Cure Kinetics of Epoxy/Anhydride Thermosetting Matrix Systems

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Synopsis

The kinetics of bisphenol-A diglycidyl ether epoxy (DGEBA) cured with trimellitic anhydride (TMA) were studied using differential scanning calorimetry (DSC) and FT-IR under isothermal temperatures in the range of 100–200°C. The effects of an onium salt catalyst and styrene monomer (a reactive diluent additive) on cure kinetics of the DGEBA/TMA resin systems were also investigated. For the uncatalyzed DGEBA/TMA system, the reaction was found to be second order up to a fractional conversion of 0.8, where a diffusion-limited reaction regime was observed as the matrix gelled. The apparent activation energy was calculated to be 11.3 kcal/mol. The cure reaction of the catalyzed DGEBA/TMA system was found to be second order up to a fractional conversion of 0.3 and first order thereafter. The apparent activation energy of the catalyzed resin system was calculated to be 12.3 kcal/mol. In the FT-IR investigation, it was discovered that the KBr powder catalyzed the cure reaction. Additionally, the styrene component in the styrene–DGEBA/TMA resin system polymerized independently in the later stage of the cure reaction of the epoxy component. Therefore, the styrene monomer had little effect on the kinetics of cure reaction of the epoxy system.

INTRODUCTION

The kinetics of cure reactions of thermosetting resins are critical for laminate processing and for continuous composite processing such as pultrusion or filament winding. In this study, an epoxy resin based on diglycidyl ether of bisphenol-A (DGEBA) formulated with or without a reactive styrene diluent to be cured with an anhydride curing agent, trimellitic anhydride (TMA), was investigated. The styrene is a reactive diluent incorporated in the epoxy formulations to improve processability by lowering the viscosity. Anhydride-cured epoxy systems are generally for fast-curing applications and the reaction rate can be further increased by an onium salt (a quaternary ammonium salt). The effects of the onium salt accelerator and the reactive styrene diluent on the cure kinetics was investigated. Catalysts for anhydride-cured epoxy systems are not limited to onium salts. Other catalysts also commonly used are tertiary amines, alcohols, imidazoles, or acids. In some cases, a tertiary amine may require an acid (such as benzoic acid) as a co-catalyst. In such cases, the tertiary amine reacts with the co-catalyst acid and forms a complex with structure similar to a quaternary ammonium salt.

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The mechanisms of curing reactions of epoxy resins with anhydrides have been investigated by several authors[1-5] using chemical analysis, FT-IR, torsional braid analysis, or differential scanning calorimetry techniques. In general, these reactions are quite complex, and the cure kinetics are not always easily elucidated. Phenomena such as autocatalysis at early stages[6] and onset of gelation at later stages of cure reaction[7,8] can further complicate the analysis. Reaction kinetics differing from first to third order have been reported.[7-9] Determination of the reaction order from experimental data can be difficult and confusing in some reaction systems, and one must be careful in analysis. In an investigation of DGEBA cured with methylnadic anhydride using the FT-IR technique, Antoon and Koenig report that the overall kinetics are first-order but the data can be fit to zero- and second-order kinetics almost as well.[4]

DSC has been a useful technique for studying cure kinetics of crosslinking reactions of thermosetting epoxy resins.[6-12] The basic assumption is that the heat evolution monitored and recorded by DSC is proportional to the extent of consumption of the functional groups, such as the epoxide groups in the epoxy resin or the anhydride (or acid) groups in the curing agent. In this study, cure kinetics of the epoxy/anhydride resins were examined using the DSC as well as FT-IR techniques. The nth-order rate expressions in both differential and integral forms were used, and cure kinetics parameters were derived by fitting the rate expressions with the data generated from the isothermal differential scanning calorimetry measurements during cure. In this study, both the integral and differential rate equations were used to investigate the reaction order. The resulting rate laws were then shown to describe the cure behavior of the resin systems during an isothermal cure.

EXPERIMENTAL

Materials

The unmodified epoxy resin system was Shell EPON® Resin 828 based on diglycidyl ether of bisphenol-A (DGEBA) cured with Shell EPON® CURING AGENT 9150 based on 95% by weight of trimellitic anhydride (TMA) and 5% of an antidusting agent. The styrene-modified epoxy system was Shell EPON® Resin 9102, which is essentially a homogeneous liquid mixture of DGEBA with 19.8 wt % of monomeric styrene as a processing aid and minor (1.0%) proprietary additives including an onium salt accelerator. The epoxide equivalent weight of the EPON Resin 9102 is 240 g/mol. The EPON Resin 9102 and CURING AGENT 9150 fall under the class of compositions described in a U.S. patent.[13] The recommended concentration of the curing agent is 35–41 parts of TMA per hundred parts (35–41 phr) of the epoxy resin. All materials, supplied by the Shell Development Co., were commercial grades and used as received. The three formulated resin systems were used in this study. System A (uncatalyzed DGEBA/TMA) is a formulation of the DGEBA resin with the TMA curing agent. System B (catalyzed DGEBA/TMA) is essentially of the same components as in system A, plus an onium salt accelerator. System C (catalyzed styrene–DGEBA/TMA) is a formulation of EPON Resin 9102 and EPON CURING AGENT 9150.

Apparatus and Procedures

Differential Scanning Calorimetry

The DuPont 910 DSC coupled to the 9900 Thermal Analysis System was used for data acquisition and analysis. Resin samples of approximately 8–10 mg were weighed accurately to the nearest 0.1 mg into an aluminum DSC sample pan. Typical isothermal temperatures used were 100, 120, 140, 160, and 180°C. At high temperatures, the resin could be cured completely in a few minutes. Therefore, kinetic studies on fast-curing resins were more difficult since the initial temperature ramping and equilibration would cause the reactions to start prematurely before the heat evolution could be recorded by the instrument. A simple procedure was employed in the DSC experiments to minimize the error caused by the unrecorded heat of reactions. The DSC cell was equilibrated at the desired temperature before the sample was introduced. A typical temperature drop of 10–30°C was noticed immediately after the insertion of the sample to the DSC cell. The data acquisition was not started until the DSC cell regained the temperature equilibration, which usually took about one minute or less. Even with a short time lapse, some of the exotherm might not have been recorded due to the fast-curing nature of the resins. Some temperature fluctuation in the DSC cell occasionally was observed at the initial stage of equilibration immediately after the insertion of the sample. However, the temperature fluctuation period was generally short, and it could be reasonably assumed that experimental errors of these sources were negligible.

Isothermal reaction data were acquired by placing the sample in the DSC cell at a certain isothermal temperature for one hour, during which the exotherm of reactions was recorded. Subsequently, dynamic scanning was performed on the same sample in order to determine the overall conversion at the end of each isothermal treatment by measuring the residual heat of reaction of the sample. Both the glass transition temperature and residual heat of reactions were measured using DSC at a heating rate of 10°C/min. After the dynamic scanning, the resin samples were assumed to be completely cured. The baseline for the integration of the cure exotherms was then determined at the same isothermal temperature by running DSC again on the very same sample that was previously used in the DSC isothermal cure. The integration of the peak associated with the cure exotherm was done either graphically or numerically by using a computer.

