(8) Jin, J.-I.; Choi, E.-J.; Ryu, S.-C.; Lenz, R. W. *Polym. J. (Tokyo)* **1986**, *18*, 63.
(9) Ober, C. K.; Jin, J.-I.; Lenz, R. W. *Adv. Polym. Sci.* **1984**, *59*, 103.
(10) Lenz, R. W.; Jin, J.-I. *Macromolecules* **1981**, *14*, 1405.
(11) Luise, R. R. U.S. Patent 4 183 895, 1980.
(12) Chivers, R. A.; Blackwell, J. *Polymer* **1985**, *26*, 997.
(13) Blackwell, J.; Cheng, H.-M.; Biswas, A. *Macromolecules* **1988**, *21*, 39.
(14) Calundann, G. W. U.S. Patent 4 184 996, 1980.
(15) Inoue, T.; Okamoto, M.; Hirai, T. *Kobunshi Ronbunshu* **1986**, *43*, 253.

Curing Mechanism and Thermal Properties of Epoxy–Imidazole Systems

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ABSTRACT: The role of imidazoles in the curing of epoxy resins and their effects on the thermal properties of the network were investigated. Fourier transform infrared spectroscopy and differential scanning calorimetry were used to identify and analyze the individual reactions occurring during the cure of the diglycidyl ether of bisphenol A with various 1-unsubstituted imidazoles (2-ethyl-4-methylimidazole and imidazole) and 1-substituted imidazoles (1,2-dimethylimidazole and 1-methylimidazole). Two types of etherification reactions were found to occur in 1-unsubstituted imidazoles. These etherification reactions, which occur at imidazole concentrations of 25.0 mol % or less, are characterized by a rapid increase in the glass transition temperature. The curing mechanism and the glass transition temperature were shown to be strongly dependent on the concentration and on the reactivity of the imidazole.

Introduction

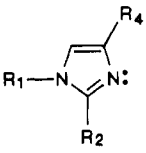
Imidazoles are used as hardeners in a variety of commercial epoxy resin systems. They are added to epoxy–anhydride systems to initiate the esterification reaction and to epoxy–cresol systems to catalyze selectively the epoxy–phenolic hydroxyl reaction. Imidazoles also catalyze the homopolymerization of epoxy compounds. The cured product exhibits excellent chemical stability and high heat resistance and, consequently, is used in the electronics industry as a molding and sealing material.[1] However, despite the widespread commercial use of imidazoles, little is known about their role in the curing process.

In previous work[2-8] on epoxy/imidazole systems, the reaction between phenyl glycidyl ether (PGE) and imidazoles was investigated. The formation of epoxy/imidazole adducts was shown to be the first step in the curing process. It was proposed that both nitrogens were involved in forming adducts; consequently, the imidazole became permanently incorporated into the polymer network.[2,3] Barton and Shepard[3] and Dearlove[4] concluded that the formation of both 1:1 and 2:1 epoxy/imidazole adducts resulted from the opening of the epoxide ring by basic "pyridine-type" nitrogens. The 2:1 adduct, which contains the nucleophilic alkoxide ion, was believed to be the catalyst that initiated the polymerization process.

Considerable research has been conducted on the adduct reaction between PGE and various imidazoles which occurs at high catalyst concentrations; however, the etherification reaction that occurs at low catalyst concentrations has not been extensively explored. These etherification reactions cross-link the epoxy resins and determine the final properties of the network. Initial studies[5,9] on a cross-linking epoxy resin cured at low imidazole concentrations, specifically the diglycidyl ether of the bisphenol A (DGEBA)/2-ethyl-4-methylimidazole (EMI-24) system, revealed a complex curing mechanism. Figure 1 shows the proposed reaction mechanism for DGEBA based on previous PGE adduct reaction studies.[3] There are four possible reactions: two adduct reactions and two etherification reactions.

The objective of this work was to identify the different reactions occurring in DGEBA/imidazole systems and to analyze their effect on the thermal properties of the network. Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were used to monitor the curing reactions and to evaluate the resin properties during the cure. Four model imidazoles with different reactivities and selectivities were used to differentiate the curing reactions.

Table I
Chemical Structure of Imidazoles Used to Cure DGEBA



	designation	R_1	R_2	R_4
2-ethyl-4-methylimidazole	EMI-24	H	C_2H_5	CH_3
1,2-dimethylimidazole	DMI-12	CH_3	CH_3	H
1-methylimidazole	MI-1	CH_3	H	H
imidazole	IMDZ	H	H	H

Experimental Section

High-purity DGEBA (X-22) was supplied by the Shell Development Co. The epoxide equivalent weight, determined by titration, was 170 g/mol epoxide. The imidazoles, with purities ranging from 98 to 99%, were obtained from Chemical Dynamics Corporation. The four imidazoles used in this study are shown in Table I. Samples with different imidazole concentrations were prepared by dissolving both components in methyl ethyl ketone (MEK). The homogeneous sample was recovered by solvent flashing followed by crystallization.

