A Study on Isothermal Cure Behavior of an Epoxy-Rich/Anhydride System by Differential Scanning Calorimetry

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ABSTRACT: Cure behavior of a catalyzed epoxy/anhydride system was investigated for an epoxy-rich formulation using differential scanning calorimetry (DSC). The mixture was isothermally cured at different times and temperatures, and the cure behavior of the samples was analyzed by the peak exothermic temperature (T_{peak}) and the extent of cure reaction (X) from DSC thermograms. For the excess epoxy sample, two exothermic peaks at a low temperature from esterification reaction and at a high temperature from etherification on DSC curves appeared in the early stage of cure and shifted to a lower temperature scale with curing. However, the esterification peak disappeared and the remaining etherification peak shifted to a higher temperature with further cure. The shift of the peaks may be attributed to the change of reaction mechanism from kinetically controlled to diffusion-controlled. The extent of cure of esterification and etherification was also considered separately in this article. The result shows that esterification reaction mainly occurs in the early stage of cure and then etherification slowly proceeds after the completion of the esterification. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1101–1108, 1998

Key words: epoxy; anhydride; imidazole; exotherm; esterification; etherification

INTRODUCTION

The cure process of various epoxy resin–hardener systems has been extensively studied by many workers.[1–7] In the previous article,[8] we investigated the cure behavior of diglycidyl ether of bisphenol-A (DGEBA) with methyltetrahydrophthalic anhydride (MTHPA) in the presence of 1-cyanoethyl-2-ethyl-4-methyl imidazole (2E4MZ-CN) as a catalyst. Samples with stoichiometric and epoxy-rich formulations were isothermally cured at various cure temperatures (T_{cure}) for different cure times. The parameter to analyze the cure behavior of the samples was the glass transition temperature (T_g), determined by differential

scanning calorimetry (DSC). One of the results for the variation of the T_g with cure time in the excess epoxy system is shown in Figure 1.[8] This figure shows that the T_g gradually increases with cure time and the increase levels off after an extended length of time. Plateaus, which do not clearly appear in a stoichiometric ratio, are observed at $T_g = \sim 80°C$ for all cure temperatures. Isothermal vitrification times (t_v) determined at $T_g = T_{cure}$ and marked by arrows for the cure temperatures of 75, 85, 95, and 105°C were 235, 210, 130, and 83 min in this figure, respectively.

Normally, the epoxy/anhydride reaction is so slow that a small amount of accelerators such as tertiary amines or imidazoles is added to speed up the cure process. It is known that esterification and etherification are the principal curing reactions in the catalyzed system. Although the conflicting cure mechanisms are reported,[9–13] the most recent reaction scheme[14] is represented in
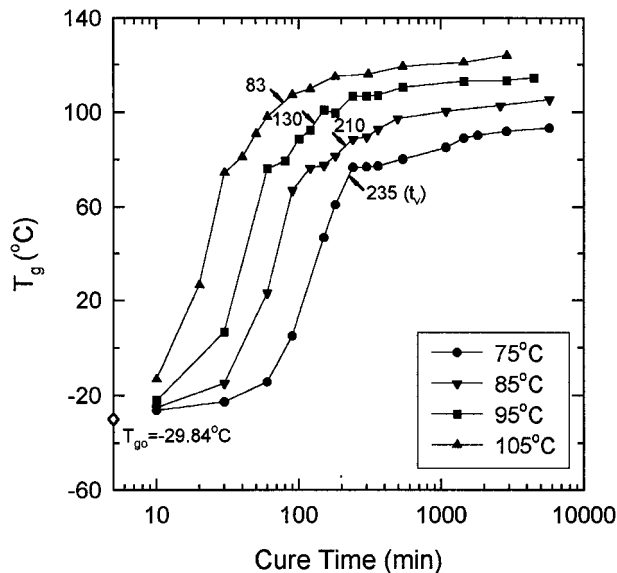
Figure 1 T_g versus cure time of samples cured at various cure temperatures. Isothermal vitrification times (t_v) at $T_g = T_{cure}$ for different cure temperatures are marked by arrows. T_{go} is the glass transition temperature of an uncured sample.

