Cure Behavior of an Epoxy-Anhydride-Imidazole System

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ABSTRACT: The cure behavior of an epoxy-anhydride system with one of imidazole derivatives as an accelerator was investigated for both stoichiometric and epoxy-rich formulations. The mixtures were isothermally cured for different times at various temperatures, and the glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC). There was a considerable increase in the T_g during curing, and master curves were formed by shifting and superposing the T_g vs. cure time curves. The activation energies obtained by the shift were $15.2 \text{ kcal mol}^{-1}$ and $16.5 \text{ kcal mol}^{-1}$ for the stoichiometric and epoxy-rich systems, respectively. For the epoxy-rich one, plateaus were observed on the T_g vs. cure time curves, and two exothermic peaks appeared on DSC curves in the early stage of cure and became one thereafter. This phenomenon is related to the competitive reactions between esterification and etherification reactions. We found that the maximum T_g s were 80°C for esterification and 125°C for etherification in the excess epoxy system.

KEY WORDS Epoxy / Anhydride / Imidazole / Glass Transition Temperature / Esterification / Etherification /

During curing of thermosetting materials, low molecular liquids are transformed to high molecular solids by chemical reactions. As the cure proceeds, there is a considerable increase in the glass transition temperature (T_g). It is known that the T_g can be used as a measure of chemical conversion, especially, in the later stages of cure, where the T_g changes more sensitively with conversion.¹ Variation of T_g with cure time has been studied for dicyanate ester-polycyanurate^{2,3} and epoxy-amine systems.^{1,4,5} Since T_g is an important parameter in analyzing cure behavior, we examined the variation of T_g in the relation to the cure reaction mechanisms for a catalyzed epoxy-anhydride system.

It is known that catalyzed reaction of epoxy resins with anhydrides proceeds through two principal curing reactions; esterification and etherification. Although the conflicting initiation mechanisms are reported,^{6–8} the initiation of epoxy group by tertiary amine produces a zwitterion as in eq 1.⁹

An alkoxide anion from the epoxy backbone reacts with the anhydride to give a monoester (eq 2), which reacts with an epoxy group to give the diester (eq 3). A competing reaction is the epoxy with an alkoxide anion resulting in an ether linkage (eq 4).

The etherification reaction of an epoxy with alkoxide anion has been known to be slower than the esterification reaction of alkoxide anion with anhydride or carboxylate anion with epoxy.^{10,11} Etherification of epoxy resins in epoxy-amine curing systems has already been reported by many researchers.^{4,5,12}

EXPERIMENTAL

Materials

Epoxy resin for this study was a diglycidyl ether of bisphenol A (DGEBA) (Kumho Shell Chemical Co., Epikote 828, equivalent weight = 186 g mol^{-1}). It was cured with a mixture of methyltetrahydrophthalic anhydride (MTHPA) and hexahydrophthalic anhydride (HHPA) (Lonza Italia, equivalent weight = 161 g mol^{-1} , mixing ratio by weight = 6/4) as a hardener in the presence of a 1-cyanoethyl-2-ethyl-4-methyl imidazole (2E4MZ-CN, shikoku Chemicals Co.) as an accelerator. The chemical structures of the reactants are shown in Figure 1.

The chemicals were mechanically well mixed for 10 min at 40°C to obtain a homogeneous mixture. After mixing, the mixture was immediately stored in a refrigerator maintained at -70°C to prevent any further reaction. The compositions of the epoxy/anhydride/imidazole by weight were 100/90/1.5 (I) for a stoichiometric ratio, and 100/50/1.5 (II) for an epoxy-excess formulation.

Cure Monitoring Technique

Differential scanning calorimetry (DSC, Du Pont 910)

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Epoxy resin

DGEBA ($n=0.11$)

Hardener

MTHPA

HHPA

Accelerator

2E4MZ-CN

Figure 1. Chemical formulae of the reactants.

was employed to measure T_g in this experiment. The initial mixture in a vial was taken out of a refrigerator, and allowed around 15 min at room temperature until the condensed moisture on the surface of the vial with the cold material 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 with sample was isothermally cured in dry oven for prespecified periods (10 min to 72 h) at different cure temperatures.

