure Kinetics of Epoxy / Imidazole Resin Systems

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Synopsis

The reaction kinetics for the cure of epoxy resins with imidazoles were determined from Fourier transform infrared spectroscopy and differential scanning calorimetry studies. The diglycidyl ether of bisphenol A and phenyl glycidyl ether were cured with various concentrations of 2-ethyl-4-methyl-imidazole ranging from 4.0 to 100.0 mol %. The first step in the curing process is the formation of epoxide/imidazole adducts. These adducts initiate the etherification reaction which crosslinks the resin. The kinetics were determined and confirmed for both the adduct and the etherification reactions as a function of the imidazole concentration. A model was developed and used to predict the concentrations of the unreacted epoxide groups and the reaction products for a wide range of imidazole concentrations and cure temperatures.

INTRODUCTION

Recent studies[1,2] have demonstrated that epoxy resins cured with imidazoles have superior physical properties compared to those cured with tertiary amines. Imidazole-cured resins are widely used in the electronics industry as molding and sealing compounds because they exhibit a better heat resistance, less tensile elongation, a higher modulus, and a wider range of cure temperatures than amine-cured systems.[1,2] Imidazoles are added to epoxy–anhydride systems to initiate the esterification reaction and to epoxy–phenol systems to catalyze selectively the epoxy–phenolic hydroxyl reactions; they also catalyze the homopolymerization of epoxide groups.

Most of the previous work[3-9] on epoxy/imidazole systems has focused on the reaction between phenyl glycidyl ether (PGE) and various imidazoles to form adducts. Barton and Shepard[4] and Dearlove[5] concluded that both 1 : 1 and 2 : 1 adducts were formed from the epoxide ring opening by "pyridine-type" nitrogens. These adducts were assumed to be the catalysts that initiated the polymerization process and, therefore, the imidazole became permanently incorporated into the epoxy network.[3,4] The proposed reaction mechanism[10] for a diepoxide/imidazole system consists of both adduct and etherification reactions, as shown in Figure 1. 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.[6,11]

The objectives of this study were threefold. First, the adduct and the etherification reactions were differentiated and analyzed by curing with a wide range of imidazole concentrations. High imidazole concentrations were

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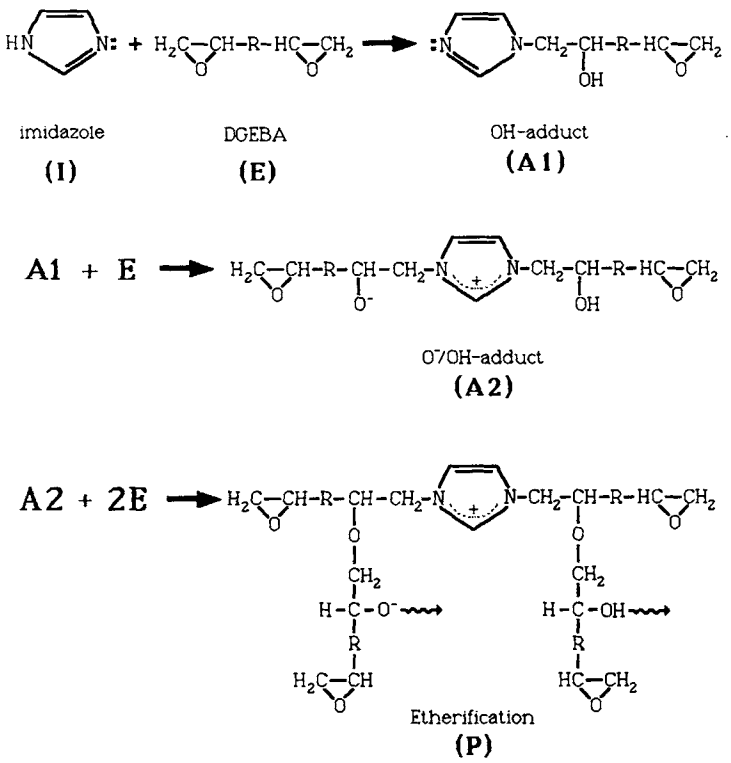

Fig. 1. Reaction mechanism for the curing of a diepoxide with a 1-unsubstituted imidazole.[10]

used to study the adduct formation process by suppressing the etherification reaction; low imidazole concentrations were used to analyze the etherification reaction. Second, the reaction kinetics for the individual curing reactions were determined from Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) analyses. Because the curing studies were performed over a wide range of imidazole concentrations, the effect of the imidazole on the epoxy homopolymerization reaction could be determined. Third, a kinetic model was developed which describes the curing behavior of the epoxy/imidazole system. This model forms the basis for developing structure–property relations and performing network modeling studies.[12]

EXPERIMENTAL

Two epoxy compounds were used in this study. The epoxy resin (X-22), a highly pure form of the diglycidyl ether of bisphenol A (DGEBA), was supplied by the Shell Development Co. The epoxide equivalent weight, determined by titration, was 172 g/mol epoxide. Phenyl glycidyl ether (PGE), obtained from the Aldrich Chemical Co. with a purity of 99.5 + %, was used as the noncrosslinking epoxy. The imidazole, 2-ethyl-4-methyl-imidazole (EMI-24), was obtained from Chemical Dynamics Co. with a purity of 99% Samples with different molar imidazole concentrations (mol imidazole/100 mol epoxide groups) were prepared by dissolving both components in methyl

ethyl ketone. The DGEBA/imidazole samples, used for DSC analysis, were recovered by solvent flashing followed by crystallization.

FTIR studies were performed using an IBM Instruments IR/32S equipped with a temperature-controlled sample holder which allowed for *in situ* analysis of the curing reaction. Thin films of the epoxy/imidazole system were prepared by solvent casting with methyl ethyl ketone on NaCl cells. The cells were placed in a vacuum desiccator to remove the solvent prior to the reaction. The samples were then secured in the sample holder that had been preheated to the desired isothermal temperature. Spectra were taken every 90 s for at least 1 h. Peak areas were calculated for the epoxide asymmetric ring stretch at 915 cm^{-1} and for the N — H stretch between 3400 and 3200 cm^{-1}. The Ar — C — Ar stretch at 1184 cm^{-1} was used as the reference peak for the DGEBA samples; the =C — H out-of-plane deformation at 693 cm^{-1} was used as the reference for the PGE samples.