Isothermal and temperature ramp studies were performed using a Mettler DSC-30 equipped with a low-temperature cell. Isothermal studies were performed by rapidly ramping (100 °C/min) the sample from 0 °C to the isothermal temperature, holding for various periods of time, and quenching to −50 °C. The sample was then scanned to 300 °C at 10 °C/min to determine the glass transition temperature (T_g) and the residual heat of reaction; the conversion was calculated by assuming that all the reactions have similar heats of reaction. Temperature ramp (dynamic) studies were performed at various heating rates and over a temperature range of 0 to 300 °C. The temperature corresponding to the onset of the endothermic deflection of the base line was taken to be

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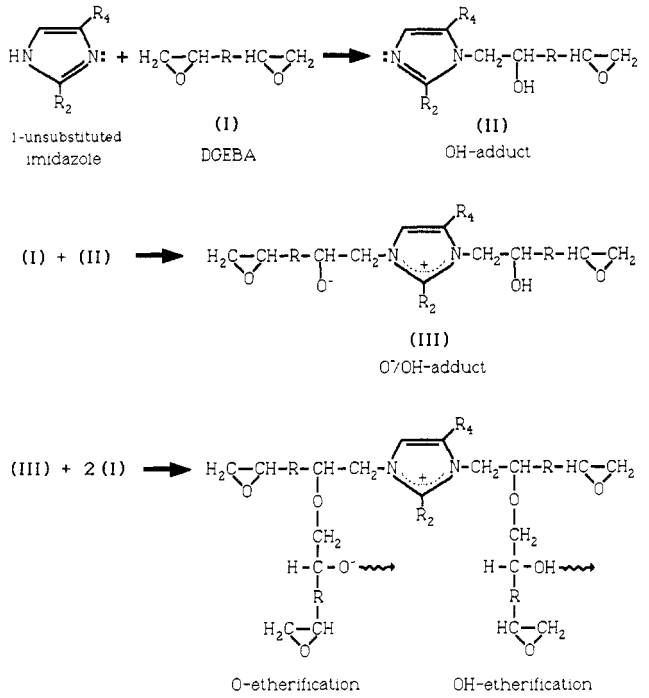

Figure 1. Proposed reaction mechanism for the curing of a diepoxide with a 1-unsubstituted imidazole.

the T_g; the heat of reaction was calculated from the exotherm area. The total heat of reaction was determined from dynamic experiments performed at various heating rates.

FTIR studies were performed by 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 DGEBA/imidazole system were prepared by solvent casting with MEK 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 in the 1-unsubstituted imidazoles between 3400 and 3200 cm^{-1}. The Ar–C–Ar stretch at 1184 cm^{-1} was used as the reference peak.

Results and Discussion

The proposed reaction mechanism for the DGEBA/imidazole system consists of two adduct and two etherification reactions, as shown in Figure 1. The reaction of the imidazole with an epoxide group forms the 1:1 molar adduct (OH adduct) which contains a hydroxyl group resulting from a proton rearrangement. The OH adduct can react with another epoxide ring to form the 2:1 molar adduct (O^-/OH adduct) with a highly reactive alkoxide ion. The reaction of additional epoxide groups with the O^-/OH adduct causes chain growth by two different etherification reactions: O-etherification and OH-etherification. These etherification reactions cross-link the resin and determine the final properties of the network.

Dynamic and isothermal studies, at various imidazole concentrations ranging from 0.5 to 100.0 mol % (moles of imidazole per 100 moles of epoxide groups), were used to separate and to identify the different curing reactions. Previous work[9] showed that the adduct formation was necessary prior to the etherification reaction. Thus, high imidazole concentrations were used to study the adduct formation by suppressing the etherification reactions; low imidazole concentrations were used to analyze different etherification reactions. Although the majority of these curing studies were performed with EMI-24, the number of reactions occurring in the curing process was reduced

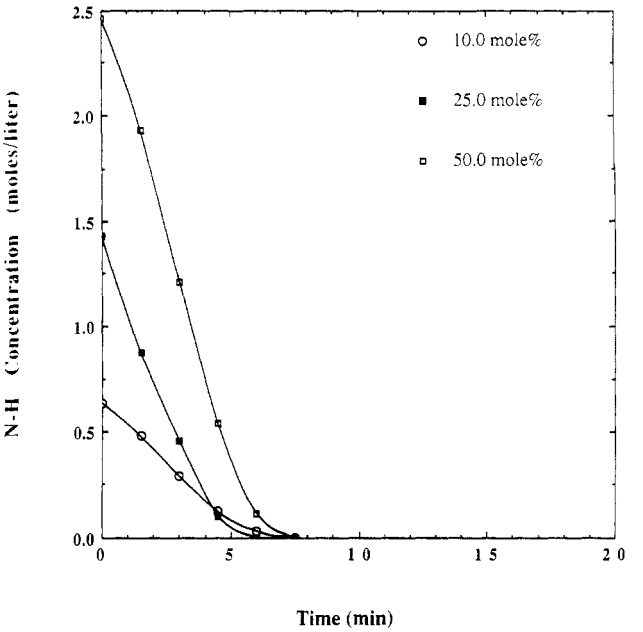

Figure 2. N–H concentration profile from isothermal FTIR analysis for the cure of DGEBA with various concentrations of EMI-24 at 80 °C.

by using 1-substituted imidazoles, DMI-12 and MI-1. Because no hydrogen migration is possible for DMI-12 and MI-1, only the 1:1 adduct (O^- adduct) can be formed; consequently, only the O-etherification reaction is possible. The analyses of the individual curing reactions are discussed below.

