Characterization of Imidazole-Cured Epoxy–Phenol Resins

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SYNOPSIS

The physical and chemical properties of the diglycidyl ether of bisphenol A (DGEBA) cured with different concentrations of bisphenol A (BPA) and 2-ethyl-4-methylimidazole (EMI-24) were examined using Fourier transform infrared spectroscopy, differential scanning calorimetry, dynamic mechanical and dielectric analyses, and solvent extraction studies. The effects of the phenol–epoxide and the secondary hydroxyl (R–OH)–epoxide reactions on the network formation process were analyzed using a recursive modeling technique to obtain expressions for the weight-averaged molecular weight, the weight fraction solubles, and the gel point as a function of the extent of cure and the epoxide–phenol reactant ratio. The sol fraction and the gel point predictions from recursive modeling studies of the network formation process agreed with the results obtained from the extraction studies. The results from the network modeling studies were also related to the thermal and rheological properties of the resin during cure.

INTRODUCTION

Epoxy–phenol resins are widely used in the electronics industry as molding and sealing compounds for electronic packaging; however, few published studies on this system are available. These thermosetting resins have a variety of useful properties including excellent insulating characteristics, good adhesive properties, outstanding chemical resistance, retention of properties under severe operating conditions, low moisture absorption, and no reaction by-products that could cause void formation or act as plasticizers.

There are two types of etherification reactions that can occur during the cure of an epoxy–phenol resin system. The first reaction occurs between the phenolic hydroxyl and the epoxide group to form an aromatic ether and a secondary hydroxyl group (R–OH). This secondary hydroxyl group can react with another epoxide group to form an aliphatic ether. The extent of the (R–OH)–epoxide reaction has been shown to be a function of the nature and con-

centration of the catalyst as well as the cure temperature.[1-3]

Initial studies on epoxy–phenol resins cured with imidazoles have indicated that the reaction selectivity is strongly dependent on the imidazole concentration.[4,5] Hale et al.[4] showed that for cresyl glycidyl ether cured with 50 mol % m-cresol and 0.75 wt % 2-methylimidazole at 125°C, the (R–OH)–epoxide reaction was suppressed and the final epoxide conversion was 50%. When the imidazole concentration was raised to 1.5 wt %, the epoxide conversion reached 90%, indicating that the (R–OH)–epoxide reaction was occurring. The results of this study illustrate the complexity of the epoxy–phenol-imidazole curing process and the need to understand the role of the imidazole in the individual curing reactions.

The objectives of this study were threefold. First, the epoxy–phenol cure chemistry was examined and the corresponding cure kinetics were determined. Second, the network formation process was examined by developing a recursive model for predicting the weight-averaged molecular weight, the sol fraction, and the conversion at the gel point as a function of the resin composition. Third, extraction studies were conducted to determine the gel point and the weight fraction solubles during the cure. These re-

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sults were then compared with the values obtained from the network modeling studies.

EXPERIMENTAL

The epoxy resin (X-22), a highly pure form of diglycidyl ether of bisphenol A (DGEBA), was supplied by the Shell Development Company. The epoxide equivalent weight, determined by titration, was 172 g/mol epoxide. The imidazole, 2-ethyl-4-methylimidazole (EMI-24), was obtained from the Chemical Dynamics Corporation with a purity of 99%. The difunctional alcohol, bisphenol A (BPA), was obtained from the Aldrich Chemical Company with a purity of > 99%. Samples with different molar concentrations were prepared by dissolving the resin components in methyl ethyl ketone. The samples were recovered by solvent flashing followed by crystallization. All resin compositions are expressed as mole percent EMI-24 and mole percent BPA. The mole percent EMI-24 designation corresponds to moles of imidazole per 100 mol epoxide groups whereas the BPA concentrations are expressed as moles of phenol groups (Ar-OH) per 100 mol epoxide groups.

Fourier transform infrared spectroscopy (FTIR) studies were conducted using an IBM Instruments IR/32S equipped with a temperature-controlled sample holder that allowed for the *in situ* analysis of the curing reaction. Thin films of the epoxy–phenol–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 secured in the sample holder that had been preheated to the desired isothermal temperature. Spectra were then taken every 90 s for at least 1 h. Peak areas were calculated for the epoxide asymmetric ring stretch at 915 cm^{-1}; the Ar–C–Ar stretch at 1184 cm^{-1} was used as the reference peak.

Both dynamic and isothermal differential scanning calorimetry (DSC) 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 at 10°C/min over a temperature range from 25 to 300°C were used to determine the total heat of reaction. Isothermal DSC studies were performed by rapidly ramping the sample temperature from 0°C to the isothermal temperature, holding for various periods of time, and quenching to −50°C. The sample was then scanned after the initial cure to 300°C at 10°C/min to determine the glass transition temperature 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 T_g; the heat of reaction was calculated from the exotherm area.