Both dynamic and isothermal DSC studies were performed using a Mettler DSC-30 equipped with a low temperature cell. Samples used in the dynamic analysis were melted at 40°C for 1 min prior to the curing study to achieve a consistent thermal baseline. Dynamic scans from 2.5 to 20°C/min over a temperature range of 25–300°C were used to cure the DGEBA/EMI-24 samples. Isothermal DSC studies were performed by rapidly ramping (100°C/min) the sample from 0°C to the desired isothermal temperature which ranged from 60 to 100°C, holding for various periods of time, and quenching to −50°C. Both the dynamic and isothermal samples were then scanned after the initial cure to 300°C at 10°C/min to determine the T_g and the residual heat of reaction. The temperature corresponding to the onset of the endothermic deflection of the baseline was assigned to be the T_g; the heat of reaction was calculated from the exotherm area.

ANALYSIS OF THE CURING MECHANISM

The first step in the curing process is the reaction of an epoxide group with an imidazole as shown in Figure 1. In 1-unsubstituted imidazoles such as EMI-24, the 1 : 1 adduct (OH — adduct) is formed by the nucleophilic attack of the 3-N, followed by the rearrangement of the zwitterion intermediate through a proton transfer. This proton transfer can be analyzed with FTIR by monitoring the N — H stretching peak. The epoxide and N — H concentration profiles for DGEBA cured with 25.0 mol % EMI-24 are shown in Figure 2. The N — H concentration decreases during the initial stages of the reaction as the 1 : 1 adduct is formed.

The reaction of the second epoxide group to form the 2 : 1 adduct (O^-/OH — adduct) can be followed by monitoring the epoxide concentration. The change in slope in the epoxide concentration profile, indicated by the arrows in Figure 2, represents a change in the reaction mechanism and is marked by the appearance of the aliphatic ether peak (1110–1140 cm^{-1}) in the IR spectra. The epoxide conversion, prior to the appearance of aliphatic ether peak, is approximately 40–45% for DGEBA cured with 25.0 mol % EMI-24; this corresponds to a depletion of almost 2 mol epoxide/mol imidazole. The change from the adduct formation reactions to the etherification reaction is characterized by an increase in the epoxide reaction rate, a sharp

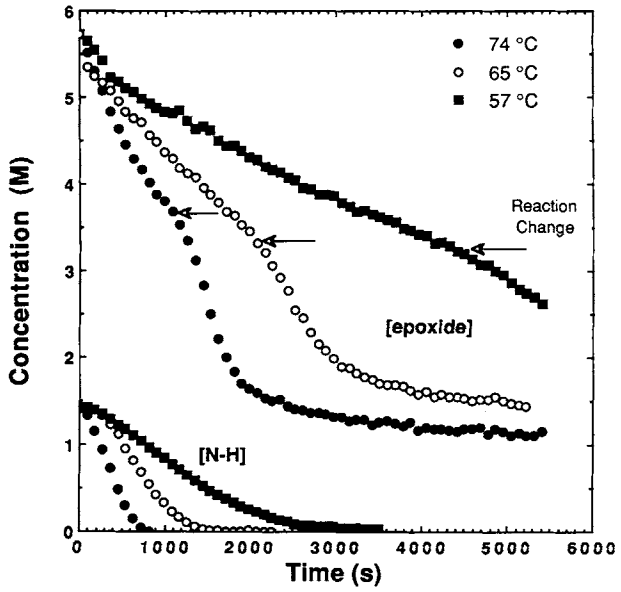

Fig. 2. Epoxide and N — H concentration profiles from isothermal FTIR studies for the cure of DGEBA with 25.0 mol % EMI-24 at various reaction temperatures. (The arrows indicate the change in the reaction rate.)

increase in the T_g, and the appearance of the aliphatic ether peak in the IR spectra.[10]

In the DSC isothermal traces for DGEBA cured with 25.0 mol % EMI-24, shown in Figure 3, there are two distinct exothermic peaks. As the imidazole concentration is decreased, the area under the first peak decreases while the

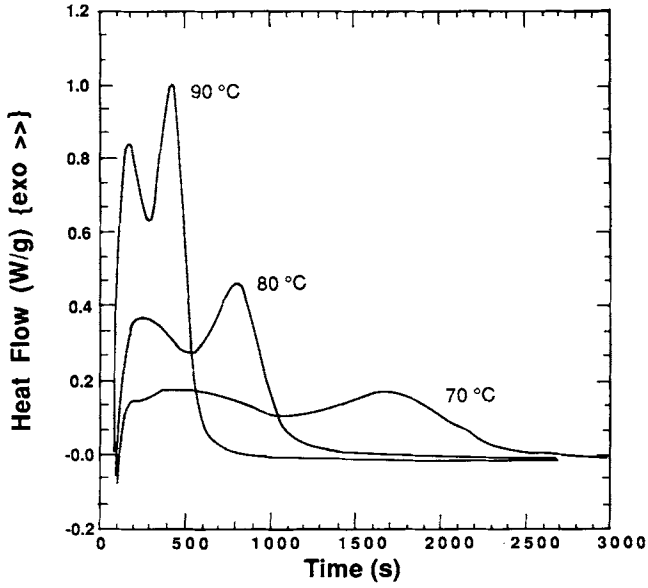

Fig. 3. DSC thermograms for DGEBA cured with 25.0 mol % EMI-24 at different cure temperatures.