Some limitations of the DSC technique were considered. Due to the fast-curing nature of the present epoxy systems, the reaction rate became too high at high temperatures to be measured accurately. At low temperatures, the reaction could terminate prematurely at a low conversion irrespective of continuation of isothermal treatment when the T_g of the reacting resin approached the isothermal temperature T_c.[7-9]

FT-IR Technique

The infrared spectra of the DGEBA/TMA (system A) samples were obtained using an IBM FT-IR Spectrometer (IR-32 operated with an IBM 9000 computer system for data acquisition). Reaction at three different isothermal tempera-

tures (155, 140, and 130°C) were characterized. Since the resin samples were not optically transparent, transmission spectroscopy would not be suitable. Also, there was no hot stage accessory available for the transmission mode. Instead, a technique was employed using an IBM Diffuse Reflectance Accessory designed for use in the IBM FT-IR spectrophotometer, which was equipped with a hot stage capable of heating to above ambient temperature. Mirror alignment and baseline calibration were done according to the procedures recommended by the manufacturer. For diffuse reflectance, the proper y axis to use is the Kubelka–Munk units, which as a function of reflectance is given as[14]

$$f(R) = (1 - R)^2/2R \tag{1}$$

where R is the reflectance at infinite depth. This scale is loosely equivalent to the absorbance plot mode.[14] The quantitative aspects of diffuse reflectance methods were discussed by several authors.[15] Griffiths et al. also discussed the correlations between the spectral intensity in Kubelka–Munk units and sample concentrations.[16] The liquid resin sample was mixed with finely ground KBr powder at a resin/powder ratio of 1/10. After mixing, the mixture became a partially dry paste. The paste was then transferred into a sample pan, which was then placed on the heating stage inside the diffuse reflectance accessory equilibrated at a chosen isothermal temperature. It was assumed that the sample reached thermal equilibrium with the heating stage within a minute or so. Subsequently, data acquisition was started at 32 scans at a resolution of 4 cm^{-1}.

The benzene ring modes at 1502 and 1608 cm^{-1} have been proven to be independent of the reaction. They were used as an internal reference for determination of epoxide conversions based on the rate of the epoxide peak disappearance. The absorption due to $\nu_s(CH_2)$ of the epoxide ring at 3008 cm^{-1} was crowded and hence could not be resolved properly. The following reacting species were found to exhibit absorption decreases at 1780 and 1858 cm^{-1} [$\nu_{as}(C=O)$ and $\nu_s(C=O)$], and at 915 cm^{-1} (epoxide). The anhydride absorption is located at a slightly lower wave number of 910 cm^{-1} as a shoulder next to the epoxide absorption. The epoxide absorption decrease at 915 cm^{-1} was used to derive kinetic data of epoxide conversion as a function of time. Absorption intensity increase due to formation of the ester group was observed at 1743 cm^{-1} [$\nu(C=O)$ester]. The peak at 1778 cm^{-1} due to $\nu(C-O)$ of the ester was not observed.

RESULTS AND DISCUSSION

Figure 1 shows a typical DSC exotherm of the heat flow, dH/dt in mV/mg, as a function of time for the reaction of DGEBA cured with 40 phr of TMA with no accelerator (system A) at an isothermal temperature of 200°C. The figure shows how heat flow is related to reaction conversion. The distance, dH, between the exotherm curve and baseline is related to the rate of conversion, $d\alpha/dt$, through $d\alpha/dt = (1/\Delta H_{tot})(dH/dT)$, where ΔH_{tot} is the total heat of reaction, as represented by the area under the curve and above the baseline. The conversion α at time t is related by $\alpha(t) = \Delta H(t)/\Delta H_{tot}$, where $\Delta H(t)$ is

DATA   ■ - 160 °C   ——— **Model**

△ - 120

▲- 100

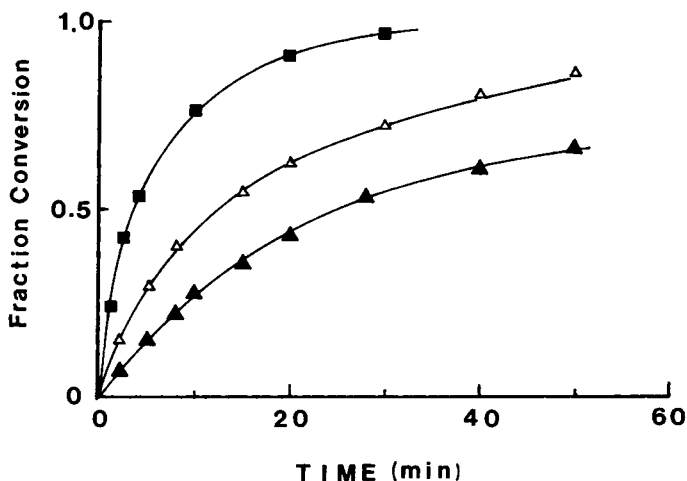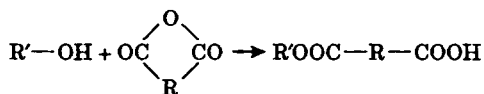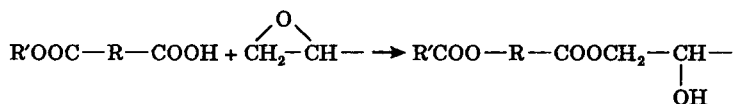
Fig. 5.   Isothermal conversion data of DGEBA/TMA (40 phr) compared with the second-order reaction model at 100, 120, and 160°C.

to the networks, they are called accelerators rather than catalysts. This study does not try to distinguish the difference between them. An epoxy/anhydride system may be difficult or slow to cure in the absolute absence of catalysts and/or co-catalysts. In practice, however, it may be impossible to preclude all species that may inherently act as catalysts or accelerators. For example, most epoxy resins contain hydroxylic species ($R-OH$) as part of the structure, which may catalyze an epoxy reaction with anhydride, shown as follows:

Monoester formation:

$$R'-OH + OC \underset{R}{\overset{O}{\diamond}} CO \rightarrow R'OOC-R-COOH$$

Diester formation:

$$R'OOC-R-COOH + CH_2-CH- \rightarrow R'COO-R-COOCH_2-CH- \atop OH$$

experimental errors. However, the advantage of using the differential form of rate expressions is that the dependence of the kinetic constant can be easily detected. Also, by plotting $(d\alpha/dt)/(1-\alpha)^n$ as a function of α, it is possible to examine the reaction order and possible shift of reaction order in a wide conversion range.