Figure 2. Initiation of the cure involves the reaction of the epoxy group with the tertiary amine, producing a zwitterion [reaction (1)]. An alkoxide

anion from the epoxy backbone reacts with the anhydride to give a monoester [reaction (2)], which reacts with an epoxy group to give the diester [reaction (3)]. Reaction (4) is an epoxy homopolymerization which is a competing reaction of the epoxy with an alkoxide anion resulting in an ether linkage.

One of the factors influencing the properties of the cured epoxies is epoxy/anhydride composition, and optimum mixing ratios generally are less than the stoichiometric equivalents.[15–19] The etherification reaction, which has been known to be slower than the esterification,[11] is responsible for the optimum cured properties. The esterification reaction is expected for a 1 : 1 stoichiometry of epoxy to anhydride. In this study, the cure behavior of samples with excess epoxy for which more etherification occurs was examined by the variations of the exothermic peak temperature and the extent of cure reaction determined by the area under the peak in the DSC thermograms.
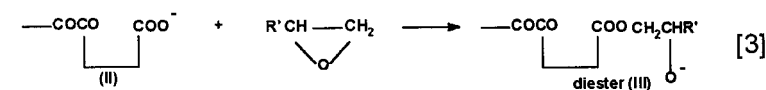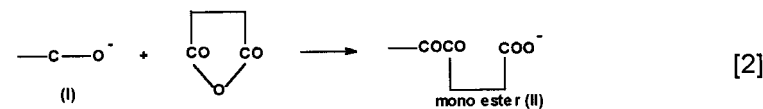
EXPERIMENTAL

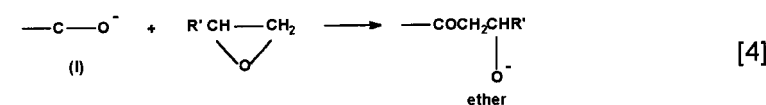A diglycidyl ether of bisphenol-A epoxy resin (Kumoh Shell Chemical Co., Epikote 828, equivalent
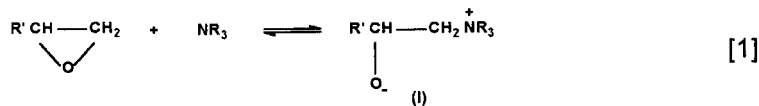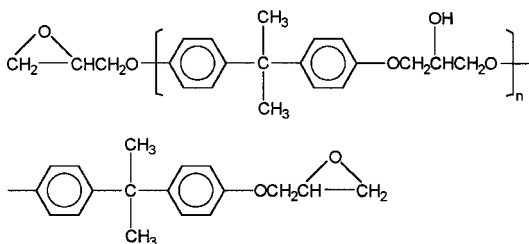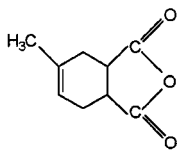

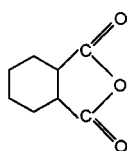**Figure 2** Reaction scheme of a catalyzed epoxy/anhydride system.

Epoxy resin

DGEBA (EEW=186g/mole, n=0.11)

Hardener

MTHPA (methyltetrahydrophthalic anhydride)

HHPA (hexahydrophthalic anhydride)

Accelerator
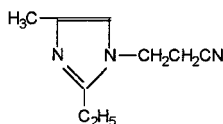
2E4MZ-CN (1-cyanoethyl-2-ethyl-4-metyl imidazole)

Figure 3 Chemical structures of materials used.

weight = 186 g/mol) and a methyltetrahydrophthalic anhydride hardener mixed with 40% hexahydrophthalic anhydride (Lonza Italia, equivalent weight = 161 g/mol) were used in this experiment. The cure reaction was accelerated by 1-cyanoethyl-2-ethyl-4-methyl-imidazole (Shikoku Chemical Co.). The chemical structures of the reactants are represented in Figure 3.

The chemicals were mechanically mixed for 10 min at 40°C to obtain a homogeneous mixture. After mixing, the mixture was immediately stored in a freezer maintained at −70°C to prevent any further reaction. The mixing ratio for the excess epoxy formulation was epoxy/anhydride/accelerator = 100 : 50 : 1.5 by weight. The stoichiometric ratio of this system is epoxy/anhydride = 100 : 90.

Differential scanning calorimetry (DSC, Dupont 910) was employed to observe the peak temperatures on exothermic curves and to measure the area under the curves in this experiment. The initial mixture in a vial was taken out of the freezer and allowed to warm up for ∼ 15 min at room temperature until the condensed moisture on the surface of the vial was completely evaporated. Approximately 10–15 mg of the mixture was put into a DSC hermetic pan and then sealed by crimping. The sealed pan containing the sample was cured in a dry oven at 75, 85, 95, and 105°C for times from 10 min to ∼ 6000 min.