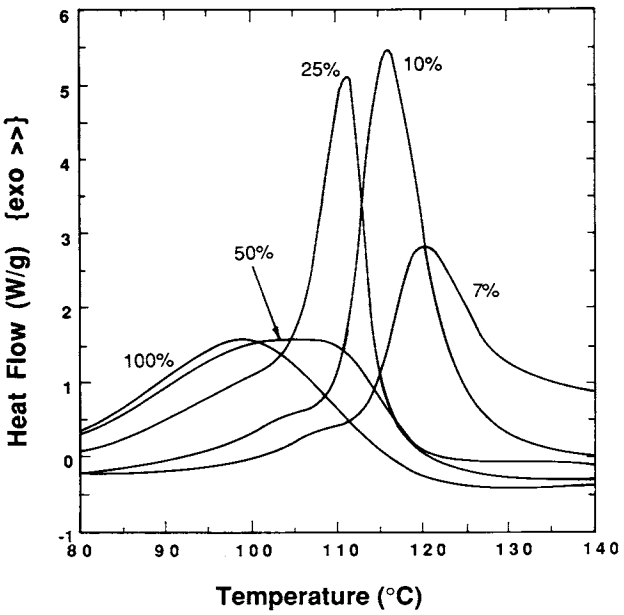

Fig. 4. DSC dynamic traces at 10°C/min for the cure of DGEBA with various molar concentrations of EMI-24.

area under the second peak increases; therefore, the first peak is attributed to the adduct reactions and the second peak is attributed to the etherification reaction.[10] This peak assignment was confirmed by monitoring the T_g during the isothermal cure of DGEBA and EMI-24.[10,11] Because adduct formation is not a crosslinking process, the T_g does not change appreciably during the first exothermic reaction. The initiation of the etherification reaction is marked by the appearance of the second exothermic peak and a rapid increase in the T_g as ether crosslinks are formed. The second exothermic peak does not appear at concentrations greater than 50.0 mol % EMI-24. For these concentrations, the imidazole consumes most of the epoxide groups to form adducts.

Dynamic DSC traces for DGEBA cured with various concentrations of EMI-24 are illustrated in Figure 4. At high imidazole concentrations of 50.0 mol % or greater, the DSC thermograms exhibit a single exotherm that corresponds to the adduct formation reactions. At imidazole concentrations lower than 50.0 mol %, there are unreacted epoxy groups remaining after the adduct formation and, consequently, the etherification reaction can occur. The etherification reaction occurs as the largest exothermic peak and is characterized by a high heat flow corresponding to a rapid reaction rate. At EMI-24 concentrations of 25.0 mol % or less, the adduct formation reactions appear as a low temperature shoulder on the large exothermic peak.

DETERMINATION OF REACTION KINETICS

The reaction kinetics for the adduct and the etherification reactions were determined by three different methods: isothermal FTIR, isothermal DSC, and dynamic DSC. The reaction order and kinetic parameters (activation

energy and frequency factor) were evaluated for DGEBA and PGE cured with a wide range of imidazole concentrations. This analysis is the basis for the kinetic model developed in the following section.

FTIR Analysis

The reaction kinetics for both the adduct and etherification reactions were calculated from isothermal FTIR studies. There are three distinct regions present in the epoxide concentration profiles displayed in Figure 2. The first region is marked by the adduct formation reactions which have a relatively slow rate of reaction. Barton and Shepard[4] showed that the rates of formation for the 1 : 1 and 2 : 1 adducts of PGE and EMI-24 were similar. This result implies that the "pyridine-type" nitrogens on the imidazole have similar reactivities; hence, an overall rate for the adduct formation was determined. The second region is characterized by the appearance of the aliphatic ether band and by a rapid decrease in the epoxide concentration during the etherification reaction. The third region occurs when the sample vitrifies; here, the etherification reaction becomes diffusion-limited with a very slow rate of reaction.

First-order rate expressions describe both the adduct and the etherification reactions. The kinetic analyses are displayed in Figures 5 and 6 for the cure of DGEBA with 25.0 mol % EMI-24 for a wide range of temperatures. The rate expressions for the curing reactions are given by:

$$\text{Adduct reactions:} \quad \ln[\mathrm{E}]/[\mathrm{E}]_0 = k_a t \tag{1a}$$

$$\text{Etherification reaction:} \quad \ln[\mathrm{E}]/[\mathrm{E}]_0 = k_e t \tag{1b}$$

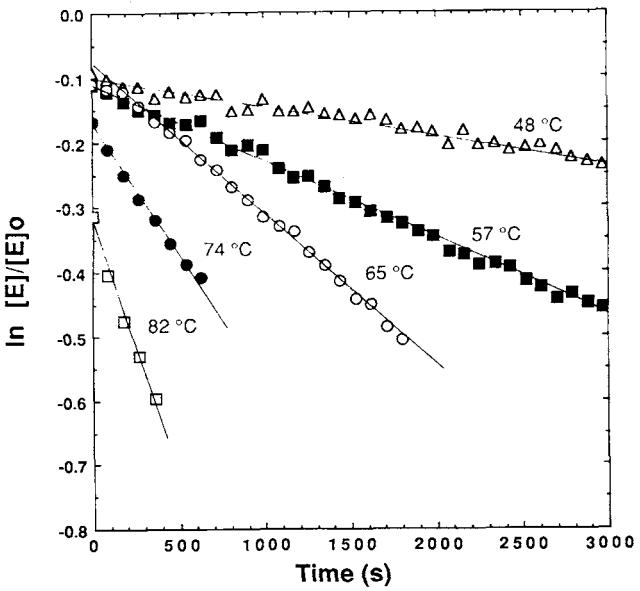

Fig. 5. First-order kinetic analysis of the adduct reactions for the cure of DGEBA with 25.0 mol % EMI-24.

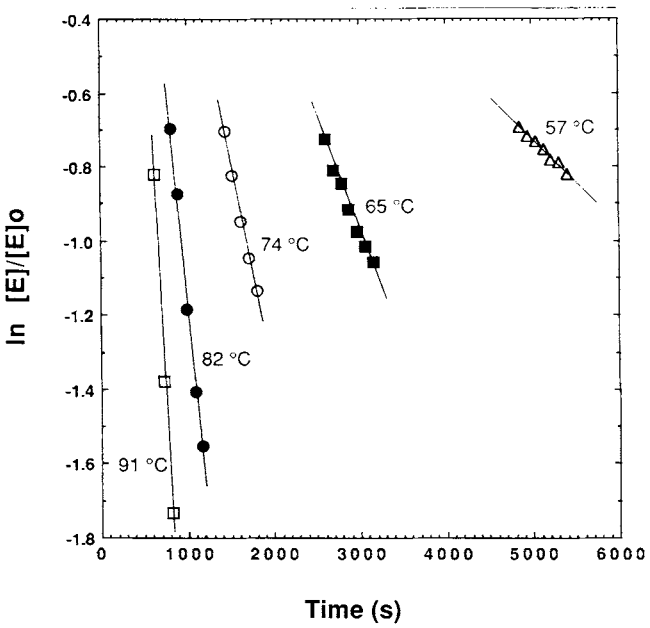

Fig. 6. First-order kinetic analysis of the etherification reaction for the cure of DGEBA with 25.0 mol % EMI-24.