Figure 2 shows the plots of the kinetics data according to the differential form of the rate expression [Eq. (3)] at an isothermal temperature of 120°C for the first-, second-, and third-order kinetics, respectively. Only the second-order plot yielded a horizontal line. The results suggested that the reaction was second order with no autocatalysis. Similar plots of the data were constructed at other isothermal cure temperatures of 100, 140, and 160°C and the constant $k(T)$ was determined. Finally, the activation energy (E) and the preexponential constant (A) were then estimated from the Arrhenius equation: $\ln[k(T)]$ $= \ln[A] - (E/R)(1/T)$. The Arrhenius plot yielded the kinetic parameters as $\ln[A] = 11.8$ min^{-1} and $E = 10.9$ kcal/mol.
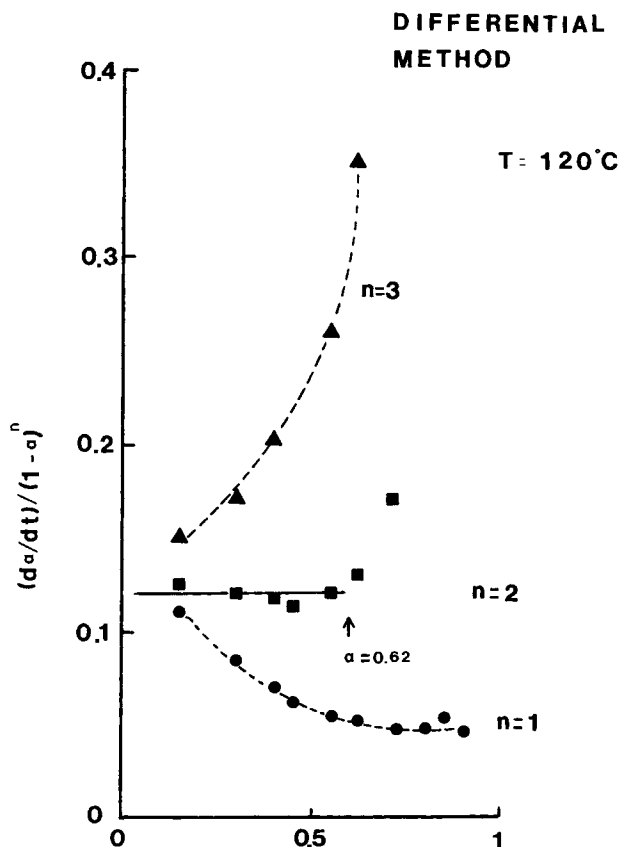

Fig. 2.   Isothermal conversion data (120°C) of DGEBA/TMA (system A) resin plotted according to the differential form of the nth-order rate expressions.

Integral forms of the rate expression were also used to examine the kinetics of the curing reaction, as follows:

For $n = 1$ (first order):

$$-\ln(1 - \alpha) = k(T, \alpha)t \qquad (4a)$$

For $n \neq 1$ (nth order):

$$[1/(1 - n)][(1 - \alpha)^{1-n} - 1] = k(T, \alpha)t \qquad (4b)$$

By plotting the left-hand side of Eqs. (4a) and (4b) as a function of time, a straight line indicates the correct reaction order and the slope gives the reaction constant $k(T)$ at the isothermal temperature T.

Figure 3 gives the plots according to the integral forms of the rate expression [Eq. (4a) or (4b)] as a function of time at 100 and 120°C, respectively. Both plots showed that the second-order kinetic analysis provides the best fit. The same reaction order was observed for the data at other isothermal cure temperatures of 140, 160, and 180°C. A sharp decrease in the reaction rate at a certain conversion, termed by some investigators as the "onset" of a diffusion-controlled reaction mechanism,[8] was not observed in this study.

Figure 4 shows the logarithm of the slopes, $\ln[k(T)]$, plotted versus $1/T$, the inverse of temperature. The kinetic constants, $k(T)$, were obtained from the slopes of the plots according to the integral forms of the rate expression. The Arrhenius analysis yielded the activation energy as 11.3 kcal/mol and the preexponential constant as $\exp[12]$ min^{-1}. This compares quite favorably with
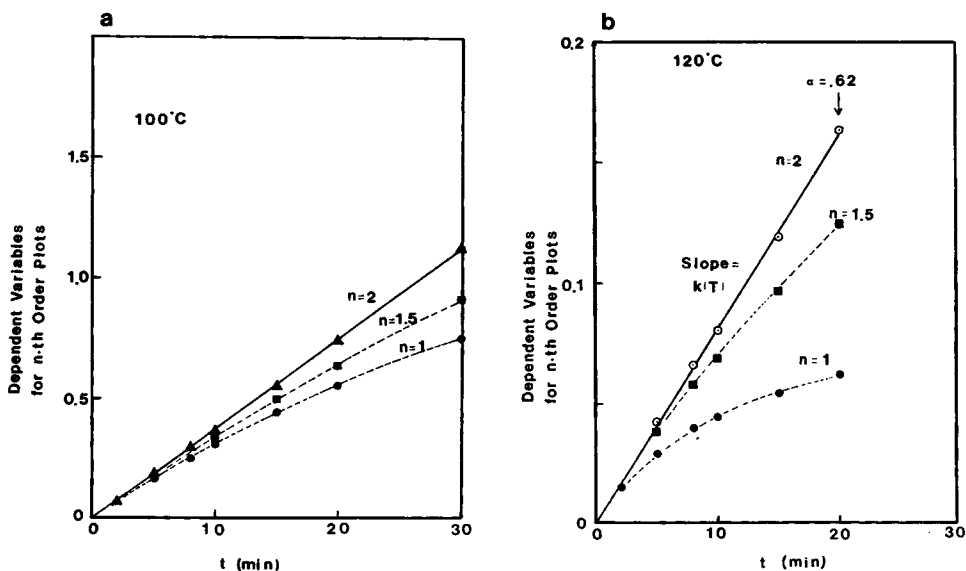

Fig. 3.   Isothermal conversion data of system A resin plotted according to the integral form of rate expressions at (a) 100°C; (b) 120°C.
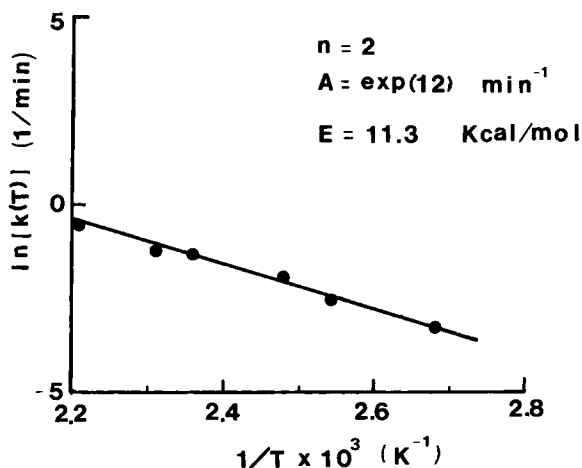
Fig. 4.   Arrhenius plot of $\ln[k(T)]$ vs. $1/T$ for DGEBA/TMA (system A) resin.

the activation energy ($E = 10.9$ kcal/mol) obtained from the differential form of the rate expressions. Typical values of the activation energy for most epoxy/amine resin systems are 10–16 kcal/mol for autocatalytic reactions[9] and 19–20 kcal/mol for normal nth-order reactions.[17] For epoxy/anhydride systems, the activation energies are lower compared to most epoxy/amine systems. Tanaka et al.[1] report 13.5–14.1 kcal/mol for the apparent activation energies of various tertiary amine-catalyzed epoxy/hexahydrophthalic anhydride systems. The apparent activation energies (10.9–11.3 kcal/mol) are relatively lower for the trimellitic anhydride-cured epoxy system.

Figure 5 shows that the second-order reaction model describes well the isothermal conversions of the epoxy system with no onium salt accelerator (system A) at three isothermal temperatures: 100, 120, and 160°C. The good fit between the model and the experimental data of conversion confirms the kinetics of second-order reactions.