The samples uncured and cured at shorter periods were quenched down to −60°C and then subjected to temperature scans from −60°C to 220°C at a heating rate of 10°C/min. The temperature scans for other samples were made from room temperature to 220°C at the same rate of heating.

RESULTS AND DISCUSSION

A DSC thermogram of an uncured epoxy-rich mixture (epoxy/anhydride/accelerator = 100 : 50 : 1.5) is shown in Figure 4. The thermogram exhibited two exothermic peaks and the glass transition. We denote the peak at a lower temperature the first (P_I), and at a higher temperature the second (P_{II}). It is known that the P_I is due to esterification and the P_{II} to etherification. The area under the peak for the enthapies (ΔH) was determined by drawing a straight base line between the onset and the end of the exotherm in such a way that the base line is tangent to the DSC curve at those two points. Multipeaked thermograms have been observed for uncured epoxy/anhydride systems with imidazole accelerators
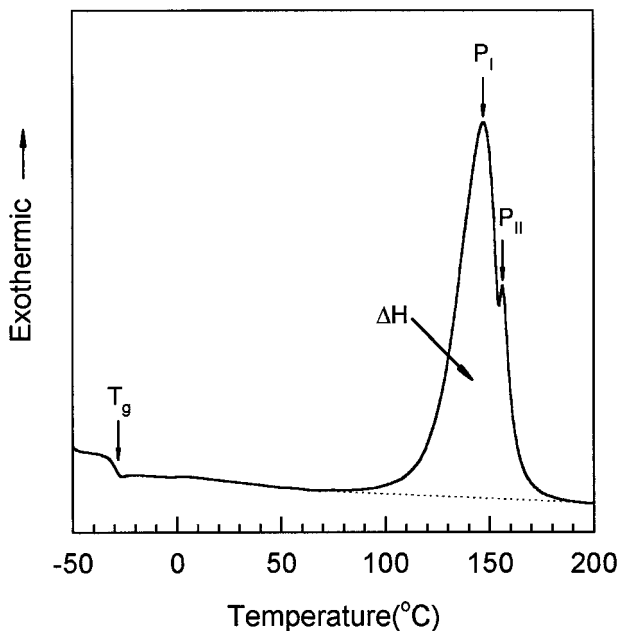
Figure 4 Typical DSC scan showing the T_g and the exotherm for an uncured sample.
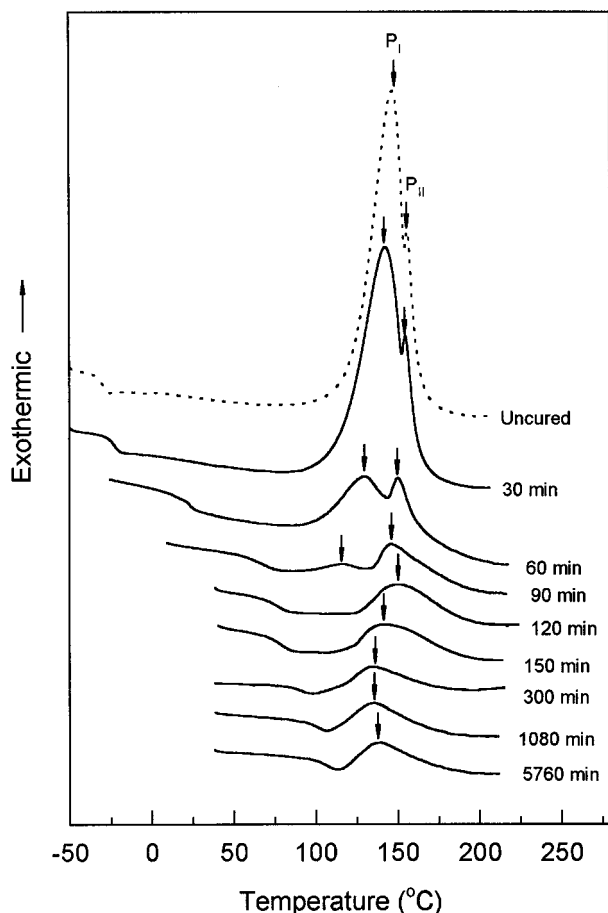
Figure 5 DSC thermograms of samples isothermally cured at 85°C for various cure times.

which were known to be effective for etherification reaction.[15-18] At a stoichiometric ratio, only P_I was observed for an uncured sample, but small P_{II} appeared at the later stage of cure.