Adduct Formation. The first step in the curing process for the DGEBA/EMI-24 system is the nucleophilic attack by the 3-N of the imidazole to open the epoxide ring. An OH adduct is formed by the rearrangement of the zwitterion intermediate through a proton transfer. Farkas and Strohm[2] assumed that the hydrogen on the secondary nitrogen (1-N) reacted with the epoxide ring in a manner similar to an amine curing agent. This theory was subsequently revised when further studies revealed that pyrrole has no activity as an epoxy curing agent[4] and that the 1:1 and 2:1 molar adducts have similar rates of formation.[3] These results imply that the same functionality, the "pyridine-type" nitrogen, is involved in both adduct reactions.

The formation of the OH adduct occurs only in 1-unsubstituted imidazoles such as EMI-24 and IMDZ. The hydrogen migration can be used to track the formation of the OH adduct by use of FTIR to monitor the disappearance of the N–H stretch. Figure 2 shows the N–H concentration profile for DGEBA cured with 50.0, 25.0, and 10.0 mol % EMI-24 at 80 °C. The N–H stretch vibration disappears within the first 10 min of the cure. In the DSC isothermal trace at 80 °C, shown in Figure 3, the OH-adduct reaction appears as part of the first exothermic peak; this peak decreases during the first 10 min of the cure and also decreases as the EMI-24 concentration is lowered. In the dynamic DSC traces, the OH-adduct reaction appears at low EMI-24 concentrations as a shoulder on the main exotherm. This shoulder occurs between 110 and 120 °C in the dynamic traces for the 7.0, 4.0, and 3.0 mol % EMI-24 samples shown in Figure 4. In the 5.0 mol % IMDZ dynamic trace, shown in Figure 5, the OH-adduct reaction appears as a distinct low temperature peak. The heat of reaction for OH-adduct peak is approximately 5% of the total heat of the curing reaction.

The formation of the zwitterion occurs in all of the model imidazoles but on different nitrogen functionalities

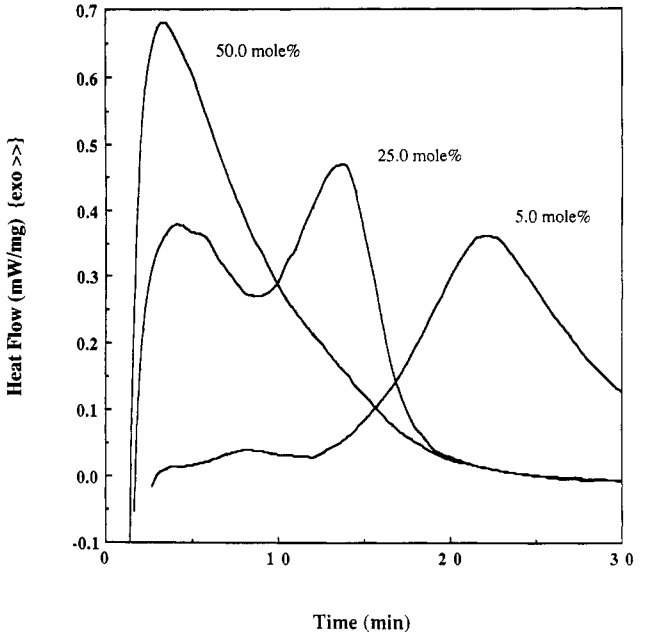

Figure 3. Isothermal DSC thermogram at 80 °C for the cure of DGEBA with various concentrations of EMI-24.

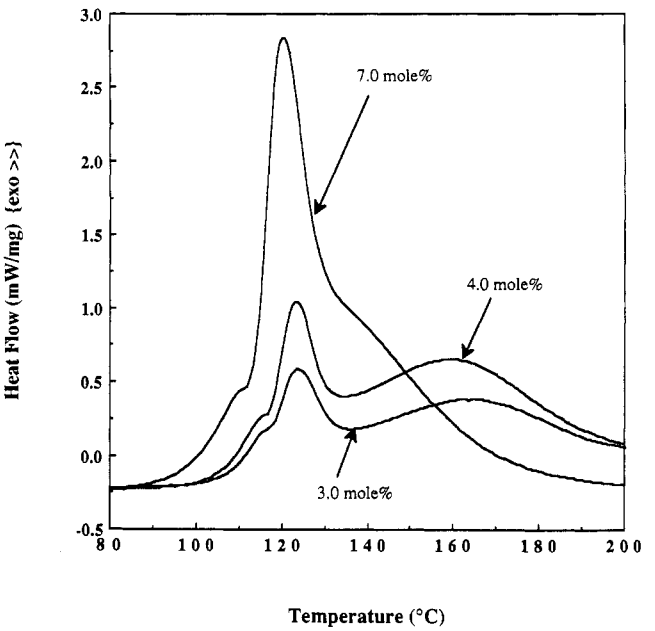

Figure 4. DSC dynamic trace at 10 °C/min for the cure of DGEBA at low EMI-24 concentrations.