Effect of Onium Salt Accelerator

For most anhydride-cured epoxy systems, cure reactions may be slow without a catalyst or an accelerator. For the present case, cure reactions of the uncatalyzed systems could still proceed at reasonable rates at normal curing temperatures. This might be due to the ($-COOH$) group in the TMA curing agent in addition to the regular anhydride group. The carboxylic group was capable of reacting with the epoxide to produce the carboxylic anions necessary to propagate the reaction. Also, the epoxy resin used in this study contained hydroxyl group ($-OH$), which might have some catalytic effect. Generally, cure reactions of epoxy/anhydride systems require some added accelerators or catalysts. The catalyst of choice for this system was an onium salt of bromide, tetra-n-butylammonium bromide (TBAB). Additionally, both acidic or basic catalysts as well as water or hydroxyl species may act as accelerators for the cure reactions. Since some of the catalyzing species may be permanently bound
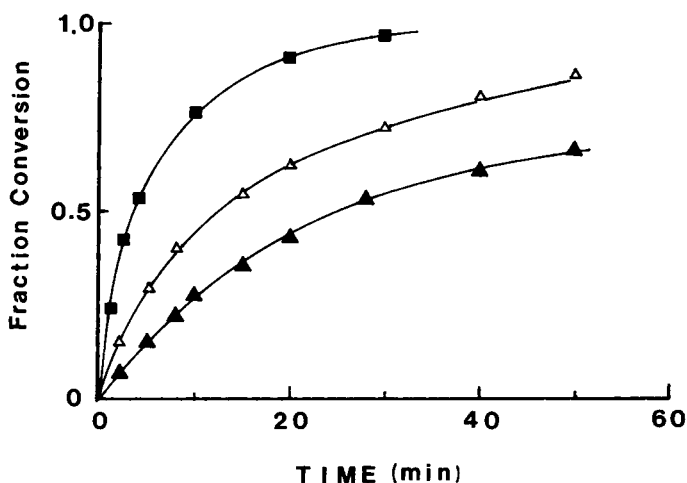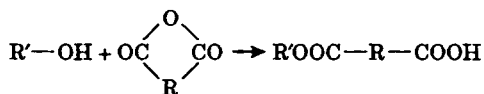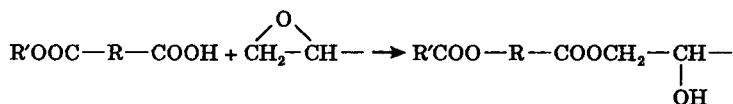
DATA ■ - 160 ˚C ——— **Model**
△ - 120
▲- 100

Fig. 5. Isothermal conversion data of DGEBA/TMA (40 phr) compared with the second-order reaction model at 100, 120, and 160°C.

to the networks, they are called accelerators rather than catalysts. This study does not try to distinguish the difference between them. An epoxy/anhydride system may be difficult or slow to cure in the absolute absence of catalysts and/or co-catalysts. In practice, however, it may be impossible to preclude all species that may inherently act as catalysts or accelerators. For example, most epoxy resins contain hydroxylic species (R—OH) as part of the structure, which may catalyze an epoxy reaction with anhydride, shown as follows:
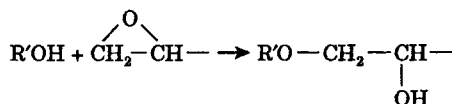
Monoester formation:

$$R'{-}OH + OC \overset{O}{\underset{R}{\diamond}} CO \rightarrow R'OOC{-}R{-}COOH$$

Diester formation:

$$R'OOC{-}R{-}COOH + CH_2{-}CH{-} \overset{O}{\diamond} \rightarrow R'COO{-}R{-}COOCH_2{-}CH{-}$$
$$\underset{OH}{|}$$

Etherification:

$$R'OH + CH_2-CH- \longrightarrow R'O-CH_2-CH- $$
$$\overset{O}{\diagup \diagdown}$$
$$\underset{OH}{|}$$

Tri-ester formation is, of course, the reaction that follows the diester formation and primarily responsible for the network structure. Etherification is not expected to proceed significantly in the presence of the curing agent.

Figure 6 shows the DSC thermograms of temperature scans for the epoxy/ TMA (35 phr) resins with various accelerator concentrations (0, 0.2, 0.5, and 1.0 phr). The figure shows that the accelerator at concentrations below 1 phr only marginally affects the kinetics of the reaction as the DSC thermograms are similar to that of the uncatalyzed DGEBA/TMA resin (system A). However, the DGEBA/TMA resin with 1 phr of the onium salt catalyst (system B) exhibited drastically different exothermic peak characteristics. The reaction peak is much narrower and at a lower temperature, indicating a change in the reaction mechanism that enhances the rate of cure reaction. At the same heating rate, the uncatalyzed system (0 phr) did not reach a full cure until $T = 250°C$ while the epoxy system with 1 phr of the onium salt accelerator attained a complete cure state at a lower temperature of 150°C.

Figure 7 shows plots according to the integral forms of the rate expression [Eqs. (4a) and (4b)] as functions of time at two isothermal temperatures of
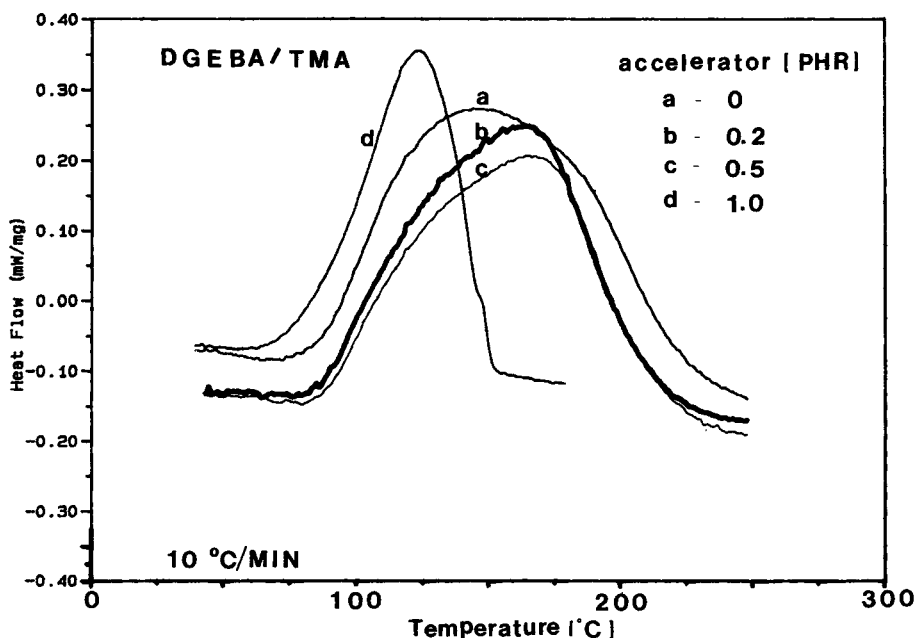