DSC studies were also made for the excess epoxy samples isothermally cured at various temperatures for different times. The variations of the peak temperature and the area under the residual exotherms for the partially cured samples were examined. Figure 5 contains DSC thermograms of samples isothermally cured at 85°C for different times, showing the variation of the exotherm and the glass transition. As shown in this figure, the exotherm changes greatly in terms of the peak temperature and the area as cure proceeds. The exothermic peak temperatures are indicated by arrows in this figure.

Exothermic Peak Temperature

In Figure 6, the variations of the peak temperatures (T_{peak}) taken from the exotherms with cure time from Figure 5 are shown for samples cured at cure temperatures of 75, 85, 95, and 105°C. The T_{peak} for the uncured and the cured samples are shown by open and closed triangles (P_I) and squares (P_{II}), respectively. The isothermal vitrification points (t_v) from Figure 1 are indicated by arrows. The variations may be divided into three regions in cure time as shown in Figure 6. The first region (R_I) is where both peaks (P_I and P_{II}) exist simultaneously. Then both peaks are shifted to lower temperatures and the amount of the shift is larger for P_I for all cure temperatures than that for P_{II}. The time range of R_I becomes much smaller at higher cure temperatures (T_{cure}) than that at lower T_{cure}; for example, t_{RI} = 150 min at 75°C and 20 min at 105°C. In the second region (R_{II}), only P_{II} appears as P_I becomes a shoulder or almost disappears. The T_{peak} of P_{II} in this region decreases further with cure time. The time range of R_{II} is reduced greatly at higher T_{cure} than that at lower T_{cure}; that is, t_{RII} = 1280 min at 75°C and 55 min at 105°C. In the final region (R_{III}), where only P_{II} exists, an interesting phenomenon was observed. The T_{peak} of the P_{II} in this region begins to increase with cure time. Although the increase of the T_{peak} at 75°C was not noticeable, the increase becomes larger with increasing cure temperature. The T_{peak} increase at 105°C in the R_{III} is over 20°C. The time between each region and the t_v are listed in Table I.

It is well known that thermosetting resins undergo kinetically controlled and diffusion-controlled curing processes, and the cure reactions become diffusion-controlled after vitrification.[21-22] The decrease of the T_{peak} in the initial stage of cure (R_I and R_{II}), where cure reaction is kinetically controlled, may be due to the relative increase of concentration of accelerator with curing. As the cure proceeds further, the change of reaction mechanism to diffusion-controlled may cause the increase of the T_{peak} of P_{II} in the later cure (R_{III}) because distance between functional groups becomes farther away with cure so that the reaction occurs at a higher temperature. As shown in Figure 6 and Table I, the time at which the P_{II} begins to increase is very close to the t_v except at the cure temperature of 75°C. It means that the increase of the P_{II} is due to the diffusion-controlled reaction in R_{III}.

Extent of Cure

The thermograms in Figure 5 also shows that there are large changes of the areas under the DSC curves during the isothermal curing. In the
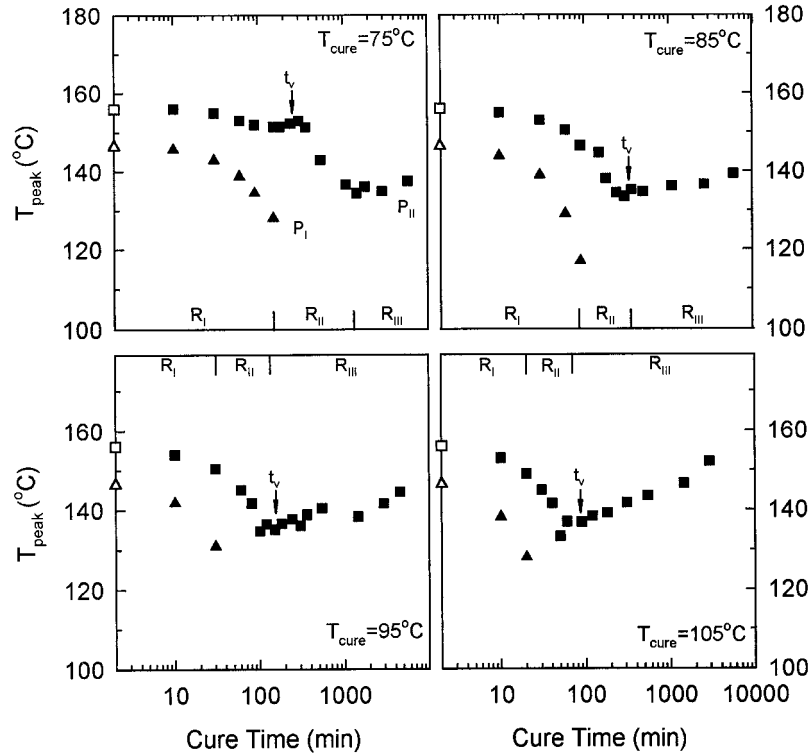
Figure 6 T_{peak} versus cure time of samples cured at various temperatures. Arrowmarks in the figure are the vitrification points.