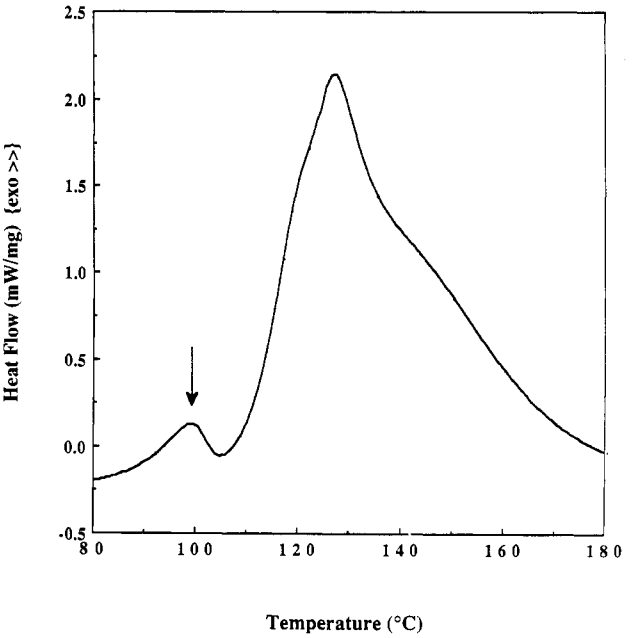

Figure 5. DSC dynamic trace for the dynamic cure of DGEBA with 5.0 mol % IMDZ at 10 °C/min. (The arrow identifies the exothermic OH-adduct reaction.)

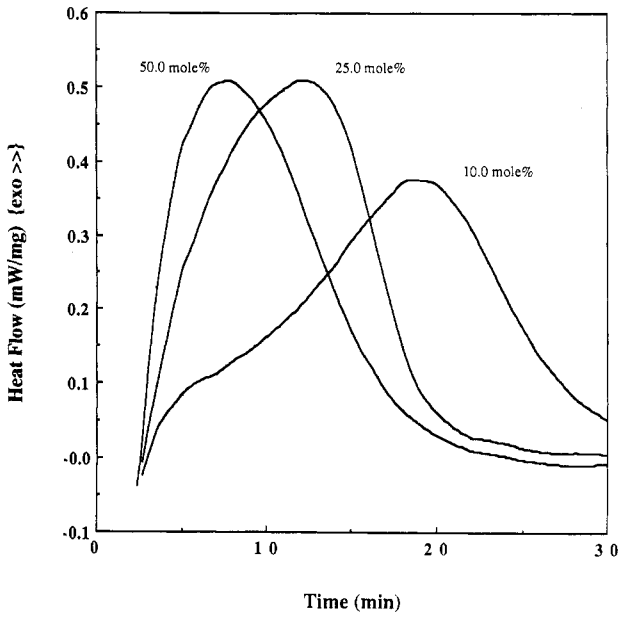

Figure 6. Isothermal DSC thermogram at 80 °C for the cure of DGEBA with various concentrations of DMI-12.

depending on whether the imidazole is substituted in the 1-position. For the EMI-24 and IMDZ, 1-unsubstituted imidazoles, the O^-/OH adduct (2:1 adduct) is formed by the basic attack of the 1-N of the OH adduct (1:1 adduct) with an epoxide group. In DMI-12 and MI-1, the OH adduct is not formed; only the O^- adduct (1:1 adduct) is formed by the reaction of the 3-N with the epoxide ring. In the DMI-12 isothermal trace at 80 °C, shown in Figure 6, there is no evidence of a large initial exotherm similar to the one present during the adduct formation for the EMI-24 system.

Although the OH-adduct reaction can be monitored with FTIR through the disappearance of the N–H stretching peak, the O^-/OH adduct must be followed indirectly by tracking the epoxide concentration. The epoxide concentration as a function of time at 80 °C for 25.0, 10.0, and 5.0 mol % EMI-24 is shown in Figure 7. A change of slope in the epoxide concentration profile, representing a change in the reaction rate, occurs between 10 and 15 min. The epoxide concentration at this point corresponds to a depletion of approximately 2 mol of epoxide groups per mole of imidazole. Also, there is no IR evidence of the formation of aliphatic ethers. Thus, at imidazole concentration of less than 25.0 mol %, and at a reaction temperature of 80 °C, the adduct formation approaches completion prior to the etherification or polymerization reaction.