The dynamic mechanical and dielectric properties were measured simultaneously by embedding a dielectric sensor into the lower plate of a Rheometrics System Four Rheometer; this arrangement is described in detail by Gotro and Yandrasits.[6] The dynamic mechanical analysis (DMA) was performed using the parallel-plate geometry at 1 Hz, while the dielectric analysis was conducted at frequencies up to 10 kHz using a Micromet Eumetric System II Microdielectrometer.
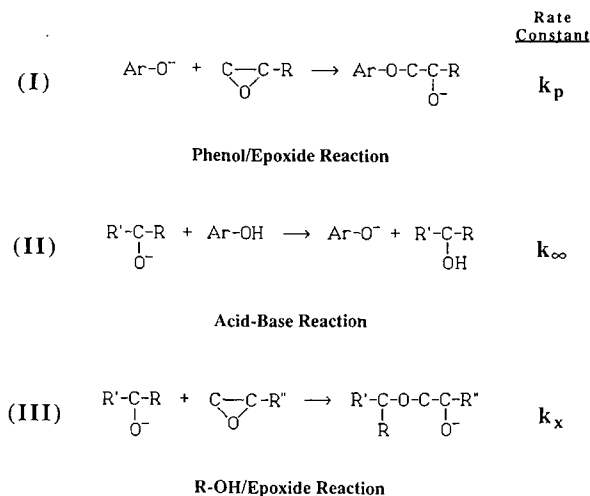
The sol fraction, which is a measure of the amount of soluble material in the network, was determined through extraction experiments. Samples were cured isothermally in the DSC and then removed at various reaction times and quenched in liquid nitrogen. Part of the sample was used for DSC analysis to determine the residual heat of reaction and the sample T_g. The remaining sample was placed in an extraction thimble with tetrahydrofuran. The sol fraction was determined from the difference between the initial and the final weights of the sample.

RESULTS AND DISCUSSION
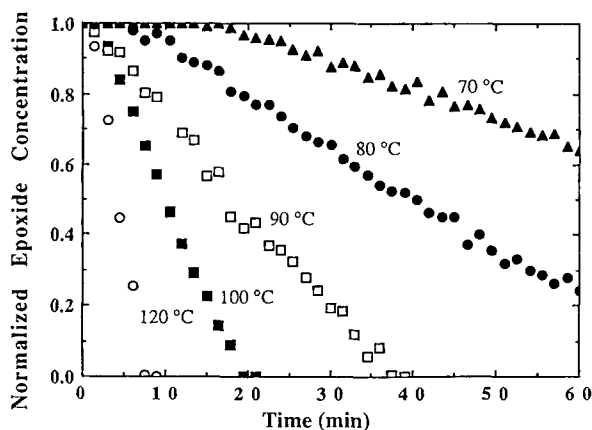
Cure Chemistry and Reaction Kinetics

Studies on the two-component DGEBA/EMI-24 system showed that the formation of epoxide–imidazole adducts was the first step in the curing process.[7-15] The formation of 2 : 1 epoxide–imidazole adducts creates active alkoxide ions that are capable of opening epoxide rings to cause the anionic polymerization of the epoxy resin.[11,14,15] In the presence of unreacted phenolic hydroxyls, this anionic homopolymerization reaction is suppressed since the alkoxide ion is a stronger nucleophile than the phenoxide ion. The acid–base reaction between an alkoxide ion and a phenolic hydroxyl group creates a secondary hydroxyl group and a phenoxide ion,[2,16] as illustrated in Figure 1. The phenoxide ion can react with an epoxide group to form an aromatic ether group and an alkoxide ion. The alkoxide ion then reacts immediately with a phenol group to create a secondary hydroxyl group and another phenoxide ion; hence, the phenoxide ion concentration remains constant during the phenol–epoxide reaction.

At 100.0 mol % BPA, the (R–OH)–epoxide reaction is inhibited and only the phenol–epoxide re-
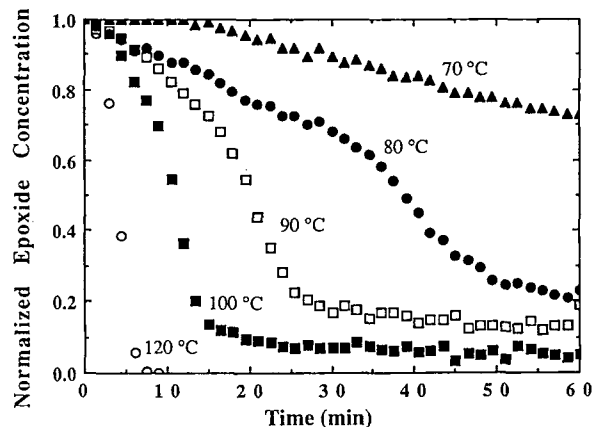
Rate Constant

(I) $Ar-O^- + C\!\!-\!\!C\text{-}R \longrightarrow Ar\text{-}O\text{-}C\text{-}C\text{-}R$ k_p

Phenol/Epoxide Reaction

(II) $R'\text{-}C\text{-}R + Ar\text{-}OH \longrightarrow Ar\text{-}O^- + R'\text{-}C\text{-}R$ k_∞

Acid-Base Reaction

(III) $R'\text{-}C\text{-}R + C\!\!-\!\!C\text{-}R'' \longrightarrow R'\text{-}C\text{-}O\text{-}C\text{-}C\text{-}R''$ k_x

R-OH/Epoxide Reaction

Figure 1   Reaction mechanism of an epoxide group with a phenol group.