initial stage of cure (or cured for shorter times like 10, 60, and 90 min), where two exothermic peaks exist on the DSC curve, the area of P_I decreases significantly with cure time, while that of P_{II} hardly changes until the P_I completely disappeared. However, in the later stage (or cured for longer times like 120, 150, 300, 1080, and 5760 min), the area of the remaining second exotherm gradually decreases with further curing. From the changes of the areas, we can estimate the extent of cure (X) during curing. The X was calculated by[23]

$$X = 1 - \frac{\Delta H_r}{\Delta H_T} \qquad (1)$$

Table I   Time Range of the R_I and R_{II} Regions and the Vitrification Time during Isothermal Cure at Different Temperatures

T_{cure} (°C)	t_{RI} (min)	t_{RII} (min)	t_v (min)
75	150	1280	235
85	90	150	210
95	30	120	130
105	20	55	83

where ΔH_r is the residual heat of enthalpy obtained from rescanning the partially cured sample and ΔH_T is the total heat of exothermic reaction for an initially uncured sample. The variations of X with cure time at four different cure temperatures are shown in Figure 7. It can be seen that the X with t_c is made of roughly two linear regions with a transitional region (X_{tr}) between them. The X_{tr} region widens and the temperature of the X_{tr} increases with cure temperature. The X_{tr} region appears to initiate at approximately $T_g = 80$°C, as can be seen in Figure 1. The transition was not observed at a stoichiometric ratio.

Since the main reactions in our epoxy system are esterification and etherification, the total extent of reaction (X) considered above can be separated into the two reactions. The extents of esterification (X_1) and etherification (X_2) were respectively calculated from P_I and P_{II}, appearing on the DSC curve by the following equations:

$$X_1 = 1 - \frac{\Delta H_{r1}}{\Delta H_{T1}} \qquad (2)$$

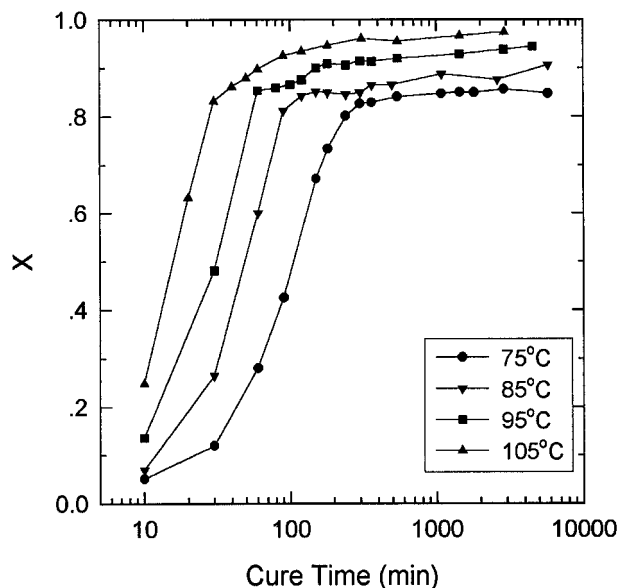$$X_2 = 1 - \frac{\Delta H_{r2}}{\Delta H_{T2}} \qquad (3)$$

Figure 7 X versus cure time of samples cured at various cure temperatures.