Fig. 6. DSC thermograms of resins with different accelerator concentrations: (Curve a) 0 phr; (b) 0.2 phr; (c) 0.5 phr; (d) 1.0 phr.
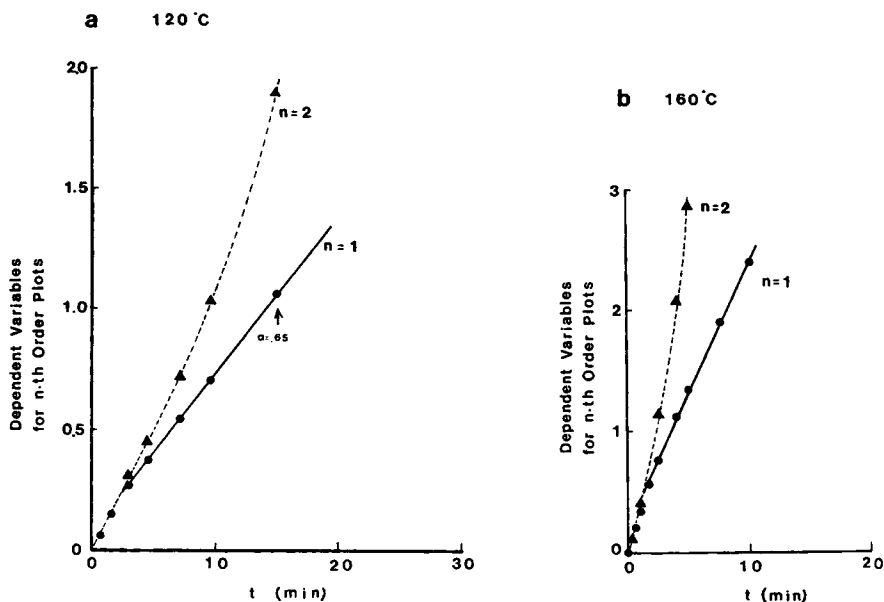
Fig. 7. Isothermal conversion data of catalyzed DGEBA/TMA (system B) resin plotted according to the integral form of rate expressions: (a) 120°C; (b) 160°C.

120 and 160°C, respectively. Isothermal DSC data were obtained at four different temperatures, but only the data at these two temperatures are shown in the figure. Apparently, the reaction data fit the second-order kinetics only for the early stages of reaction, where conversions are lower than 0.3. The data at conversions higher than 0.3 could be fit to the first-order kinetics up to a fractional conversion of 0.8. The results therefore may suggest a shift in the reaction order during cure from a second-order reaction at low conversions to a first-order reaction at high conversions. Since the deflection point is at a relatively low conversion, both plots of the data according to the first- and second-order rate expressions may seemingly fit to a straight line. However, extra care must be exercised in determining the proper reaction order.

These results were further examined by plotting the same data according to the differential form of the rate expression [Eq. (3)]. Figure 8 shows plots of the data at an isothermal temperature of 120°C. Apparently, the second-order plot yielded a horizontal line only up to approximately a conversion of 0.3. Beyond that conversion, the first-order plot fit a horizontal straight line. Again, it suggested a shift of the cure reaction from second to first order. From these results, it was concluded that the cure reaction is second order up to a fractional conversion of 0.3 before it changes to first order at higher conversions.

Figure 9 is the Arrhenius plot of $\ln[k(T)]$ as a function of $1/T$; $k(T)$ was obtained from the slopes of integral plots of the experimental data at several isothermal cure temperatures. In this figure, the slope of the first-order straight line was taken as the kinetic constant of the first-order reaction, which represents the cure reaction at fractional conversions higher than 0.3. The plot yielded $A = \exp[13]$ min^{-1} and $E = 12.3$ kcal/mol. The kinetic parameters for
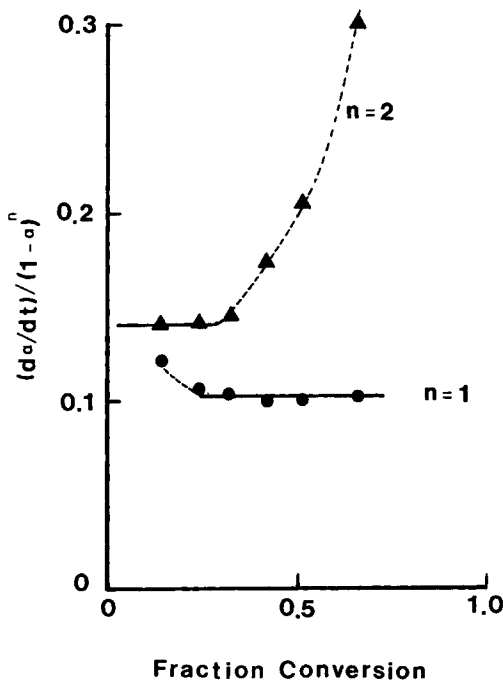
SYSTEM B

T = 120°C

Fig. 8.   Isothermal reaction conversion of system B resin plotted according to the differential form of rate expression.

the second-order reaction at fractional conversions lower than 0.3 were obtained separately from the slopes of the plots according to the second-order rate expressions. The second-order kinetic parameters at fractional conversions lower than 0.3 were determined to be $\ln[A] = 12.2$ min^{-1} and $E = 11.5$ kcal/mol. Kinetic parameters of the rate expressions were also determined from the differential form. Arrhenius plots of $\ln[k(T)]$ versus $1/T$ yielded the kinetic parameters for the first-order reaction at fractional conversions higher than 0.3. They were determined to be $\ln[A] = 11.8$ min^{-1} and $E = 10.9$ kcal/mol. The activation energy is quite comparable with the activation energy obtained from the analysis according to the integral form of the rate expressions.

Figure 10 shows the comparison of the model (solid curves) of shifting reaction order and the model (dashed curves) of first-order reaction with the experimental conversion data of the epoxy system with the onium salt (system B) at four isothermal cure temperatures: 100, 120, 140, and 160°C. The solid curves were calculated according to the model of shifting reaction order, while
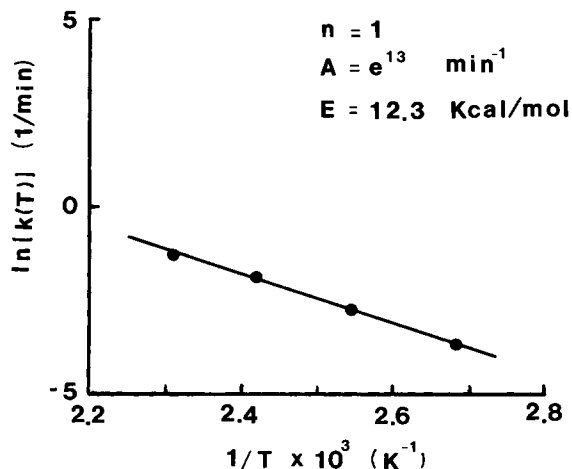
Fig. 9.   Arrhenius plot of $\ln[k(T)]$ vs. $1/T$ for catalyzed DGEBA/TMA (system B) resin.

the dashed curves were calculated according to the model of first-order reaction (constant order). Apparently, the model of shifting reaction order describes better the experimental conversion data.