Figure 3   Epoxide concentration profiles from FTIR studies of the cure of DGEBA with 25.0 mol % BPA and 2.0 mol % EMI-24 at various reaction temperatures.

action occurs. The epoxide concentration profiles for DGEBA cured with 100.0 mol % BPA at an EMI-24 concentration of 2.0 mol % are shown in Figure 2. Because only the phenol–epoxide reaction is occurring, there is no evidence of aliphatic ethers in the IR spectrum even at high epoxide conversions. At BPA concentrations below 100.0 mol %, there are epoxide groups remaining after the phenol–epoxide reaction. These epoxide groups react with alkoxide groups to form aliphatic ether crosslinks, as shown in Figure 1. The concentration profiles for DGEBA cured with 25.0 mol % BPA and 2.0 mol % EMI-24 are shown in Figure 3. The initiation of the (R–OH)-epoxide reaction at an overall epoxide conversion of approximately 30% is characterized by an increase in the rate of epoxide conversion and

the appearance of the aliphatic ether band in the IR spectrum at wave numbers between 1110 and 1140 cm^{-1}. During the later stages of the cure, the rate of epoxide depletion decreases rapidly when the sample vitrifies.

In order to determine the kinetics of the etherification reactions for the DGEBA–BPA–EMI-24 resin system, a wide range of reactant concentrations was studied. Resin formulations with BPA concentrations ranging from 25.0 to 100.0 mol % and EMI-24 concentrations ranging from 0.5 to 2.0 mol % were tested. The kinetic behavior of the epoxy–phenol–imidazole system is complicated because the rate of epoxide conversion depends on the epoxide, the phenol, the EMI-24, and the R–OH concentrations. To simplify the kinetic analysis, first-order rate expressions were fitted to the FTIR epoxide concentration data in order to determine the rate constants for both the phenol–epoxide and the (R–OH)-epoxide reactions. The results from these analyses were then used to compare the relative rates of the etherification reactions as a function of the resin composition. The first-order rate expressions for these etherification reactions are

Phenol–epoxide reaction:

$$\ln([E]/[E]_0) = k_p t \quad (1)$$

(R–OH)-epoxide reaction:

$$\ln([E]/[E]_0) = k_x t \quad (2)$$

Figure 2   Epoxide concentration profiles from FTIR studies of the cure of DGEBA with 100.0 mol % BPA and 2.0 mol % EMI-24 at various reaction temperatures.

where $[E]$ is the epoxide concentration at time t, $[E]_0$ is the initial epoxide concentration, and k_p and k_x are the rate constants.

Table I   Rate Constants at Various Cure Temperatures for Phenol–Epoxide Reaction Determined from Isothermal FTIR Kinetic Analysis for DGEBA and BPA Cured with EMI-24

Composition of BPA–EMI-24 (mol %)	k_p, $\times 10^3$ (s^{-1})					
	70°C	80°C	90°C	100°C	110°C	120°C
100 : 2	0.17	0.45	0.88	1.95	—	5.80
75 : 2	0.16	0.36	0.78	1.47	—	—
50 : 2	0.12	0.26	0.55	1.00	—	—
25 : 2	0.12	0.21	0.41	0.82	—	—
100 : 1	0.08	0.17	0.44	0.90	1.59	—
75 : 1	0.08	0.17	0.39, 0.39	0.82	1.42	—
50 : 1	0.08	0.16	0.32	0.67	1.33	—
25 : 1	0.06	0.12	0.28	0.57, 0.52	—	—
100 : 0.5	—	0.09	0.24	0.57	1.08	2.15
75 : 0.5	—	0.09	0.22	0.46	0.99	1.86
50 : 0.5	—	0.08	0.17	0.37	0.64	1.20
25 : 0.5	—	0.06	0.13	0.27	0.54	—

The rate constants for the phenol–epoxide reaction were determined for a wide range of resin compositions and cure temperatures; the results are listed in Table I. The rate constants for the phenol–epoxide reaction decrease as the BPA and EMI-24 concentrations are lowered. At an EMI-24 concentration of 2.0 mol % and at a cure temperature of 100°C, the rate constants for the 100.0 mol % BPA sample are 2.5 times greater than for the 25.0 mol % sample. At a BPA concentration of 100.0 mol % and a cure temperature of 100°C, the rate constants for an EMI-24 concentration of 2.0 mol % are three times greater than those for the 0.5 mol % EMI-24 sample. These trends were observed over the entire range of BPA and EMI-24 concentrations studied.

The rate constants for the (R–OH)–epoxide reaction were measured from the initiation of the (R–OH)–epoxide reaction until vitrification. The results

from fitting the first-order rate expressions to the epoxide concentration data are listed in Table II. The rate constants for the (R–OH)–epoxide reaction increase as the BPA concentration is decreased. At a given EMI-24 concentration and cure temperature, the rate constants for the 25.0 mol % BPA sample are two to three times greater than for the 50.0 mol % sample. At a given BPA concentration and cure temperature, the rate constants for the 2.0 mol % EMI-24 samples are four to six times greater than for the 0.5 mol % samples.