Since the adduct formation is not a cross-linking reaction, the T_g of the sample should not change appreciably until the etherification reaction begins. During the first 15 min of the reaction between DGEBA and 5.0 mol % EMI-24 at 80 °C, the T_g increases slightly, as shown in Figure 8. At about 15 min, the T_g begins to increase rapidly indicating the initiation of the etherification reaction. The reaction rate changes at approximately 15 min, as shown by the epoxide concentration profile displayed in Figure 7. That is, the adduct reaction is characterized

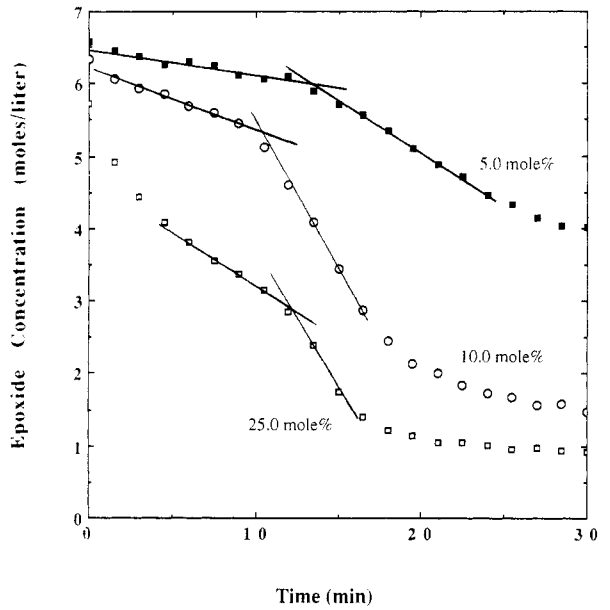

Figure 7. Epoxide concentration from the isothermal FTIR analysis for the cure of DGEBA at various concentrations of EMI-24 at 80 °C. (The lines show the change of slope in the concentration profile.)

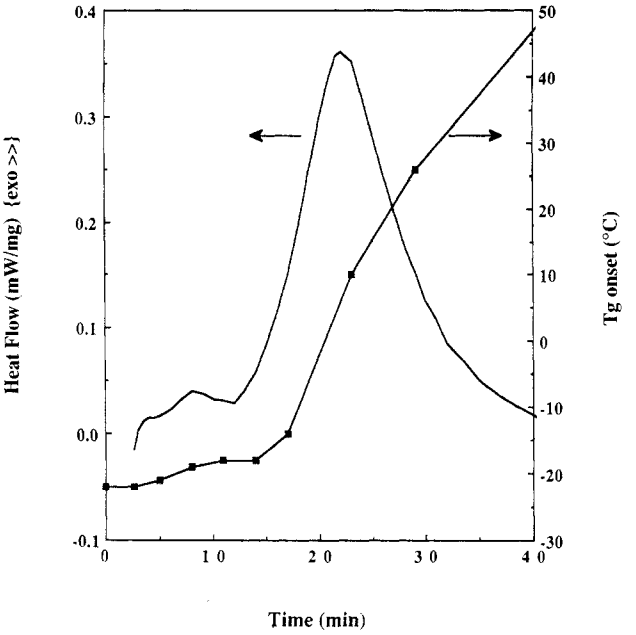

Figure 8. DSC thermogram and T_g onset for the isothermal cure of DGEBA with 5.0 mol % EMI-24 at 80 °C.

by a slow rate of epoxide conversion and a relatively constant T_g. The initiation of the etherification reaction is marked by a sudden increase in the T_g, by an increase in the rate of epoxide conversion, and by the appearance of a broad aliphatic ether band between 1140 and 1110 cm^{-1}.

Etherification Reaction. The FTIR results demonstrate that the adduct formation approaches completion prior to the start of the etherification reactions; therefore, the O-etherification reaction appears as part of the second exotherm in the isothermal DSC analysis shown in Figure 3. At 50.0 mol % EMI-24, the adduct formation is the major reaction and consumes most of the epoxide groups. However, at 25.0 mol % EMI-24, only one-half of the epoxide groups are used by the imidazole in forming adducts; the remaining groups are available for the etherification reaction. The second exotherm increases as the imidazole concentration decreases since fewer epoxide

Table II
Heat of Reaction and T_g for DGEBA Cured with Various Concentrations of EMI-24 by Dynamic DSC Traces at a Rate of 10 °C/min

EMI-24, mol %	concn phr	ΔH_{rxn}, J/g of total	ΔH_{rxn}, J/g of epoxide	T_g onset, °C
100.0	64.8	315	519	57
50.0	32.4	378	500	85
25.0	16.2	434	504	105
10.0	6.5	478	509	145
7.0	4.5	492	514	151
5.0	3.2	490	506	150
4.0	2.6	404	414	133
3.0	1.9	193	197	82
2.0	1.3	47	49	-7
0.5	0.3	14	14	-13