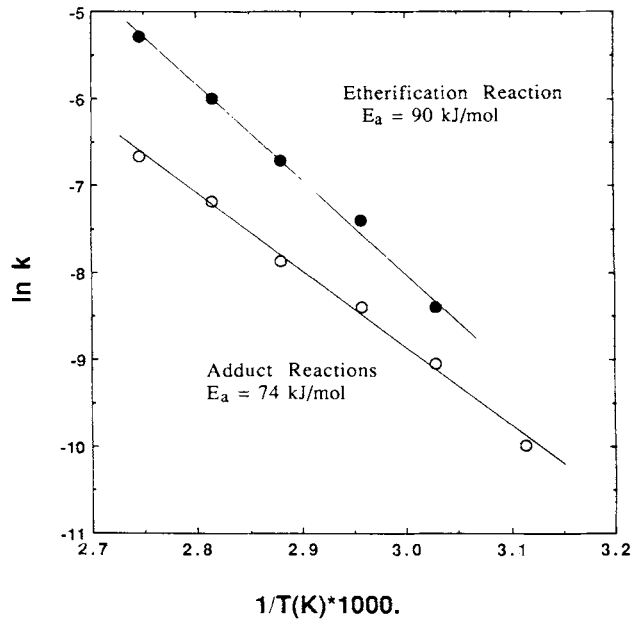

Fig. 7. Arrhenius plot determined from first-order kinetic analysis for the cure of DGEBA with 25.0 mol % EMI-24.

TABLE I
Activation Energies (E_a) and Frequency Factors (A) Determined from First-Order Isothermal FTIR Analysis for DGEBA and PGE Cured with Various Concentrations of EMI-24

Composition	Adduct reactions		Etherification reaction	
	E_a (kJ/mol)	ln A (s^{-1})	E_a (kJ/mol)	ln A (s^{-1})
PGE/100%EMI-24	78	21.3	—	—
PGE/50%EMI-24	78	20.4	—	—
DGEBA/50%EMI-24	77	19.7	—	—
PGE/25%EMI-24	71	16.9	89	24.3
DGEBA/25%EMI-24	74	17.8	90	24.1
DGEBA/10%EMI-24	82	19.3	93	25.5
DGEBA/5%EMI-24	—	—	88	22.0

where [E] is the epoxide concentration at time t, $[E]_0$ is the initial epoxide concentration, and k_a and k_e are the rate constants for the adduct and the etherification reactions, respectively.

The activation energies and frequencies factors were determined from the Arrhenius plots shown in Figure 7. This kinetic analysis was performed for both DGEBA and PGE cured with imidazole concentrations ranging from 5.0 to 100.0 mol %. A summary of the results appears in Table I. The activation energies for the adduct formation reactions vary between 71 and 82 kJ/mol, depending on the imidazole concentration, while the activation energies for the etherification reaction ranged from 88 to 93 kJ/mol.

The rate constants for the adduct and the etherification reactions for DGEBA cured with various concentrations of EMI-24 are shown in Table II. The rate of adduct formation decreases rapidly as the imidazole concentration is lowered. The rate of the adduct formation at 50.0 mol % EMI-24 is approximately three times greater than at 25.0 mol % EMI-24. The rates of the etherification reaction for 10.0 and 25.0 mol % EMI-24 are similar and are about seven to eight times faster than the reaction rate for 5.0 mol % EMI-24. At a constant imidazole concentration, the rate of etherification is always greater than the rate of adduct formation.

TABLE II
Rate Constants k_a and k_e for the Adduct and the Etherification Reactions Determined from Isothermal FTIR Kinetic Analysis

Composition	Adduct reactions $k_a \times 10^3$ (s^{-1})			Etherification reaction $k_e \times 10^3$ (s^{-1})		
	65°C	74°C	82°C	65°C	74°C	82°C
DGEBA/50%EMI-24	0.57	1.05	2.01	—	—	—
DGEBA/25%EMI-24	0.23	0.39	0.76	0.61	1.21	2.49
DGEBA/10%EMI-24	0.07	0.11	0.23	0.43	1.27	2.43
DGEBA/5%EMI-24	—	—	—	—	0.16	0.35

DSC Analysis

In order to determine reaction kinetics by DSC analysis, the amount of heat evolved during a given time period is related to the number of reacting molecules. Both dynamic and isothermal studies were performed to determine the individual kinetics for the adduct and the etherification reactions. The objective of this analysis was to compare the DSC reaction kinetics with the results obtained from the isothermal FTIR analysis and with previous DSC kinetic results obtained for the PGE/EMI-24 adduct formation reactions.[4,13]

Isothermal Studies

The reaction kinetics were determined for DGEBA cured with 50.0, 25.0, and 5.0 mol % EMI-24. At 50.0 mol %, most of the epoxide groups are used to form adducts whereas, at 25.0 and 5.0 mol % EMI-24, there are unreacted epoxide groups remaining after the formation of the adducts and the etherification reaction appears as a second exotherm.

The thermal conversion during the isothermal cure was determined by two different methods. The first method involved multiple peak integrations from a single isothermal experiment to determine the heat of reaction as function of the cure time. Isothermal experiments usually underestimate the heat of the curing reaction because part of the curing reaction is lost while the system is reaching thermal equilibrium. To avoid this problem, the total heat of reaction and the residual heat of reaction, determined from dynamic studies, were used to determine the thermal conversion which is given by

$$\alpha_t = \Delta H_t / \Delta H_{\text{total}} = \left\{\Delta H_{\text{total}} - \Delta H_{t \text{ to } t_f} - \Delta H_{f(\text{res})}\right\} \Big/ \Delta H_{\text{total}} \qquad (2)$$

where α_t is the thermal conversion at time t, ΔH_t is the heat of reaction from the start of the curing reaction to time t, ΔH_{total} is the total heat of reaction determined from multiple dynamic DSC studies, $\Delta H_{t \text{ to } t_f}$ is the heat of reaction from time t to the time at the end of the isothermal cure, t_f, and $\Delta H_{f(\text{res})}$ is the residual heat of reaction determined from a dynamic scan of the sample that was cured to time t_f.