For all of the resin compositions tested, the rate constant for the (R–OH)–epoxide reaction is greater than the rate constant for the phenol–epoxide reaction. Because the rate constant for the acid–base reaction between an alkoxide ion and a phenol group, k_α, is much greater than the rate constants for the etherification reactions, the phenol–epoxide and the

Table II   Rate Constants at Various Cure Temperatures for (R–OH)–Epoxide Reaction Determined from Isothermal FTIR Kinetic Analysis for DGEBA and BPA Cured with EMI-24

Composition of BPA–EMI-24 (mol %)	k_x, $\times 10^3$ (s^{-1})					
	70°C	80°C	90°C	100°C	110°C	120°C
50 : 2	—	0.40	0.92	2.16	—	—
25 : 2	—	0.91	2.20	4.49	23.95	—
50 : 1	—	—	0.46	1.03	2.06	—
25 : 1	—	—	1.30	2.95	4.89	—
50 : 0.5	—	—	—	0.47	1.13	1.91
25 : 0.5	—	—	0.38	1.00	1.78	—

(R–OH)–epoxide reactions occur separately since the anion remains as a phenoxide ion until the phenol groups are depleted. Comparison of the results in Tables I and II shows that changing the imidazole concentration has a greater effect on the (R–OH)–epoxide reaction rate than on the phenol–epoxide reaction rate. The differences in the rates of these two etherification reactions depend on the BPA concentration. At high BPA concentrations (75.0–100.0 mol %), the rate difference is 1.5 to 2 times; whereas at low BPA concentrations (25.0 mol %), this difference is four to six times.

The rate constants determined from the isothermal FTIR studies were used to calculate activation energies and frequency factors; the results are summarized in Table III. The activation energies for the phenol–epoxide reaction vary between 68 and 92 kJ/mol while the activation energies for the (R–OH)–epoxide reaction range from 86 to 93 kJ/mol.

Network Modeling

The network formation process was analyzed using the recursive modeling technique developed by Macosko and Miller[17,18] for deriving expressions for the weight-averaged molecular weight (MW_w), the sol fraction, and the gel point as a function of the processing conditions and the resin composition. In the model development, several simplifying assumptions are made. First, only phenolic hydroxyl groups and alkoxide ions or secondary hydroxyl ions are assumed to react with an epoxide group. Second, all of the epoxide, phenol, secondary hydroxyl, and alkoxide ions are assumed to react independently. Finally, intramolecular reactions are not considered. Applying these assumptions and using the results from the kinetic studies, the concentrations of the various reaction products can be determined.[16] Since this reacting system is similar to an epoxy–amine system, the recursive modeling[16] is patterned after the work performed by Bidstrup[19] on the DGEBA–diamino-diphenylsulfone resin system.

The weight-averaged molecular weight is based on the configurational probabilities for an epoxide group. There are five possible configurational probabilities: (1) an epoxide group is unreacted (p_0); (2) an epoxide group has reacted with a phenol group (p_B); (3) an epoxide group has reacted with a phenol group and another epoxide group (p_{AB}); (4) an epoxide group has reacted with an alkoxide ion (p_A); and (5) an epoxide group has reacted with an alkoxide ion and another epoxide group (p_{AA}). Based on the recursive nature of the branching process and the laws of conditional probability, the expected weight attached to each of these configurations can be determined and used to develop an expression for MW_w.[16] The weight-averaged molecular weight is given by

$$MW_W = [n_4 + (2 - n_4)w_E]$$
$$\times \frac{n_1 M_E + n_2[n_3 M_E + M_B]}{1 - n_1 - n_2 n_3}$$
$$+ [n_4(1 - w_E) + w_E]M_E + (1 - w_E)M_B \quad (3)$$

Table III   Activation Energies (E_a) and Frequency Factors (A) Determined from Isothermal FTIR Kinetic Analysis for DGEBA and BPA Cured with EMI-24

Composition of BPA–EMI-24 (mol %)	(Ar–OH)–Epoxide Reaction		(R–OH)–Epoxide Reaction	
	E_a (kJ/mol)	ln A (s⁻¹)	E_a (kJ/mol)	ln A (s⁻¹)
100 : 2	79.1	19.1	—	—
75 : 2	79.5	19.1	—	—
50 : 2	74.9	17.2	92.9	23.7
25 : 2	68.2	14.8	87.4	22.8
100 : 1	82.4	19.5	—	—
75 : 1	80.3	18.7	—	—
50 : 1	78.2	17.8	86.6	21.1
25 : 1	78.7	17.8	92.5	23.9
100 : 0.5	91.6	21.9	—	—
75 : 0.5	87.4	20.6	—	—
50 : 0.5	79.1	17.6	85.8	20.1
25 : 0.5	77.4	18.1	90.0	22.0