The cure temperatures in this study were 60, 75, 90, 105, 120°C for sample (I), and 75, 85, 95, 105°C for sample (II). The samples uncured or cured at shorter periods were quenched down to -60°C and then subjected to temperature scans from -60°C to 220°C at $10^\circ\text{C min}^{-1}$. Temperature scans for other samples were from room temperature to 220°C at the same rate of heating. From these scans, we are able to determine T_g and examine residual exothermic peaks by cure reactions.

The T_g appeared as an endothermic shift over a temperature interval in the DSC scan. When an endothermic peak was developed during the first scanning up through T_g , the peak was eliminated and obtained a stepwise transition by heating the samples to just above the endothermic peak, followed by quenching to room temperature at $30^\circ\text{C min}^{-1}$ in the DSC cell. Similar methods were used for same purpose.^{1,13} Then the samples were reheated to 220°C . In this study, T_g was taken as the inflection point of the step-transition.

Figure 2. T_g vs. cure time of samples at various temperatures for a stoichiometric ratio. Figure 3. T_g vs. cure time of samples at various temperatures for an epoxy-rich formulation.

RESULTS AND DISCUSSION

The glass transition temperature (T_g) of samples cured at various times and temperatures for stoichiometric (I) and epoxy-rich (II) systems was measured and shown in Figures 2 and 3, respectively. The T_g s of uncured samples (T_{g0}) were -37°C for sample (I) and -29°C for sample (II) as marked by arrows in the figures. Since the viscosity of epoxy resin is higher than that of anhydride in our experiment, the higher T_g of sample (II) is due to the larger ratio of epoxy resin in the sample. The T_g increases up to above 120°C for sample (I) cured at 120°C for 70 min and sample (II) cured at 105°C for 400 min. The increase of the T_g levels off at long times, indicating the completion of cure reaction. The trend of the T_g increase in these figures has an S-shape as in other thermosetting systems.^{1,4} With increasing the cure temperature, the S-shaped curves shift to shorter time scales. In Figure 3 for the excess epoxy sample (II), we can observe plateaus at around $T_g = 80^\circ\text{C}$ for all samples, which become more distinct at lower temperatures. This phenomenon has also been observed in an epoxy-amine system,⁵ which will be discussed later in this study.

Figure 4. Superposition of the T_g vs. $\ln(\text{time})$ curves to form a master curve for a stoichiometric ratio ($T_r = 90^\circ\text{C}$).

Figure 5. Superposition of the T_g vs. $\ln(\text{time})$ curves to form a master curve for an epoxy-rich formulation ($T_r = 85^\circ\text{C}$).

The T_g vs. $\ln(\text{time})$ curves shown in Figures 2 and 3 were time-temperature shifted horizontally and master curves were formed at the initial stage of cure. The master curves are shown in Figures 4 and 5 at selected reference temperatures, 90°C and 85°C , respectively.

The reaction rate in a kinetically controlled region is expressed by the following Arrhenius rate equation:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_a}{RT_c}\right) f(\alpha) \quad (5)$$

where E_a is the apparent activation energy for the overall reaction, T_c is the cure temperature, and $f(\alpha)$ is a function of conversion (α) which is independent of temperature. By rearranging and integrating eq 5, we obtain

$$\ln \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \ln A + \ln t - \frac{E_a}{RT_c} \quad (6)$$

Since there is a unique relationship between α and T_g , eq 6 may be written as:

$$F(T_g) = \ln A + \ln t - \frac{E_a}{RT_c} \quad (7)$$

At the arbitrary reference temperature (T_r), eq 7 becomes

Figure 6. Arrhenius plot of the shift factors.

Table I. Activation energies for epoxy systems obtained by T_g -shift

Materials	Activation energy (kcal mol ⁻¹)	Reference
DGEBA-TMAB ^a	15.2	5
Epoxy Novolac-DDS ^b	14.6	4
DGEBA-anhydride-imidazole		
100/90/1.5	15.2	This work
100/50/1.5	16.5	This work

^a TMAB, trimethylene glycol di-*p*-aminobenzoate. ^b DDS, 4,4'-diaminodiphenylsulfone.

$$F(T_g) = \ln A + \ln t_r - \frac{E_a}{RT_r} \quad (8)$$

By subtracting eq 7 from eq 8, a shift factor ($a(T)$) may be calculated as follows:

$$a(T) = \ln t_r - \ln t = \left(-\frac{E_a}{R}\right) \left(\frac{1}{T_c} - \frac{1}{T_r}\right) \quad (9)$$

Plotting the shift factors used to form the master curves for both mixtures as a function of reciprocal temperature gives a straight line with a slope, $-E_a/R$, as shown in Figure 6. The apparent activation energy can be determined from eq 9. In this study, the activation energies calculated were $15.2 \text{ kcal mol}^{-1}$ and $16.5 \text{ kcal mol}^{-1}$ for samples (I) and (II), respectively. Table I contains the apparent activation energies obtained by the time-temperature shift of T_g with the values for other systems. It is considered that the higher value in sample (II) may indicate the slower rate of reaction involved.