The second method for determining the thermal conversion as a function of cure time involved multiple isothermal experiments. A sample was cured for various times, quenched, and then the residual heat of reaction, ΔH_{res}, was determined from a dynamic scan of the partially cured sample. The thermal conversion could then be determined from

$$\alpha_t = (\Delta H_{\text{total}} - \Delta H_{\text{res}}) / \Delta H_{\text{total}} \qquad (3)$$

The thermal conversions at various isothermal cure temperatures for both the adduct and the etherification reactions were described by first-order rate expressions. The activation energies and the frequency factors determined for DGEBA cured with different concentrations of EMI-24 are listed in Table III. The kinetic values for the adduct formation for DGEBA cured with 50.0 mol % EMI-24 agree with previous kinetic data determined by isothermal

TABLE III
Activation Energies (E_a) and Frequency Factors (A) Determined from Isothermal DSC Results for DGEBA Cured with Various Concentrations of EMI-24

Composition	Adduct reactions		Etherification reaction	
	E_a (kJ/mol)	ln A (s^{-1})	E_a (kJ/mol)	ln A (s^{-1})
DGEBA/50%EMI-24	77	20.0	—	—
DGEBA/25%EMI-24	77	19.5	99	27.7
DGEBA/5%EMI-24	—	—	85	21.8
PGE/50%EMI-24[4]	82	21.7	—	—
PGE/50%EMI-24[13]	84	22.3	—	—

DSC analysis for PGE cured with 50.0 mol % EMI-24.[4,13] The results of these previous studies are also included in Table III.

Dynamic Studies

The dynamic-multiple scan method, in which the variation of the peak exotherm temperature with the heating rate is measured, can be used to analyze curing reactions that exhibit several exotherms. This method is relatively insensitive to baseline problems, solvent effects, secondary reactions, and the degree of cure prior to the experiment.[14] The peak shift method, developed by Ozawa,[15–17] was used to calculate the activation energy for DGEBA cured with various concentrations of EMI-24 ranging from 4.0 to 100.0 mol %. The peak exotherm temperatures were measured for 10 different heating rates varying from 2.5 to 20.0°C/min. The activation energies for the adduct formation reaction determined for a wide range of imidazole concentrations varied from 65 to 71 kJ/mol. These results agree with the previous studies using this method; an activation energy for the adduct formation of 63 kJ/mol was obtained by Grentzer et al.[13] for PGE cured with 50.0 mol % EMI-24. The activation energies determined for the etherification reaction ranged from 66 to 79 kJ/mol. The frequency factors were calculated for each

TABLE IV
Activation Energies (E_a) and Frequency Factors (A) Determined from Dynamic DSC Results Using the Peak Shift Method[15–18] for DGEBA Cured with Various Concentrations of EMI-24

Composition	Adduct reactions		Etherification reaction	
	E_a (kJ/mol)	ln A (s^{-1})	E_a (kJ/mol)	ln A (s^{-1})
DGEBA/100%EMI-24	68	17.3	—	—
DGEBA/50%EMI-24	65	16.1	—	—
DGEBA/25%EMI-24	65	16.3	66	15.6
DGEBA/10%EMI-24	—	—	72	17.3
DGEBA/7%EMI-24	71	17.6	72	17.2
DGEBA/5%EMI-24	—	—	79	19.7
DGEBA/4%EMI-24	71	17.3	—	—
PGE/50%EMI-24[13]	63	—	—	—

heating rate using a relationship developed by Kissinger[18] and were then averaged. A summary of the kinetic results is given in Table IV.

The kinetic results obtained from the isothermal DSC analysis agree with the isothermal FTIR results. The activation energy values for the two methods varied by less than 5% for a given resin composition. Both isothermal methods showed that the reaction rate could be described by first-order rate expressions. The activation energies, determined from dynamic DSC studies, were 10–15% lower for the adduct reaction and 15–25% lower for the etherification reaction than the values obtained from the isothermal studies.

ANALYSIS OF INDUCTION PERIOD

In the previous section, the adduct formation and the etherification reactions were differentiated and the reaction kinetics were determined. From the FTIR results the adduct reaction was shown to approach completion prior to the etherification reaction; however, the rate of the etherification reaction was shown to be much faster than the rate of adduct formation. This anomalous behavior is caused by an adduct induction period that controls the initiation of the etherification reaction. An accurate description of this induction period is required before a kinetic model can be developed for the curing process.

Induction periods in epoxy/imidazole systems have been observed by several workers for a variety of different imidazoles. Ricciardi et al.[8] reported an induction period for PGE cured with 1-methylimidazole, 2-methylimidazole, and 1,2-dimethylimidazole. Jisova[19] observed the same phenomenon for a crosslinking epoxy resin cured with 2-phenylimidazole, 1-butylimidazole, imidazole, and EMI-24. The induction period was shown to be dependent on the reaction temperature and the effectiveness of the catalyst. This phenomenon is not unique to the cure of epoxy/imidazole systems; Tanaka et al.[20] reported a similar induction period for epoxies cured with tertiary amines.

The end of the induction period is characterized by an increase in the rate of epoxide conversion, an increase in the T_g, and the formation of aliphatic ethers. The activation of all the 2 : 1 adducts does not occur simultaneously. As a few activated adducts react with epoxide groups, the thermal energy, which is released, accelerates the activation of the other adducts. The length of the induction period was therefore determined from the change in slope in the epoxide concentration profiles; this change is indicated by the arrows shown in Figure 2.