and

$$n_1 = p_A + 2p_{AA} + p_{AB} + \frac{p_{AA}}{p_{AB}} (p_A + p_{AA})$$

$$+ \frac{p_{AA}}{p_A} (p_{AB} + p_{AA}) \quad (4)$$

$$n_2 = p_A + p_{AA} + p_{AB} + p_B \quad (5)$$

$$n_3 = (\mu - 1)\left[\frac{p_{AB}}{p_B + p_{AB}}\left(1 + \frac{p_{AA}}{p_A}\right) + 1\right] \quad (6)$$

$$n_4 = (p_{B,1} + 2p_{B,2}) \frac{n_3}{\mu - 1} \quad (7)$$

$$\mu = \frac{p_{B,1} + 4p_{B,2}}{p_{B,1} + 2p_{B,2}} \quad (8)$$

Here, $p_{B,1}$ is the fraction of BPA monomers with only one reacted site; $p_{B,2}$ is the fraction of BPA monomers that are completely reacted; w_E and w_P are the epoxide and the phenol weight fractions; M_E and M_B are the molecular weights of the DGEBA and the BPA monomers; n_1, n_2, n_3, n_4 are variables used to simplify the notation; and μ is the weight-averaged extent of reaction.

The gel point for a stepwise polymerization process can be defined as the point where the weight-averaged molecular weight diverges to infinity.[17] Examination of Eq. (3) shows that this divergence occurs when

$$n_1 + n_2 n_3 = 1 \quad (9)$$

The configurational probabilities for the epoxy and the phenol compounds as a function of the extent of cure and the stoichiometric reactant ratio can be determined by integrating the rate expressions for the individual curing reactions.[16] The theoretical molecular weight curves determined from Eq. (3) for DGEBA and 2.0 mol % EMI-24 cured with various concentrations of BPA are shown in Figure 4. The weight-averaged molecular weight increases gradually during the phenol–epoxide reaction and then increases rapidly after the (R–OH)–epoxide reaction is initiated. As the BPA concentration is increased, the weight-averaged molecular weight at a given conversion decreases. Because the phenol–epoxide reaction is a chain lengthening process, the molecular weight does not diverge until the chain branching process occurs. At a BPA concentration of 100.0 mol %, there are enough phenol groups to react with every epoxide group to form a linear copolymer, but for this resin system, the ep-
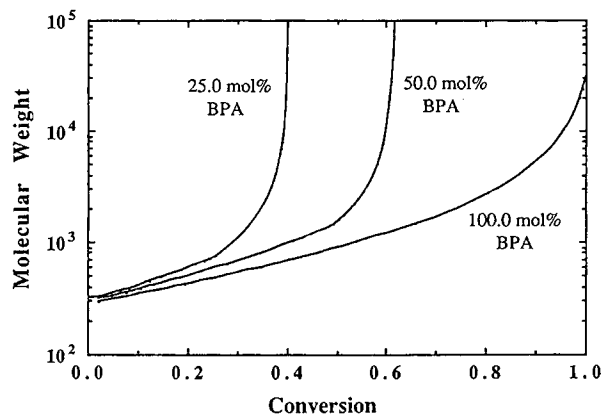
Figure 4   Weight-averaged molecular weight curves as a function of the epoxide conversion predicted from recursive modeling [Eq. (3)] for DGEBA–BPA systems cured with 2.0 mol % EMI-24.

oxide–imidazole adduct formation process consumes epoxide groups[14-16] and alters the stoichiometry. When the resin system is deficient in phenol groups, the molecular weight diverges to infinity as the (R–OH)–epoxide reaction crosslinks the resin. At 25.0 mol % BPA, the conversion at the gel point is 40%, whereas at 50.0 mol % BPA the conversion at the gel point is 60%.

Physical Properties

Thermal Properties

For DGEBA cured with 100.0 mol % BPA at 120°C, the DSC thermogram, shown in Figure 5, exhibits only a single exothermic peak. As shown in Figure 5, the T_g of the resin rises gradually throughout the reaction. For this BPA concentration, there are enough phenol groups to react with every epoxide group to form linear aromatic ether chains with secondary hydroxyl groups.