In these equations, ΔH_{r1} and ΔH_{r2} are the residual heats for P_{I} and P_{II} of partially cured samples, respectively. ΔH_{T1} and ΔH_{T2} are the total heats for both peaks of an uncured sample. In order to obtain the area of each peak under the double exotherm accurately, it is necessary to separate the overlapped exotherm as clearly as possible. According to Chataing and Vergnaud,[24] an overlapped peak can be separated by slowing the heating rate during dynamic scanning in DSC. Figure 8 shows the effect of heating rate on separation of the double peak exotherm for our uncured sample. As the heating rate decreases from 10 to 2 and 0.5°C/min, the overlapped thermogram was well separated, as shown in this figure. However, the total heat of reaction (ΔH_T) for the uncured samples at the different heating rates in our experiment was nearly unchanged: 305.6, 308.8, and 304.1 J/g for 0.5, 2, and 10°C/min, respectively.

We determined the total heat of reaction for P_{II} (ΔH_{T2}) from the DSC curves at the heating rate of 0.5°C/min by using a commercial fitting program (Jandel Scientific PeakFit, V2.01, AISN Software, USA, 1990). The ΔH_{T2} obtained in this method was 56.2 J/g. Therefore, the total heat for P_{I} (ΔH_{T1}) is 305.6 − 56.2 = 249.4 J/g at 0.5°C/min. Since total enthalpies are almost constant at the different heating rates tested, the enthalpy values at 0.5°C/min were used for the calculation of the X_1 and X_2 at 10°C/min. The fitted value of 56.2 J/g (ΔH_{T2}) was
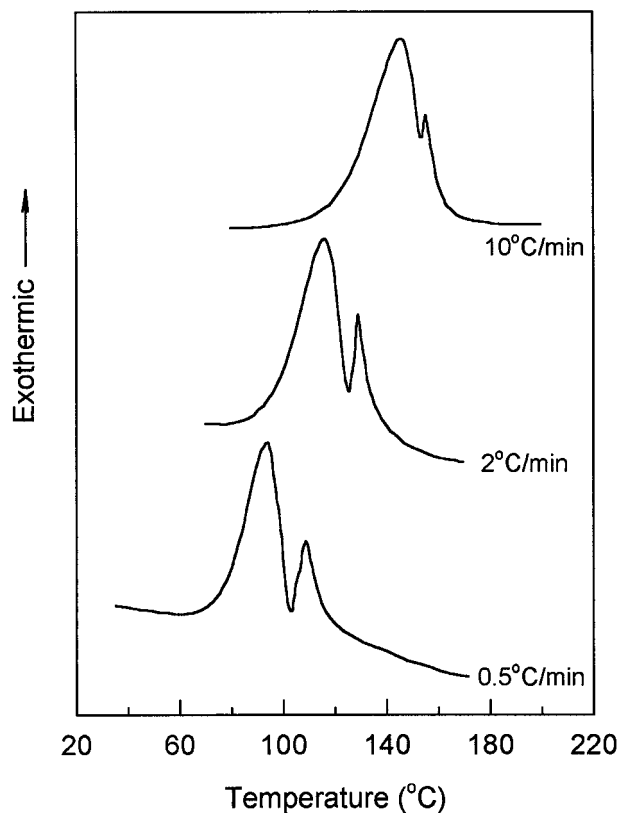

Figure 8 Exotherms for an uncured sample at different heating rates.

used for ΔH_{r2} in obtaining ΔH_{r1} ($=\Delta H_r - \Delta H_{r2}$) as long as double peaks existed. Figure 9 shows the variation of enthalpies for the exotherms with cure
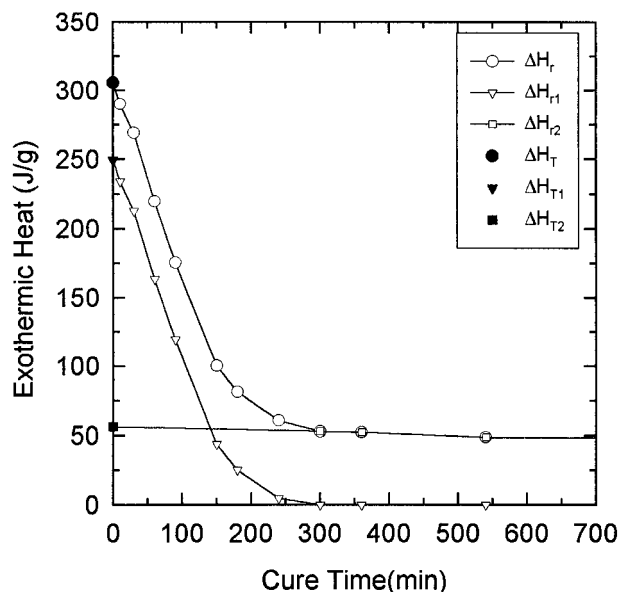