The induction time was measured for DGEBA and PGE cured with various concentrations of EMI-24; the results are listed in Table V. These results show that the length of the induction period is a strong function of the cure temperature but does not vary significantly with the imidazole concentration and the functionality of epoxy compound. A plot of the log of the induction time (t_{ind}) vs. $1/T$ is shown in Figure 8. An expression for the length of the induction period as a function of the cure temperature, determined by linear regression analysis, is given by

$$t_{ind}\,(\mathrm{s}) = \exp\{[8969/T\,(\mathrm{K})] - 18.74\} \tag{4}$$

This expression is limited only to the curing of epoxy compounds with

TABLE V
Length of the Adduct Induction Period as a Function of the Cure Temperature for Various Epoxy/Imidazole Systems

Composition	Induction time (s)				
	57°C	65°C	74°C	82°C	91°C
DGEBA/25%EMI-24	4520	2090	1110	710	370
DGEBA/10%EMI-24	—	2450	1240	610	320
DGEBA/5%EMI-24	—	—	1310	760	350
PGE/25%EMI-24	4260	2480	1120	640	—

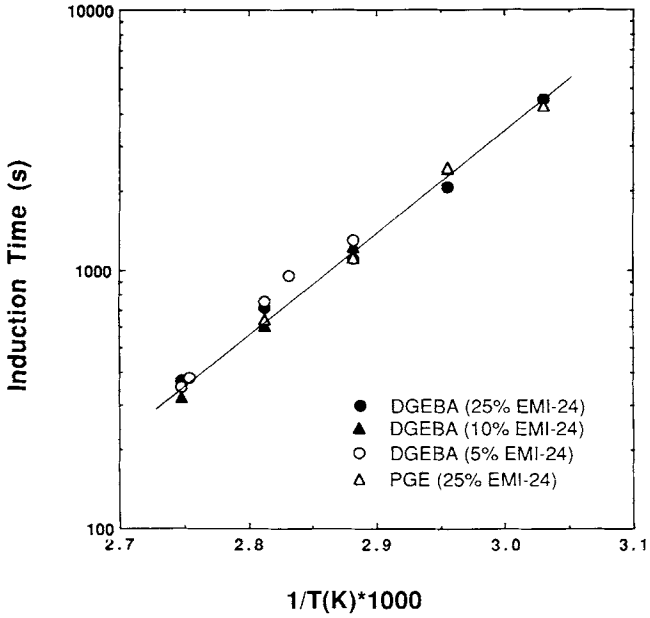

Fig. 8. The length of the induction period as a function of the isothermal reaction temperature for the cure of various epoxide/imidazole systems.

EMI-24. The length of the induction period changes with the imidazole substitution pattern.[8,10,19]

KINETIC MODELING

Based on the previous studies of the curing mechanism,[10,11] a reaction scheme consisting of three competitive series reactions with an adduct activation step can be written to describe the epoxy/imidazole curing process. This reaction scheme is shown below:

Reaction		Rate constant	
1 : 1 adduct formation	$I + E \rightarrow A1$	k_a	(5)
2 : 1 adduct formation	$A1 + E \rightarrow A2$	k_a	(6)
Adduct activation	$A2 \rightarrow A2^*$		(7)
Etherification reaction	$A2^* + E \rightarrow P$	k_e	(8)

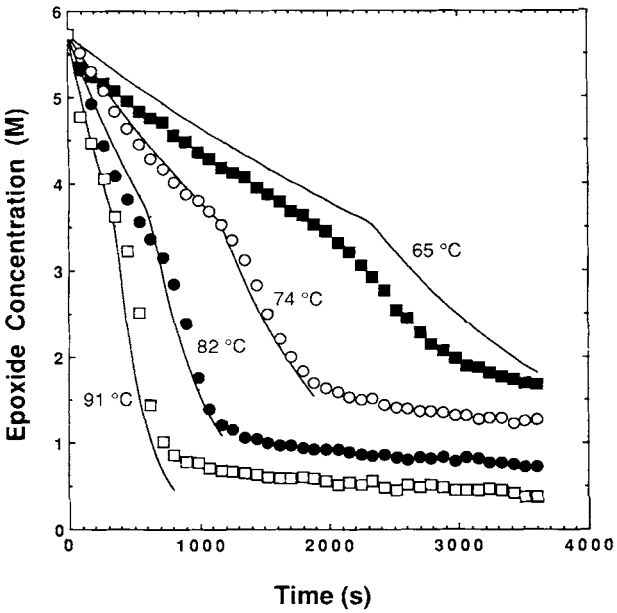

Fig. 9. Comparison of the model results (—) from first-order kinetic analysis with the experimental epoxide concentration profiles for DGEBA cured with 25.0 mol % EMI-24.

where I is a 1-unsubstituted imidazole, E is an unreacted epoxide group, A1 and A2 are the 1 : 1 and 2 : 1 adducts, respectively, A2* is a 2 : 1 adduct with an active alkoxide group that can initiate an etherification reaction, and P is an aliphatic ether group formed from the epoxide homopolymerization reaction.

First-Order Kinetics

The rate of epoxide conversion for both the adduct and etherification reactions are described by first-order kinetics. The initiation of the etherification reaction [eq. (8)] is controlled by the length of the induction period which can be determined from eq. (4). Unlike the 1 : 1 adduct, the activated 2 : 1 adduct is not consumed since A2* represents an alkoxide ion; this ion is continually regenerated during the epoxy anionic polymerization reaction. The first-order rate expressions for the chemical species included in eqs. (5)–(8) were integrated numerically to determine the concentrations of the curing species as a function of the reaction time. The FTIR kinetic parameters listed in Table I were used in the modeling studies.

A comparison of the first-order model predictions with the experimental epoxide concentration profiles for DGEBA cured with 25.0 and 50.0 mol % EMI-24 is shown in Figures 9 and 10. At 25.0 mol % EMI-24, a change in the reaction rate occurs at an epoxide conversion of 40–45%; this change marks the initiation of the etherification reaction. At long times, the sample vitrifies and the reaction rate slows. The first-order kinetic model can also be used to predict the epoxide concentration profiles for the cure of DGEBA with a stoichiometric concentration of EMI-24 (50.0 mol%). In this case, the etherification reaction is suppressed and there is no abrupt change in the epoxide concentration profile.

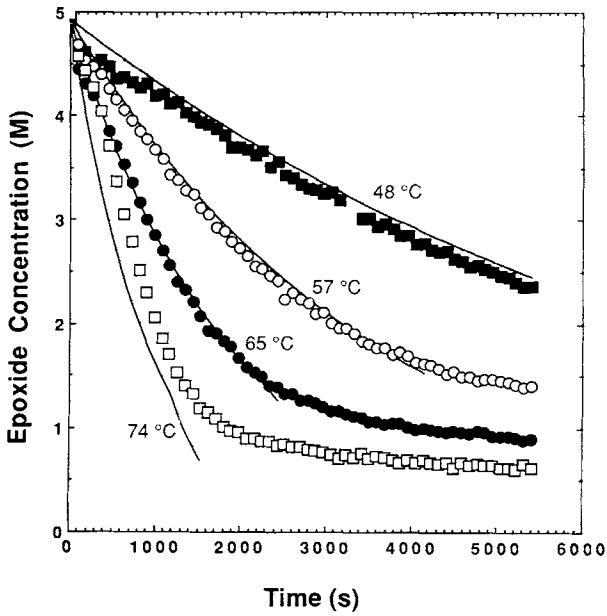

Fig. 10. Comparison of the model results (—) from first-order kinetic analysis with the experimental epoxide concentration profiles for DGEBA cured with 50.0 mol % EMI-24.