As the BPA concentration is lowered to 50.0 mol %, there are unreacted epoxide groups available for the (R–OH)–epoxide or crosslinking reaction. At 50.0 mol % BPA, the DSC thermogram at 120°C, shown in Figure 6, exhibits two exothermic peaks. Based on the FTIR studies, the initial peak can be attributed to the phenol–epoxide reaction; this reaction is characterized by a gradual rise in T_g. At a cure time of approximately 7–8 min, a second exothermic peak is observed and the T_g rises sharply. This peak corresponds to the (R–OH)–epoxide reaction that crosslinks the resin. The second peak has a higher heat flow, indicating that the reaction of the alkoxide ion with an epoxide group has a faster rate of reaction than the (Ar–OH)–epoxide reaction.
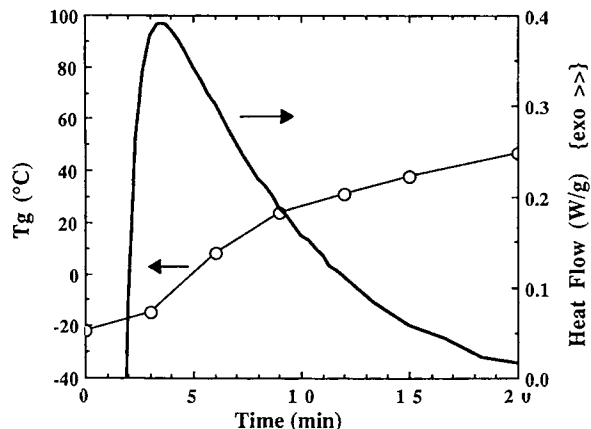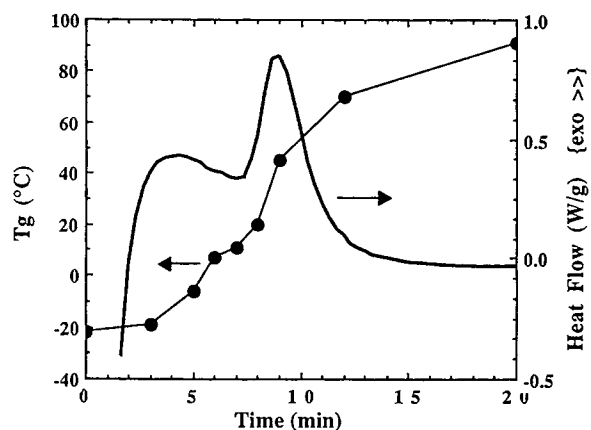
Figure 5 Heat flow and T_g as a function of the reaction time for the cure of DGEBA and 100.0 mol % BPA with 2.0 mol % EMI-24 at 120°C.

The faster reaction, however, cannot occur until the phenol concentration is almost depleted.

Extraction Studies

The experimental sol fraction values as a function of the degree of cure are shown in Figure 7. The amount of soluble material present during the cure is a strong function of the BPA concentration. At 100.0 mol % BPA, the chain branching reaction is suppressed and only soluble linear aromatic poly-ethers are formed. Throughout the curing process, the sol fraction remains near unity, indicating that only linear chains are forming and that this system does not gel. Although the sol fraction values are slightly less than unity, no gelled material was observed or could be isolated after the solvent extraction.

Figure 6 Heat flow and T_g as a function of the reaction time for the cure of DGEBA and 50.0 mol % BPA with 2.0 mol % EMI-24 at 120°C.
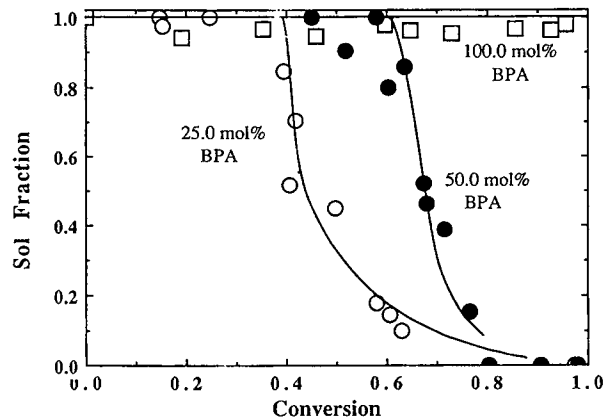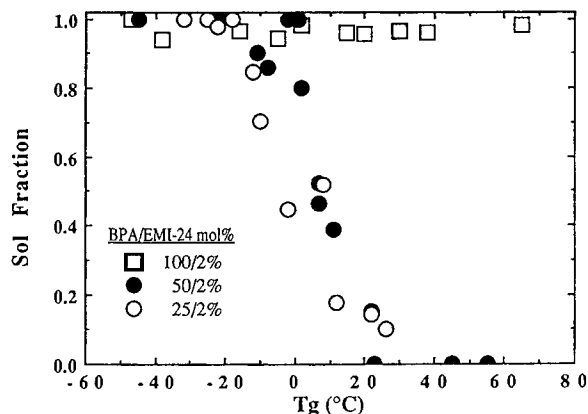

Figure 7 Sol fraction as a function of conversion for DGEBA/2.0 mol % EMI-24 cured with various concentrations of BPA. (The solid lines are the results from the network modeling studies.)

For BPA-deficient systems, the (R–OH)–epoxide reaction crosslinks the resin. Soluble molecules react with the insoluble network, causing the sol fraction to decrease. The experimental sol fraction data for 50.0 and 25.0 mol % BPA are shown in Figure 7. The sol fraction is near unity during the phenol-epoxide reaction and then decreases rapidly during the initial stages of the (R–OH)–epoxide reaction. The incipient formation of an infinite network occurs at an overall conversion of 40% for the 25.0 mol % BPA sample and at a conversion of 60% for the 50.0 mol % BPA sample.
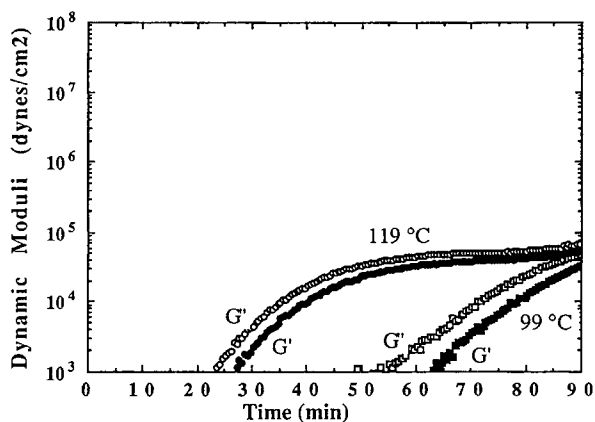
The sol fraction at a given epoxide conversion can also be determined using the recursive modeling technique by calculating the probability that a selected epoxide group is attached to a finite chain.[16,18,19] A molecule is part of the sol if all of its ends or arms are attached to parts of finite chains. Based on the finite-chain probability, the weight fraction solubles can be calculated as a function of the epoxide conversion and the resin composition. The network modeling results, which are also shown in Figure 7, agree with the experimental values for all of the BPA concentrations tested.