Figure 9 Variation of residual exothermic heats for samples isothermally cured at 75°C.
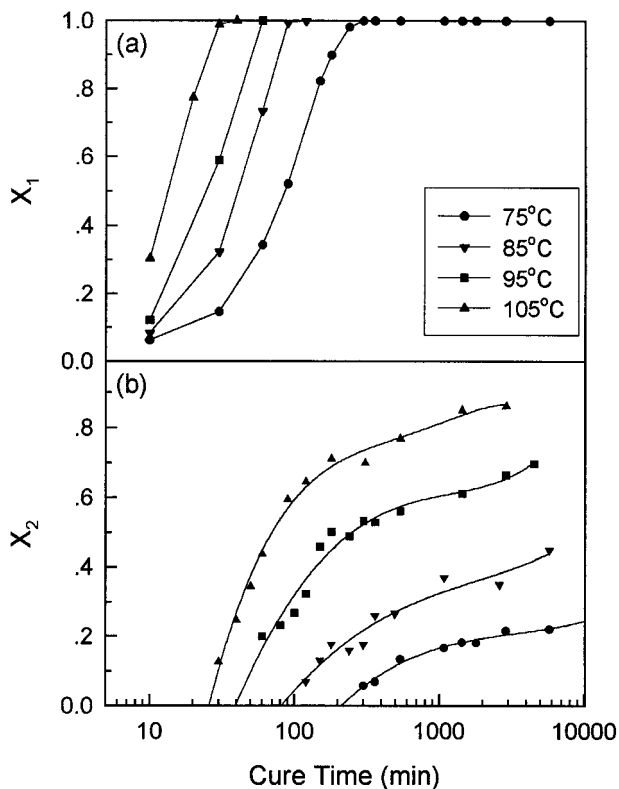
Figure 10 X_1 and X_2 versus cure time of samples cured at various cure temperatures.

time at 75°C. As shown in this figure, ΔH_{r1} decreases rapidly and becomes zero at 300 min, while ΔH_{r2} continues to decrease slowly.

The separate extents of reactions from esterification (X_1) and etherification (X_2) with cure time obtained by eqs. (2) and (3) were respectively plotted in Figure 10(a) and (b). Figure 10(a) shows that, for all cure temperatures, X_1 rapidly increases with cure time and the cure goes to completion at various times. The times for completion of the esterification reaction were 300, 120, 60, and 40 min for 75, 85, 95, and 105°C, respectively. As in Figure 10(b), X_2 begins to increase very slowly after the esterification is complete. The X_2 increases up to 0.2, 0.5, 0.7, and 0.9 for 75, 85, 95, and 105°C after long times, respectively. Therefore, isothermal cure in our epoxy system proceeds mainly through a fast esterification reaction in the early stage of cure, followed by slow etherification.

CONCLUSIONS

The isothermal cure behavior of an epoxy/anhydride/imidazole system rich in epoxy was investi-

gated by the peak exothermic temperature and the area under the exotherm using DSC. An uncured epoxy-rich sample showed a double exotherm (the first peak at a low temperature and the second at a high temperature) during dynamic scanning. In the initial stage of the isothermal cure, the two peaks on DSC thermograms shifted to a lower temperature scale with cure time. As the cure proceeded, the first peak disappeared and only the second remained. The peak temperature of the remaining second peak decreased further with time. The decrease may be due to the relative increase of concentration of the accelerator in a kinetically controlled region. In the later stage of the cure, the change of cure reaction mechanism to a diffusion-controlled reaction with curing caused the increase of the second peak.

According to the variations of enthalpy values, esterification reaction mainly occurs with almost no etherification in the beginning stage of cure and then etherification takes place very slowly compared to the esterification. In the extent of reaction versus cure time curves, there are roughly two linear regions with a transitional region between them. The transition region widens and the temperature of the region increases with cure temperature. The transition appears to initiate at approximately $T_g = 80°C$.

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