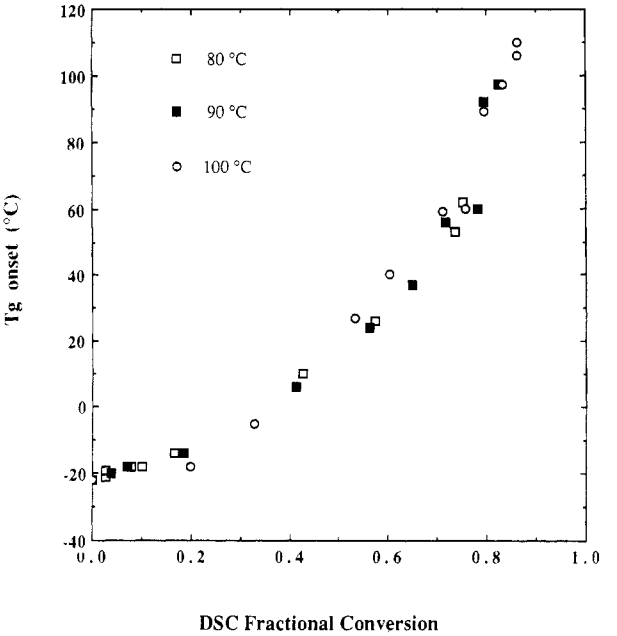

Figure 9. T_g onset as a function of DSC conversion for DGEBA cured with 5.0 mol % EMI-24 at different temperatures.

groups are used to form the adducts. Thus, the second exothermic peak in the 25.0 and 5.0 mol % EMI-24 thermograms is primarily caused by the O-etherification reaction. Imidazole concentrations of 50.0 mol % or greater are sufficient to react with all of the epoxide groups to form adducts; however, the relatively high T_g values, reported in Table II, indicate that the etherification reaction might be occurring. In this case, a broad tail on the first exotherm peak is observed instead of a second exothermic peak.

The epoxide chain begins to grow and to form cross-links during the O-etherification reaction. The T_g does not significantly increase during the first 15 min of the cure, as shown in Figure 8. During the second exotherm, the T_g begins to increase rapidly, indicating initiation of the O-etherification reaction. Values of the observed T_g for DGEBA cured with 5.0 mol % EMI-24 at different isothermal temperatures as a function of the conversion are shown in Figure 9. The T_g remains relatively constant during the adduct formation which occurs at conversions of less than 10%. The T_g increases rapidly with conversion after the etherification reaction begins.

This study shows that for imidazole concentrations of 25.0 mol % or less, the O-etherification reaction is characterized by a rapid rate of reaction compared to the rate of adduct formation. This difference in the reaction rate is illustrated in Figure 10 which shows the dynamic DSC scans at high EMI-24 concentrations. At 100.0 and 50.0

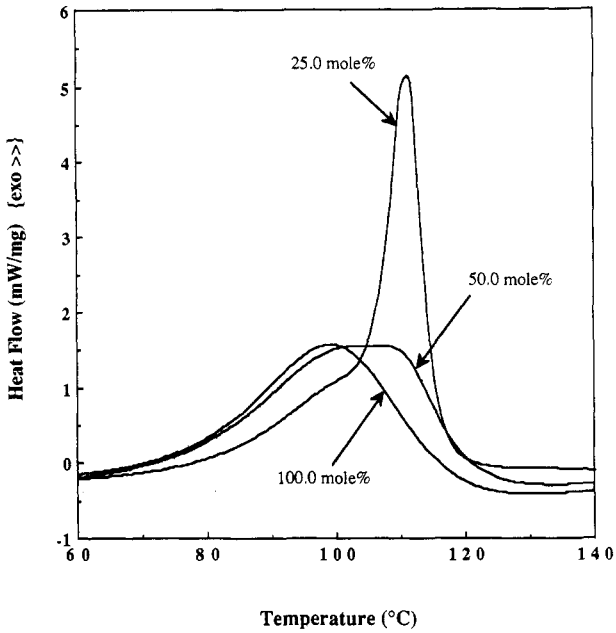

Figure 10. DSC dynamic trace at 10 °C/min for the cure of DGEBA at high EMI-24 concentrations.

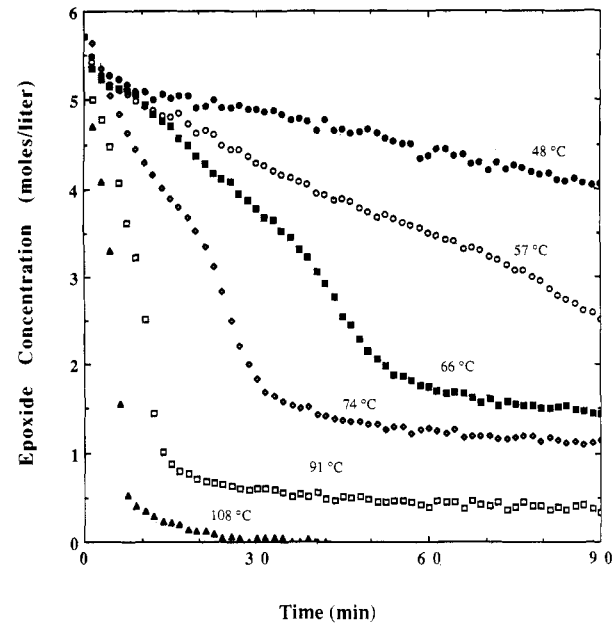

Figure 11. Epoxide concentration from the isothermal FTIR analysis for the cure of DGEBA with 25.0 mol % EMI-24 at different temperatures.

mol %, the adduct formation consumes most of the epoxide groups resulting in broad exothermic peaks. When the EMI-24 concentration is lowered to 25.0 mol %, the dynamic trace shows a broad shoulder between 90 and 100 °C followed by an extremely sharp exotherm; this exotherm represents a rapid O-etherification reaction.