The network formation process for the epoxy-phenol–imidazole is dependent on the BPA concentration. This concentration dependence can be related to the network formation process by plotting the sol fraction against the T_g of the sample; this plot is shown in Figure 8. For the 100.0 mol % BPA sample, the sol fraction remains near unity as the T_g increases to over 60°C. The 50.0 and 25.0 mol % BPA samples show a rapid decrease in the sol fraction at glass transition temperatures between −15 and 30°C. Both BPA-deficient samples are com-
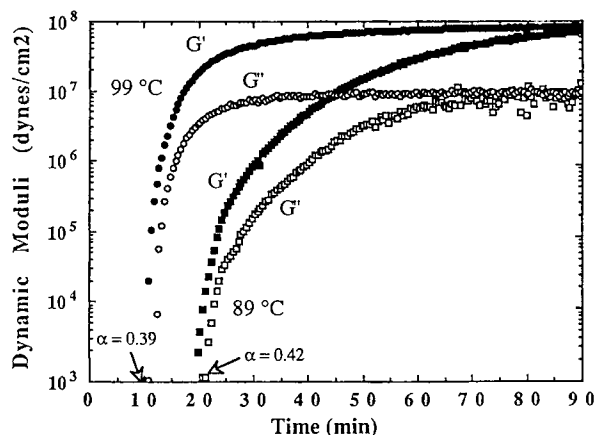
Figure 8 Sol fraction as a function of the sample T_g for DGEBA/2.0 mol % EMI-24 cured with different concentrations of BPA.

Figure 10 Dynamic shear moduli at 1 Hz as a function of reaction time for the isothermal cure of DGEBA with 25.0 mol % BPA and 2.0 mol % EMI-24. (The conversion at crossover, α, was determined from DSC studies.)

pletely gelled at a T_g of 20–30°C although the ultimate glass transition temperatures for these samples are greater than 100°C. For the 100.0 mol % BPA sample, linear polyethers are created and both high T_g and high sol fraction values are obtained. For the BPA-deficient systems, however, the molecular weight achieved by the phenol–epoxide reaction is much less than that obtained for the stoichiometrically balanced systems, as illustrated by the molecular weight curves shown in Figure 4; therefore, the T_g prior to the initiation of the chain branching reaction is only −20 to 0°C. Once the (R–OH)-epoxide reaction is initiated, the resin crosslinks and the sol fraction drops rapidly. Thus, for the BPA-deficient DGEBA–EMI-24 resin systems, T_g values of 60–80°C, which are typical values for "B-staged" materials, cannot be obtained without curing past the gel point.
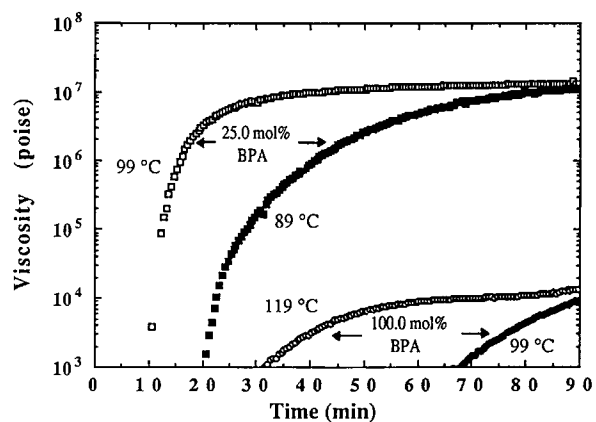
Dielectric and Dynamic Mechanical Properties

To determine if the incipient formation of an insoluble network corresponds to the dynamic moduli crossover for this resin system, dynamic mechanical studies were performed. The dynamic shear moduli at 1 Hz for DGEBA/2.0 mol % EMI-24 cured with 100.0 and 25.0 mol % BPA are shown in Figures 9 and 10; the corresponding viscosity profiles are shown in Figure 11. For the 100.0 mol % BPA, the loss modulus G'' is greater than the storage modulus G' indicating that the viscous component of the resin is dominating. This rheological behavior is consistent with the proposed curing mechanism. Because the 100.0 mol % BPA sample does not crosslink, the viscosity remains low during most of the curing reaction and exceeds 10^3 P only at long cure times.