In Figure 7, residual exothermic peaks above T_g on DSC curves were shown for the excess epoxy samples isothermally cured at different times (90, 150, 300, 540, 5760 min) at 75°C . In the initial stage of cure (90 and 150 min), there exist two exothermic peaks on the DSC curve. However, the area of the first peak decreases significantly with cure time, while that of the second hardly changes until the first one completely disappeared. In the later stage (300, 540, and 5760 min), the area of the remaining second exotherm decreases with further curing. This variation of the peaks may be due to two different cure reactions, esterification and etherification.

Figure 7. DSC scans of samples cured at 75°C for various cure times for an epoxy-rich formulation.

Figure 8. Comparison of DSC scans for epoxy-imidazole (a) and excess epoxy-anhydride-imidazole (b) systems.

During the whole curing process, the peak positions tend to shift lower temperatures. The temperature of the second peak after curing for 5760 min decreased almost down to that of the first peak in the early stage of cure.

Since it is known that the dominant reaction in an epoxy-imidazole system is etherification,^{14,15} a dynamic temperature scan was made for the epoxy resin having only imidazole (2E4MZ-CN) without anhydride by DSC. From this experiment we may figure out the reaction mechanism in the excess epoxy-anhydride-imidazole system. The mixing ratio for this test was epoxy/imidazole = 100/1.5 and the procedure for making the sample was same as the other mixtures. The DSC scans of uncured samples for the epoxy-imidazole and epoxy-rich systems are shown in Figure 8. The T_g in the epoxy-imidazole system was -13°C which is higher than that in the epoxy-rich system. This is simply because the epoxy-imidazole sample has no anhydride. And in the epoxy-imidazole system only one exothermic peak appeared at 152°C . This temperature nearly corresponds

to the peak temperature of the second exotherm in the epoxy-rich system as marked by arrows. It means that the cure reaction mechanism of the epoxy-imidazole system is identical with that of the epoxy-rich formulation at the second peak.

As a result, the first peak on the DSC curve is due to esterification reaction and the second to etherification reaction in Figure 7. Therefore, in the epoxy-rich system, the cure proceeds mainly by esterification in the beginning of cure followed by etherification until reaction is stopped. From the observation of the exotherms of DSC curves near the plateau region in Figure 3, the plateau at around 80°C is closely related to the change of reaction mechanisms from esterification to etherification. In other words, the increase of the T_g up to the plateau corresponds to the completion of esterification, and the further increase of the T_g to etherification. At higher temperatures, the larger amount of etherification reaction causes the T_g increase up to 125°C . In our laboratory, experiments are being carried out to identify the change of the reaction mechanisms by means of Fourier Transform Infra-Red Spectroscopy.

CONCLUSIONS

In order to study the cure behavior of an epoxy-anhydride-imidazole system, variation of T_g for two mixtures, one a stoichiometric and the other an epoxy-rich, was examined using differential scanning calorimetry (DSC). There was a great increase in the T_g during curing for both systems. Activation energies obtained in this experiment by the time-temperature shift were 15.2 and $16.5\text{ kcal mol}^{-1}$ for the stoichiometric and epoxy-rich formulations, respectively.

For the excess epoxy system, plateaus were observed on the T_g vs. cure time curves, which becomes more clear as cure temperature is lower. This can be explained by the residual exotherms from DSC scans. There were two exothermic peaks on the DSC curves initially. As the cure proceeds, the area of the first peak decreases first and then that of the second steadily decreases. The variation of the peaks is closely related to the competitive reactions between esterification for the first peak and etherification for the second. From the observation of the peak variation, the etherification becomes significant after esterification reaction is nearly depleted. Therefore, the increase of T_g up to the plateau observed at about 80°C in the T_g vs. cure time curves corresponds to the completion of esterification, and the further increase of the T_g is due to etherification. At higher temperatures, the larger amount of etherification reaction occurs and induces the increase of the T_g up to 125°C .

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