The epoxide concentration profiles, determined from isothermal FTIR studies, also show the same trend in the reaction rate between the adduct and the etherification reactions. The change in the epoxide reaction rate, illustrated in Figure 7, occurs between 10 and 15 min at 80 °C. The epoxide concentration profile for 25.0 mol % EMI-24 at various temperatures is shown in Figure 11. At 48 and 57 °C, the rate of adduct formation is extremely slow. The change in the reaction rate does not occur until approximately 70 min at 57 °C and does not occur in 90 min at 47 °C. At 66 and 74 °C, the reaction rate change occurs at an epoxide conversion between 40 and 50%. At

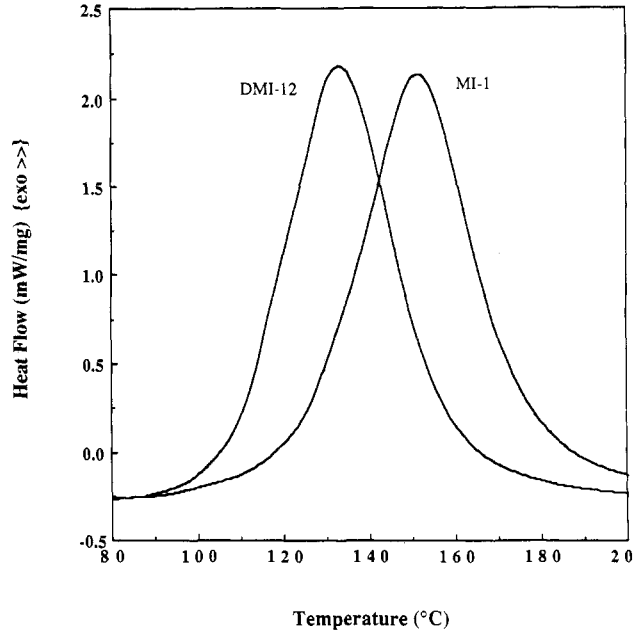

Figure 12. Comparison of DSC dynamic traces at 10 °C/min for the cure of DGEBA with 5.0 mol % DMI-12 and with 5.0 mol % MI-1.

higher reaction temperatures, the reaction rate becomes too fast to differentiate between the individual reactions.

Examination of the epoxide concentration profile in Figure 11 for DGEBA cured with 25.0 mol % EMI-24 shows that there are three regions present. The first region is marked by the adduct reactions which occur prior to the etherification reaction and is characterized by a constant T_g, exhaustion of the N–H group, an initial exothermic DSC peak, and a slow rate of epoxide depletion. The O-etherification reaction occurs in the second region, which shows a second exothermic peak, accompanied by a rapid increase in the T_g, a rapid decrease in the epoxide concentration, and the appearance of the aliphatic ether band in the IR spectra at wavenumbers between 1140 and 1110 cm^{-1}. The third region occurs when the sample vitrifies. The reaction between the epoxide groups becomes diffusion-limited, resulting in a slow increase in the T_g.

The OH-etherification reaction can occur only in the 1-unsubstituted imidazoles, since the active hydroxyl site is formed during the OH-adduct formation. This etherification reaction was only observed in the dynamic DSC traces at EMI-24 concentrations less than 7.0 mol %. The reaction appears as a broad high-temperature exotherm in the dynamic DSC traces, as shown in Figure 4. The peak shifts to higher temperatures as the scan rate is held constant and as the EMI-24 concentration is lowered, indicating that this reaction is a strong function of the imidazole concentration. The reaction is also observed for DGEBA cured with 5.0 mol % IMDZ; it appears as a broad tail on the main exotherm peak, as illustrated in Figure 5. The 1-substituted imidazoles, DMI-12 and MI-1, do not undergo the OH-adduct formation or the OH-etherification reaction and, therefore, the dynamic traces, shown in Figure 12, exhibit a single symmetric peak containing the O adduct and the O-etherification reactions. There is no low-temperature side peak or broad high-temperature peak in the dynamic scans.