The mechanism of curing reaction of epoxy resin with anhydride in the presence of tertiary amine catalysts has been investigated by several authors.[1] The general mechanism reported in the literature is shown in Figure 11. Although the catalyst in this study was not a tertiary amine, the mechanism of catalysis would be expected to be similar. Unlike a tertiary amine, the quaternary ammonium lacks a pair of unshared electrons. However, the electron negativity of one of the ions in the salt has the same function as the unshared electron in attacking the carboxylic group in the anhydride structure, which leads to the opening of the anhydride ring. This step of the reaction is fairly fast. After the ring opening, a carboxyl anion is formed on the other end of the opened ring. The reaction propagates by attacks of the anion on the epoxide group to form an ester–alkoxide anion that can, in turn, react with anhydride to form an ester linkage and another carboxyl anion to propagate the reaction. The rate-determining step is believed to be the reaction between the anion and the epoxide. The reaction is therefore first order with respect to the epoxide concentration.

The cure of the epoxy with trimellitic anhydride may involve two different reactions. One is the reaction between the epoxide and the acid group on the TMA molecule, and the other is the reaction between the epoxide and the anhydride ring on TMA. The reaction between the epoxide and the acid groups is second order and can proceed with or without a catalyst. But the reaction rate between the epoxide and the anhydride is very slow without a catalyst. With the catalyst, the reaction is first order, and its rate depends only on the concentration of the epoxide. The former reaction may proceed earlier and is faster than the latter since the former has a lower activation energy. Therefore, the reaction shifts from second order to first order during cure. The shifting of
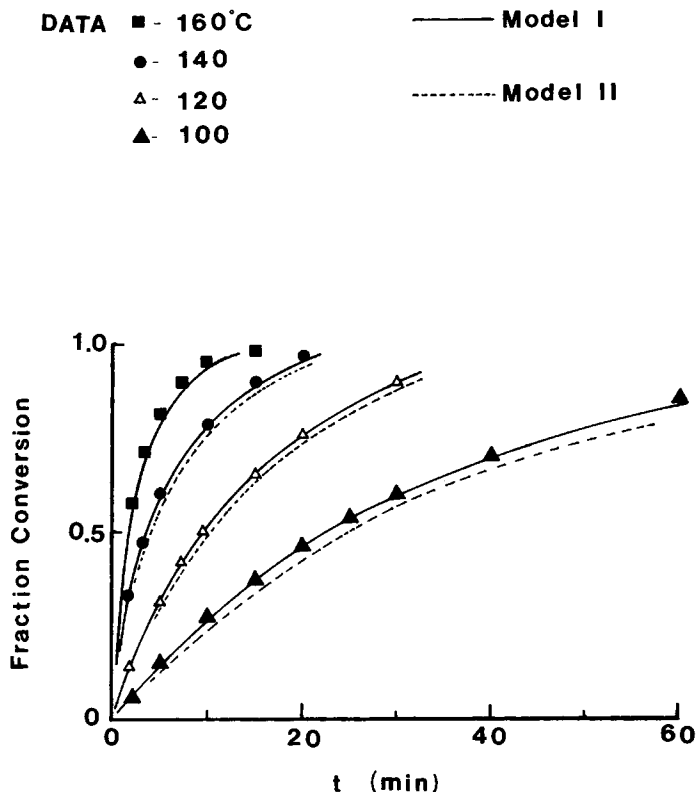
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Fig. 10. Experimental conversion data compared with the kinetic model for the catalyzed DGEBA/TMA (system B) resin.

the reaction order may be gradual, and it is assumed that there is a step change at a certain fractional conversion from second order to first order.

Figure 12 shows the infrared spectrum plotted on the Kubelka–Munk scale as a function of wave number (cm^{-1}) for the uncatalyzed DGEBA/TMA resin system (system A). Peak assignments were in accordance with those for a nadic methyl anhydride-cured DGEBA epoxy system done earlier by Antoon and Koenig.[4]

Figure 13(a) shows the plots of conversion as a function of time. A close comparison with the DSC conversion results shows that the reaction monitored using the FT-IR technique is much faster at the same temperature. A treatment of the data according to the first- and second-order integral forms of the rate expression is shown in Figure 13(b). Apparently, first-order kinetics give a good linear fit of the data, but second-order kinetics deviate significantly from linearity. This indicates that the reaction is not of second-order kinetics, which is contrary to the DSC results that the uncatalyzed DGEBA/TMA reaction was of second-order kinetics.

The discrepancy was later found to be caused by a catalytic effect of the KBr powder used as a substrate of the resins in the FT-IR diffuse reflectance experiments. Although the resin (system A) did not contain the onium salt,
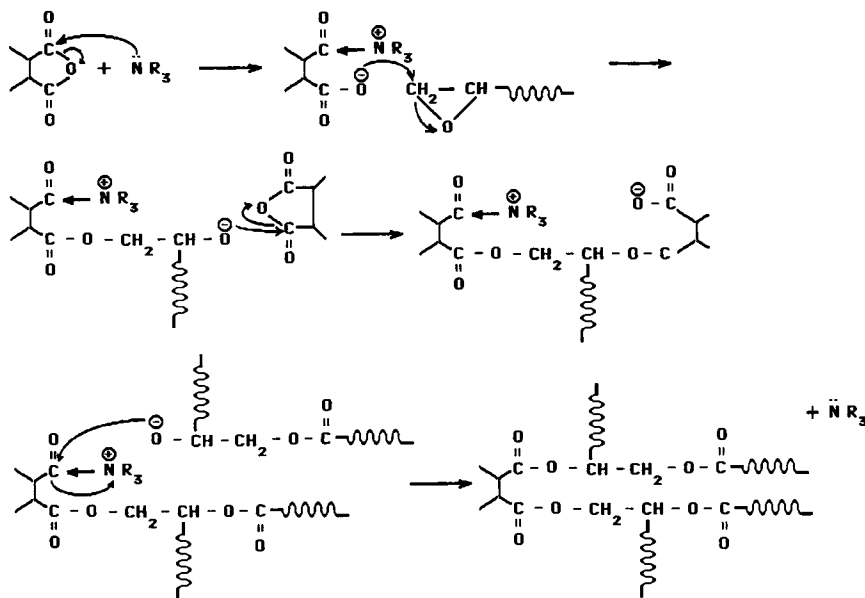
Fig. 11.   General mechanism of catalyzed cure reaction of epoxy/anhydride in presence of a tertiary amine accelerator.

the KBr powder might act as a catalyst and, as a result, the epoxy cure reaction followed a catalytic first-order reaction, rather than an uncatalyzed reaction. The catalytic effect of KBr powder on the cure reaction of the DGEBA/TMA system exemplified by the FT-IR results was further substantiated by DSC characterization of the DGEBA/TMA/KBr powder mixture used in the FT-
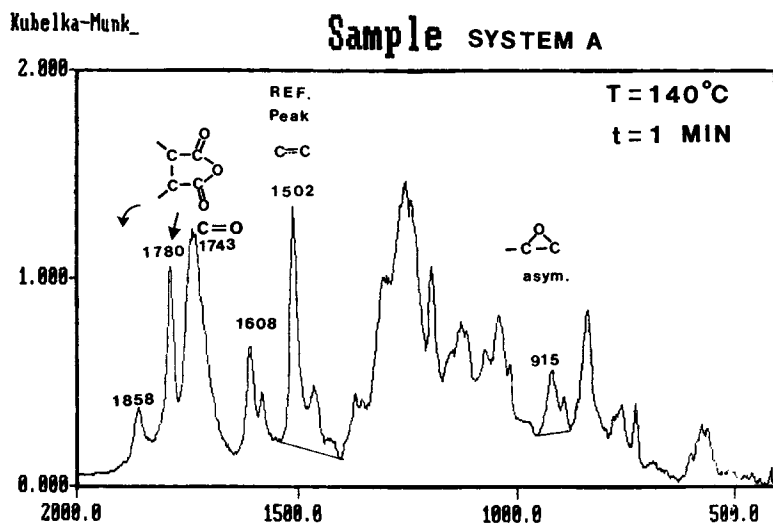