Figure 9 Dynamic shear moduli at 1 Hz as a function of reaction time for the isothermal cure of DGEBA with 100.0 mol % BPA and 2.0 mol % EMI-24.

Figure 11 Complex viscosity at 1 Hz as a function of reaction time for the isothermal cure of DGEBA/2.0 mol % EMI-24 with 100.0 and 50.0 mol % BPA.
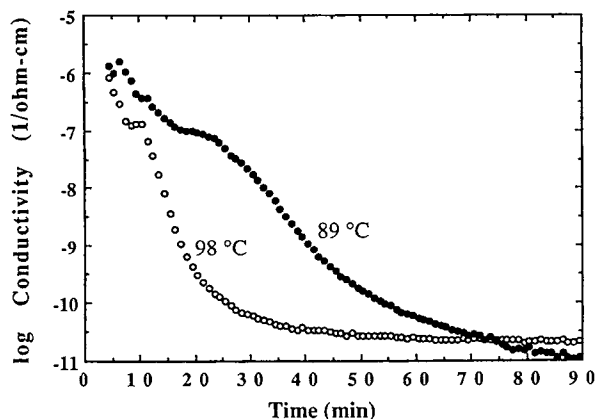
Figure 12 Ionic conductivity as a function of reaction time for the isothermal cure of DGEBA with 25.0 mol % BPA and 2.0 mol % EMI-24.

This increase can be attributed to the formation of high molecular weight chains that are created as the conversion approaches unity.

At 25.0 mol % BPA, the loss and storage moduli increase rapidly during the (R–OH)–epoxide reaction. As the resin cures, the storage modulus exceeds the loss modulus since the system is highly cross-linked. For this resin composition, the dynamic moduli change by several orders of magnitude during a cure time of 2–3 min. This increase in the moduli corresponds to a rapid increase in the viscosity. During the initial stages of the cure, the phenol–epoxide reaction is the major reaction, and therefore, the viscosity remains below 10^3 P.

The ionic conductivity, which depends on the segmental mobility of the polymer chains, was monitored for DGEBA/2.0 mol % EMI-24 samples cured with 25.0 mol % BPA; the results of these studies are shown in Figure 12. As the resin cures, the molecular weight increases, resulting in an increase in the viscosity. This increase in the viscosity causes a decrease in the chain mobility and the ion move-

ment. For the BPA-deficient resin system, the ionic conductivity profiles exhibit two different regions. The first region occurs during the initial stages of the cure. This region is characterized by a decrease in the ionic conductivity and a low viscosity. In the second region, the decrease in the ionic conductivity corresponds to a rapid rise in the viscosity as the resin crosslinks.

Gel Point

In the BPA-deficient epoxy–imidazole systems, the resin will crosslink when the phenol concentration approaches zero. In the early stages of the crosslinking process, the structural and the rheological properties change rapidly as the resin gels. A comparison of the various experimental methods for determining the gel point is given in Table IV along with the theoretical predictions determined from the network modeling studies. For the 25.0 mol % BPA sample, the sol fraction decrease, the moduli crossover, and the viscosity increase occur at an overall epoxide conversion of approximately 40%. The experimental results agree with the theoretical predictions calculated from Eq. (9). For this stepwise polymerization process, the initiation of gel formation and the moduli crossover occur at the gel point; this result agrees with the previous studies on resins cured with an excess of crosslinker.[19–24]

CONCLUSIONS

The chemical and physical properties were examined for a variety of DGEBA–BPA–EMI-24 resin compositions. In BPA-deficient systems, the chain branching reaction occurs when the phenolic hydroxyl groups are depleted. Hence, the final T_g of the resin system increases as the BPA concentration is decreased since more epoxide groups are available for crosslinking. At 100.0 mol % BPA, there are

Table IV Comparison of Experimental and Theoretical Results of Physical Properties of DGEBA Cured with BPA and 2.0 mol % EMI-24

	Conversion (%)	
	25.0 mol % BPA	50.0 mol % BPA
Experimental		
Sol fraction decrease	35–40	60
Moduli crossover ($G' = G''$)	40–44	—
Viscosity increase	38–42	—
Theoretical : Conversion at the gel point [from eq. (9)]	41	61

enough phenolic hydroxyl groups to react with every epoxide group. For this concentration, the chain branching reaction is suppressed and only linear aromatic polyethers are formed. These linear chains are soluble and exhibit a viscosity of less than 10^3 P until the final stages of the curing process.

At 25.0 and 50.0 mol % BPA, the (R–OH)-epoxide reaction causes the resin to gel. The sol fraction is unity during the phenol–epoxide reaction and decreases rapidly during the initial stages of the (R–OH)-epoxide reaction. The sol fraction and gel point predictions from the network modeling studies agree with the experimental extraction results for DGEBA/2.0 mol % EMI-24 cured with 50.0 and 25.0 mol % BPA. In the BPA-deficient systems, the storage and the loss moduli increase rapidly as the resin gels. This increase corresponds to a rapid rise in the viscosity and a sharp decrease in the ionic conductivity. The epoxide conversion at the dynamic moduli crossover agrees with the gel point conversion values determined from the theoretical modeling studies and from the extraction experiments.

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