The thermal properties of the network are strongly dependent on the imidazole concentration used to cure the epoxy resin. The heat of reaction and T_g for DGEBA cured with various concentrations of imidazoles, ranging with 0.5 to 100.0 mol % EMI-24, are displayed in Table II. The samples were cured by dynamic DSC scans from

0 to 300 °C at a rate of 10 °C/min. At high EMI-24 concentrations, the imidazole consumes most of the epoxide groups to form adducts. The T_g values for the 100.0 mol % and 50.0 mol % sample were determined to be 57 and 85 °C, respectively. As the EMI-24 concentration is lowered to 25.0 mol %, more epoxide groups are available for etherification and the T_g increases to 105 °C. The isothermal epoxide concentration profiles for 25.0 mol % EMI-24 show that complete conversion of the epoxide groups is obtained at 108 °C since the isothermal temperature exceeds the ultimate T_g of the system (see Figure 11). However, complete epoxide conversion does not occur for isothermal runs below 105 °C because the sample vitrifies when the T_g of the sample reaches the isothermal cure temperature. The highest T_g values of approximately 150 °C are obtained at EMI-24 concentrations of 7.0 and 5.0 mol %. As the EMI-24 concentration is reduced below 5.0 mol %, the T_g and the heat of reaction decrease rapidly and depend on the sample heating rate. As the heating rate decreases, the cure time increases, resulting in a higher heat of reaction and a higher T_g. The epoxy/imidazole adduct catalyzes the etherification reaction and contains the active sites for polymerization. At low imidazole concentrations, the etherification reaction rate is strongly dependent on the adduct concentration.

Conclusions

Dynamic and isothermal studies were used to identify and analyze the adduct and etherification reactions which occur during the cure of DGEBA with various 1-unsubstituted and 1-substituted imidazoles. The OH-adduct formation, which occurs only with the 1-unsubstituted imidazoles, was monitored by tracking the N–H stretching peak with IR analysis. The formation of a zwitterion adduct with an active alkoxide group occurred with all imidazoles. Overall, at imidazole concentrations of 25.0 mol % or less, the adduct formation was characterized by a slow rate of epoxide conversion compared to the rate of polymerization and by a constant T_g. The beginning of the O-etherification reaction, initiated by the alkoxide ion, was marked by a rapid increase in the T_g and by an increase in the rate of the epoxide conversion. Another etherification reaction, caused by the attack of an epoxide ring by a hydroxyl group, occurred in 1-unsubstituted imidazoles at low concentrations. The hydroxyl group was created during the OH-adduct formation through a rearrangement by a proton transfer from the 1-nitrogen. Therefore, OH-adduct reaction and the OH-etherification reaction were not observed for the curing reactions with the 1-substituted imidazoles.

The thermal properties of the network were shown to be strongly dependent on the imidazole concentration. At high imidazole concentrations (50 mol % and greater), the adduct reaction consumes most of the epoxide groups to form adducts. As the imidazole concentration is decreased, the T_g increases because fewer adducts are formed and more epoxide groups are available for chain growth and cross-linking. The maximum T_g is obtained for the DGEBA/EMI-24 system at about 5.0 mol % EMI-24. As the EMI-24 concentration is lowered below 5.0 mol %, the T_g decreases rapidly. At low imidazole concentrations, the rate of the etherification reaction decreased rapidly as the adduct concentration was decreased. The combination of DSC and FTIR studies and the use of model imidazoles has been shown to be an effective technique for analyzing the complex epoxy/imidazole curing process.

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Registry No. DGEBA, 25068-38-6; EMI-24, 931-36-2; DMI-12, 1739-84-0; MI-1, 616-47-7; IMDZ, 288-32-4; (DGEBA)(EMI-24) (copolymer), 81855-87-0.

References and Notes

(1) Ito, M.; Hata, H.; Kamagata, K. *J. Appl. Polym. Sci.* **1987**, *33*, 1843.
(2) Farkas, A.; Strohm, P. F. *J. Appl. Polym. Sci.* **1968**, *12*, 159.
(3) Barton, J. M.; Shepard, P. M. *Makromol. Chem.* **1975**, *176*, 919.
(4) Dearlove, T. J. *J. Appl. Polym. Sci.* **1970**, *14*, 1615.
(5) Barton, J. M. *Adv. Polym. Sci.* **1985**, *72*, 112.
(6) Ricciardi, F.; Romanchick, W. A.; Griscavage, A. A.; Jouillie, M. M. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 127.
(7) Ricciardi, F.; Romanchick, W. A.; Jouillie, M. M. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1475.
(8) Jones, J. R.; Poncipe, C.; Barton, J. M.; Wright, W. W. *Polymer* **1987**, *28*, 1358.
(9) Heise, M. S.; Martin, G. C. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 153.

Reactivity of Some Substituted Styrenes in the Presence of a Syndiotactic Specific Polymerization Catalyst

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ABSTRACT: The reactivities of several substituted styrenes have been tested, in the presence of a syndiotactic specific catalytic system consisting of tetrabenzyltitanium and methylalumoxane, by homopolymerization and copolymerization runs. I^+ substituents enhance the reactivity to a greater extent than was previously observed for isotactic polymerization. The stereospecificity is also affected by the substituents of the aromatic ring even when they are at the para position.

1. Introduction

Several substituted styrenes have been polymerized in the presence of homogeneous catalytic systems consisting of soluble titanium or zirconium compounds and methylalumoxane.[1-4] As previously reported, these catalytic systems promote polymerization of styrene to a syndiotactic polymer.[1-6]

In this paper we are reporting a comparison of the behavior in the polymerization of some substituted styrenes, i.e., styrene itself (S), *p*-methylstyrene (PMS), *m*-

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