Bimolecular Kinetics

Although the rates of the epoxide conversion for the adduct and etherification reactions can be described by first-order epoxy rate expressions, this kinetic scheme does not completely describe the overall curing behavior. In epoxy/imidazole systems, the epoxy is usually added in a large stoichiometric excess and, therefore, the rate of the adduct formation should slow as the imidazole is depleted. Also, the rate of formation of the 2 : 1 adduct (A2) should be dependent on the concentration of the 1 : 1 adduct (A1) as well as the epoxide concentration. These rate dependencies become more important as the imidazole concentration and the cure temperature are lowered.

To obtain a more complete description of the epoxy/imidazole curing process, a bimolecular kinetic scheme which includes the imidazole kinetics was proposed. These rate expressions depend on the epoxide concentration as well as the imidazole and 1 : 1 adduct concentration. This bimolecular reaction scheme is:

$$d[\mathrm{I}]/dt = -k_a'[\mathrm{I}][\mathrm{E}] \tag{9}$$

$$d[\mathrm{E}]/dt = -k_a'[\mathrm{I}][\mathrm{E}] - k_a'[\mathrm{A1}][\mathrm{E}] - k_e[\mathrm{E}] \tag{10}$$

$$d[\mathrm{A1}]/dt = k_a'[\mathrm{I}][\mathrm{E}] - k_a'[\mathrm{A1}][\mathrm{E}] \tag{11}$$

$$d[\mathrm{A2}]/dt = k_a'[\mathrm{A1}][\mathrm{E}] \tag{12}$$

$$d[\mathrm{P}]/dt = 0 \qquad \text{for } t < t_{\mathrm{ind}} \tag{13}$$

$$d[\mathrm{P}]/dt = k_e[\mathrm{E}] \qquad \text{for } t \geq t_{\mathrm{ind}} \tag{14}$$

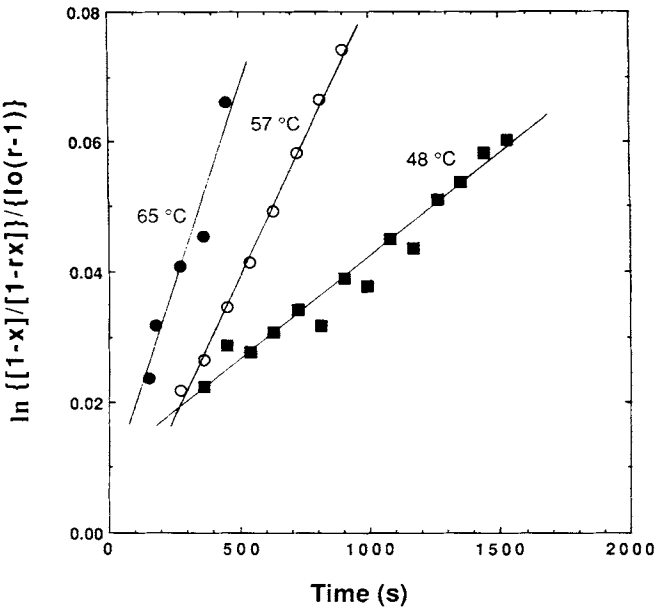

Fig. 11. Bimolecular kinetic analysis for the 1 : 1 adduct formation during the initial stages of the cure of DGEBA with 50.0 mol % EMI-24 ($r = 2$).

where k_a' is the second-order bimolecular rate constant for the adduct formation reactions and k_e is the first-order rate constant for the etherification reaction.

The second-order bimolecular kinetics for the imidazole reaction rate were determined by analyzing the epoxide conversion during the initial stages of the curing reaction when only the 1 : 1 adduct is being formed. The rate expression, given by eq. (9), was rearranged and integrated to give the following relationship:

$$\ln\{[1 - x]/(1 - rx)\}/\{[I_0](r - 1)\} = k_a' t \tag{15}$$

where $[I_0]$ is the initial imidazole concentration, x is the epoxide conversion, and r is the initial stoichiometric ratio of epoxide to imidazole.

The rate constant k_a' can be determined by plotting the left-hand side of eq. (15) as a function of the reaction time. This plot is shown in Figure 11 for DGEBA cured with 50.0 mol % EMI-24. Cure temperatures of less than 75°C were used to decrease the rate of the adduct formation since the formation of the 1 : 1 adduct could not be differentiated from the formation of the 2 : 1 adduct for cure temperatures above 75°C. The second-order rate constants were determined for DGEBA and PGE cured with 50.0 and 25.0 mol % EMI-24. An Arrhenius plot, shown in Figure 12, was used to determine the kinetic parameters. The activation energy and frequency factor were 74 kJ/mol and $9.1 \times 10^7\ M^{-1}\ s^{-1}$. The activation energy value agrees with the values obtained from the first-order kinetic analysis shown in Table I.

The bimolecular rate expressions, eqs. (9)–(14), were integrated as a function of the initial imidazole and epoxy concentrations and the cure tempera-

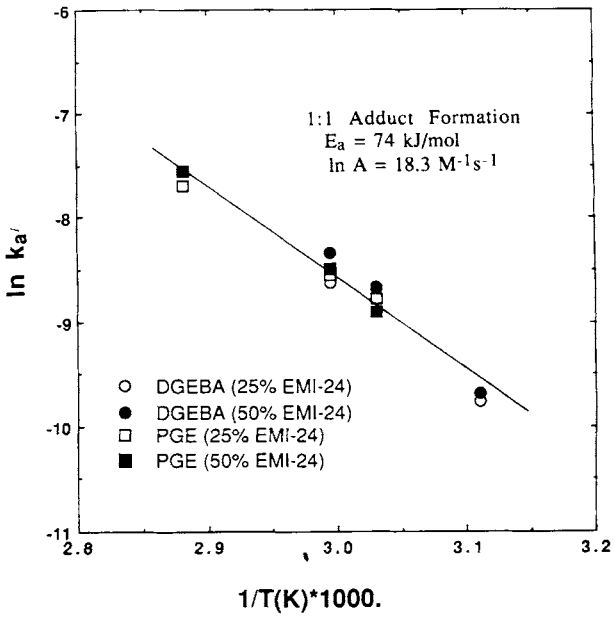

Fig. 12. Arrhenius plot determined from the bimolecular kinetic analysis for the cure of DGEBA and PGE with 50.0 and 25.0 mol % EMI-24.