Fig. 12.   Typical FT-IR spectrum of DGEBA/TMA resin (T = 140°C, t = 1 min).
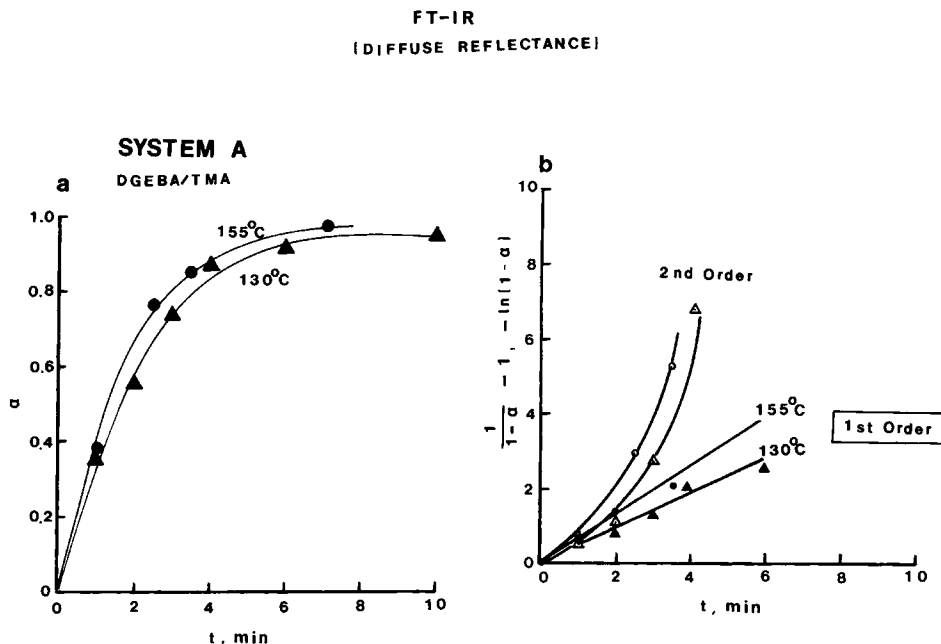
FT-IR
(DIFFUSE REFLECTANCE)

Fig. 13.   FT-IR results of isothermal cure reaction of DGEBA/TMA: (a) conversion time plot;
(b) first- and second-order plots.

IR experiment. Additionally, the time span of the critical early stage of the reaction was too short for FT-IR to acquire reaction data at sufficient number of time intervals for accurate analysis. This was because the KBr-catalyzed epoxy cure reaction was fast and reached a high conversion in relatively short time. Additionally, it would take a minute to complete a 32-scan spectrum at a 4 cm^{-1} resolution. As a result, the spectrum obtained was an average in the time interval of one minute rather than at a specific time. Due to these considerations, it was decided not to further utilize the FT-IR technique for the kinetics study.

Effect of Styrene on Epoxy Cure

Figure 14 shows the DSC characterization at a heating rate of 5°C/min on the styrene-modified epoxy resin (system C). Curve a of the figure shows the DSC thermogram of the resin cured with 30 phr of TMA, while curves b, c, and d are the DSC thermograms of the styrene/epoxy resins cured with 20, 15, and 10 phr TMA, respectively. More DSC results also concluded that the reaction exotherms exhibit only one peak when the TMA concentrations are equal or greater than 30 phr. For the resins cured with TMA below 30 phr, the DSC thermograms show a shoulder peak at the higher-temperature side of the main peak. The shoulder peak eventually separates completely as an independent peak when the concentration of TMA is 10 phr or lower. Note that the height and area of the main peak at the lower-temperature side decrease as the concentration of TMA decreases. It was concluded that the main peak is as-
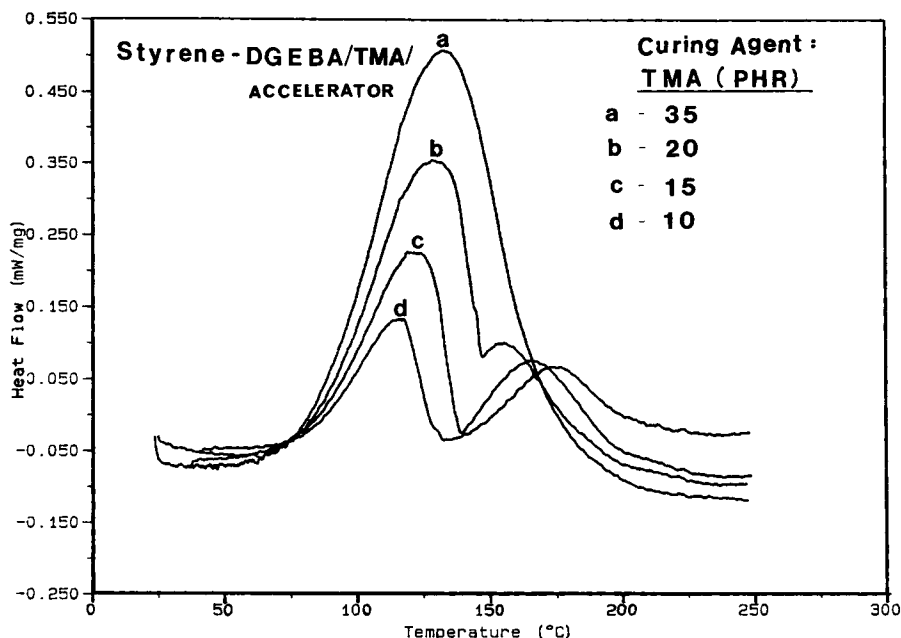
Fig. 14. DSC thermograms for the styrene-modified epoxy resin cured with anhydride concentrations: (a) 35 phr; (b) 20 phr; (c) 15 phr; (d) 10 phr.

sociated with the epoxy curing, and the shoulder peak at the higher-temperature side is associated with polymerization of the styrene monomer.

Figure 15 shows DSC thermograms of the epoxy cured with 35 phr of TMA at three different heating rates of DSC scanning. Only a single peak can be observed if the heating rate is 5°C/min or higher. There are two peaks, though not completely resolved, in the DSC traces at lower heating rates of 1–2.5°C/min. The DSC results using different heating rates demonstrated that the reaction exothermic peak may be a superposition of two different reaction peaks, one being of the epoxy curing at a lower temperature and the other being the styrene polymerization at a higher temperature. Due to the superposition of reaction peaks for resins cured with the stoichiometric quantity of TMA (35 phr), it was not possible to compare the heats of reaction of epoxy cure with or without the presence of the styrene additive.