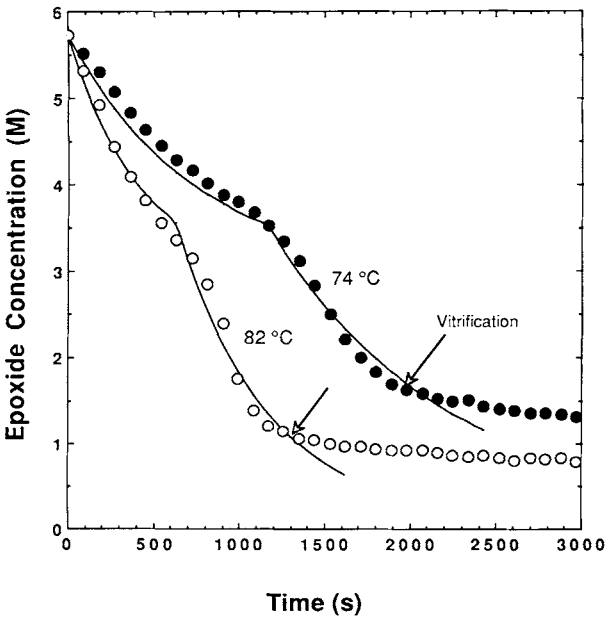

Fig. 13. Comparison of the model results (—) from bimolecular kinetic analysis with the experimental epoxide concentration profiles for DGEBA cured with 25.0 mol % EMI-24.

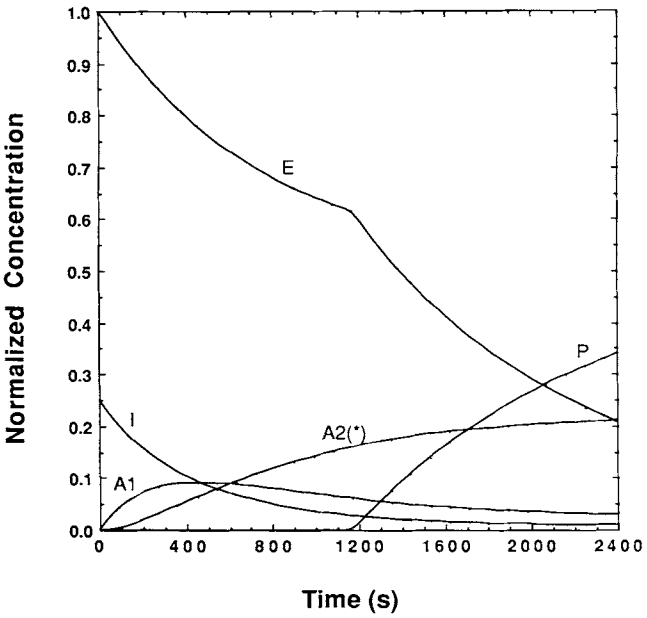

Fig. 14. Model calculations of the component concentrations from bimolecular kinetic analysis for DGEBA cured with 25.0 mol % EMI-24 at 74°C.

ture. The rate constants for the adduct reactions were assumed to be equivalent; however, in the bimolecular model the rates of adduct formation are dependent on the concentrations of both reactants. The activation energies and frequency factors used in the modeling studies for the etherification reaction were taken from Table I.

A comparison of the bimolecular model results with the experimental epoxide concentration profiles is shown in Figure 13 for the cure of DGEBA with 25.0 mol % EMI-24. The model predictions agree well with the FTIR results up to the point of vitrification. While the epoxide profile, determined from the first-order kinetic model, is essentially linear up to the time of the reaction rate change, the rate of the epoxide conversion in the bimolecular model slows as the imidazole and the 1 : 1 adduct become depleted.

Based on the results of the bimolecular modeling, the concentration profiles for the curing species were determined. These profiles for DGEBA cured with 25.0 mol % EMI-24 at 74°C are shown in Figure 14. The concentration of imidazole initially decreases rapidly as the 1 : 1 adduct is formed. Because the etherification reaction is much faster than the adduct formation reactions, the concentration of the 1 : 1 adduct decreases slowly after etherification begins. The 2 : 1 adduct forms slowly and its concentration is still increasing when the etherification reaction begins. This adduct determines the number of alkoxide ions and, therefore, controls the rate of the homopolymerization reaction.

Over a wide range of imidazole concentrations and cure temperatures, the first-order kinetic model gave a better prediction than the bimolecular model for the unreacted epoxide concentration; however, the bimolecular model can be used to predict the concentrations of all the curing species. For network formation modeling studies, the concentrations of the 1 : 1 and 2 : 1 adducts

must be known during the cure. These compounds have different degrees of crosslinking and will have different effects on network properties.

CONCLUSIONS

The reaction kinetics for the epoxy/imidazole adduct reactions and the epoxy homopolymerization reaction were determined from FTIR and DSC studies for PGE and DGEBA cured with a wide range of EMI-24 concentrations. The rates of epoxide conversion for both the adduct and the etherification reactions were described by first-order expressions. The activation energies determined from isothermal FTIR analysis for the adduct reaction ranged from 71 to 82 kJ/mol and the activation energies for the etherification reaction varied from 88 to 93 kJ/mol.

A kinetic model was developed based on the epoxy/imidazole cure chemistry. The model contained second-order bimolecular rate expressions for the formation of the 1 : 1 and 2 : 1 molar adducts, a first-order epoxy rate expression for the etherification reaction, and a relationship for the length of the induction period as a function of the cure temperature. The model was used to predict the concentration of the unreacted epoxide groups as well as the concentrations of the other curing species.

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