Figure 16 shows the DSC thermograms for the system C samples (curve a) and the system B samples (curve b), both being cured with 10 phr of TMA. For the styrene-modified epoxy resin, there are two well-separated peaks (one at 110°C and the other at 170°C), while the styrene-free epoxy sample exhibits only one peak at 110°C, which undoubtedly is the epoxy cure exotherm. These two reactions seem to be quite independent of each other. An integration of the peaks at 110°C shows that the heat of reaction for the system B sample is 106 J/g, which is comparable to the heat of reaction (102 J/g) for the system C sample. The system C sample was then scanned to 125°C to complete the first peak, presumably the epoxy curing. Curve c is the DSC trace for the same system C sample on the second scan. The disappearance of the first peak on
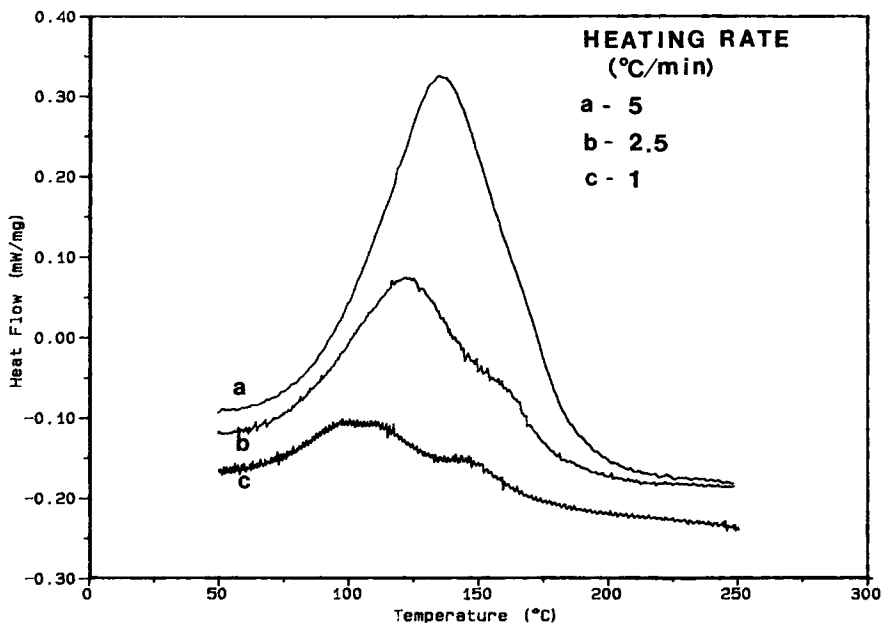
Fig. 15. DSC reaction exotherms of catalyzed styrene/DGEBA/TMA resin (system C) at various heating rate: (a) 5°C/min; (b) 2.5°C/min; (c) 1°C/min.

second scan suggested that reaction associated with the first peak was essentially completed by the time the sample was scanned to 120°C. The remaining peak has the same temperature at the maximum as the second peak in curve a, and the heats of reaction as represented by the peak areas are also comparable.

In summary, these results suggested that styrene polymerization and epoxy curing reaction are independent from one another and that the second peak at a higher temperature is associated with styrene polymerization. There may be some grafting of polystyrene blocks onto the crosslinked epoxy segments. However, the reaction associated with grafting is of much lesser extent compared to that of polymerization. The styrene polymerization was found to occur significantly only at the later stage of the cure reaction, almost near the gelation point of the epoxy matrix. It therefore had no apparent effect on the cure reaction of the epoxy component. Since the kinetic models were derived for the epoxy resin reaction prior to gelation, it could be concluded that the models are applicable to the styrene-modified resin formulations as the styrene does not react significantly before the gelation of the epoxy formulation.

CONCLUSION

Kinetics of anhydride-cured DGEBA epoxy systems with or without a catalyst and a reactive styrene diluent have been investigated using the DSC and FT-IR techniques. The DSC results indicated no evidence of autocatalysis for the uncatalyzed DGEBA/TMA system or catalyzed resin systems. The nth-order
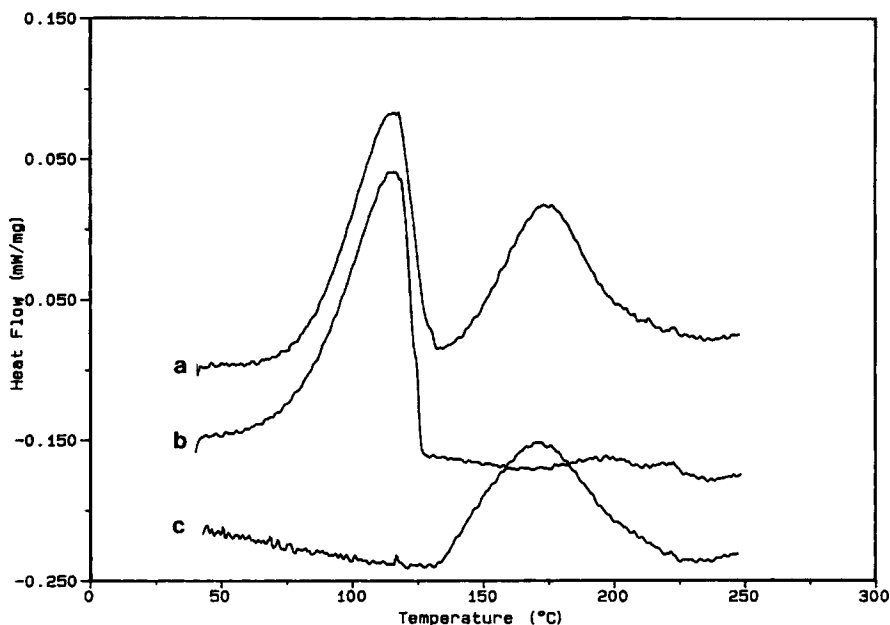
Fig. 16.   DSC thermograms of various resin systems: (a) catalyzed styrene/DGEBA/TMA; (b) catalyzed DGEBA/TMA; (c) second scan of the sample in (a).

kinetics were found to describe well all the resin systems. Specifically, the uncatalyzed DGEBA/TMA resin system was found to follow second-order kinetics. By comparison, the catalyzed resin system exhibited second-order kinetics at low conversions and shifted to first-order kinetics at fractional conversions higher than 0.3. The activation energies for both were found to be between 11 and 12.5 kcal/mol, which are slightly lower than the activation energies reported for DGEBA epoxy systems cured with amines or other anhydrides. The accelerator was found to enhance the ring opening of the anhydride groups of the TMA curing agent. The mechanism of acceleration by the quaternary ammonium salt was observed to be similar to that usually found with a tertiary amine. In the FT-IR study, it was discovered that the KBr (potassium bromide) powder had a similar catalytic effect as the onium salt of bromide. Styrene additive to the epoxy formulations was found to have little effect on the epoxy cure reactions. For this reason, the kinetic rate expressions derived for the anhydride-cured epoxy resin systems without the styrene additive are also applicable to the styrene-modified epoxy resin formulations.

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