Effects of Heat Treatment on Dynamic Mechanical Properties of Nonstoichiometric, Amine-Cured Epoxy Resins

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Synopsis

Epoxy resins cured with diethylenetriamine (37%–103% of stoichiometric composition) were heat treated at 120°C, and the dynamic elastic modulus and internal friction of the specimens were measured over the range of 85°–300°K. Results indicate that heat treatment causes the dynamic modulus to decrease at 85°K and at room temperature, but to increase over the region 150°–200°K. The γ- ($\sim$150°K) and β- ($\sim$250°K) peaks merge into a single broad peak with heat treatment, and a β'-peak is observed in the heat-treated samples. Effects of heat treatment also depend upon the amount of diethylenetriamine used.

INTRODUCTION

In most previous work on the dynamic mechanical properties of epoxy resins, the curing agent/resin ratio was stoichiometric or the samples were heat treated above room temperature. Earlier studies in this laboratory[1] examined the dynamic mechanical properties of a diglycidyl ether of bisphenol A (Shell Epon 828) cured at room temperature with a range of nonstoichiometric concentrations of diethylenetriamine (DETA). This was the first step in a program to investigate the separate effects of room-temperature curing and subsequent heat treatment.

It is well known[2] that heat treatment has important effects on the structural features of polymers and leads to changes in thier dynamic mechanical properties. Effects of heat treatment on dynamic mechanical properties have been reported by others,[3–6] but they are not well understood. The present experiments examine the effects of heat treatment at 120°C on the dynamic elastic modulus and internal friction of the room temperature-cured, nonstoichiometric epoxy/DETA formulations of the previous study.

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EXPERIMENTAL

Sample Preparation and Dynamic Mechanical Measurements

Since these procedures have been described in detail in the preceding publication,[1] only a brief description is given here. The basic molecular structure of the resin is given in Table I along with the test conditions.

TABLE I
Sample Preparation and Test Conditions

Epoxy resin: Epon 828 (diglycidyl ether of bisphenol A; Shell Chemical Co.)
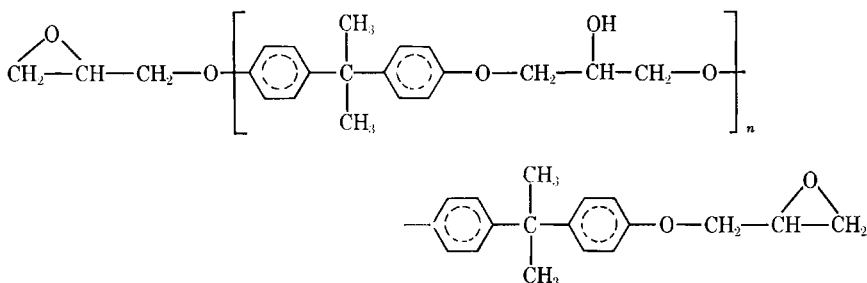
Epoxide equivalent: 185
Curing agent: diethylenetriamine (DETA; a room-temperature curing agent)

$$H_2N—CH_2—CH_2—NH—CH_2—CH_2—NH_2$$

Amounts of curing agent: 4.1–11.5 phr (37–103% of stoichiometric composition, SC)
Curing conditions: room temperature for more than 4 months
Apparatus: a free-free bar design (Förster method)[7]
Sample configuration: rod ($\sim$ 0.8 cm in diameter, $\sim$11 cm in length)
Vibration mode: fundamental transverse vibration
Frequency range: 700–2000 Hz
Temperature range: 85°–300°K

The dynamic elastic modulus E' (dynes/cm²), determined by a flexural resonance method,[7] was calculated from the resonant frequency f_r (Hz) by the relation

$$E' = 1.606 \left(\frac{L}{a}\right)^4 \frac{W}{L} f_r^2 \qquad (1)$$

where L, a, and W are, respectively, the specimen length (cm), diameter (cm), and mass (g). The internal friction Q^{-1} was determined from the relation

$$Q^{-1} = \Delta f/f_r \qquad (2)$$

where Δf is the 3-db frequency separation (the bandwidth at the half-power level of the amplitude-vs.-frequency curve).

Heat Treatment

Specimens prepared in glass tubes of 8-mm diameter, as in the previous study,[1] were cured at room temperature for four months or more. Then they were heated at a temperature of 120°C at $\sim10^{-2}$ torr in a vacuum furnace. The heating rate from 40° to 120°C was 4 C°/min, while the cooling rate from 120° to 60°C was 0.7 C°/min.

Samples were heat treated during the heating and cooling cycles in addition to the time at 120°C. Heat-treatment effects during the heating and cooling cycles have been estimated to correspond to additional heat treatment at 120°C for 1 hr. Thus, 1 hr was added to the heat-treatment time for each heat-treatment cycle. Most of the samples were heat treated for 25 hr at 120°C; however, some samples (with 44%, 59%, and 103% stoichiometric concentration of DETA) were given heat treatments of from 1.1 to 1210 hr.

RESULTS

The Effect of Heat-Treatment Time on the Dynamic Elastic Modulus

Figures 1 and 2 show the dynamic elastic modulus at room temperature of samples heated for up to 1210 hr at 120°C. We have abbreviated heat
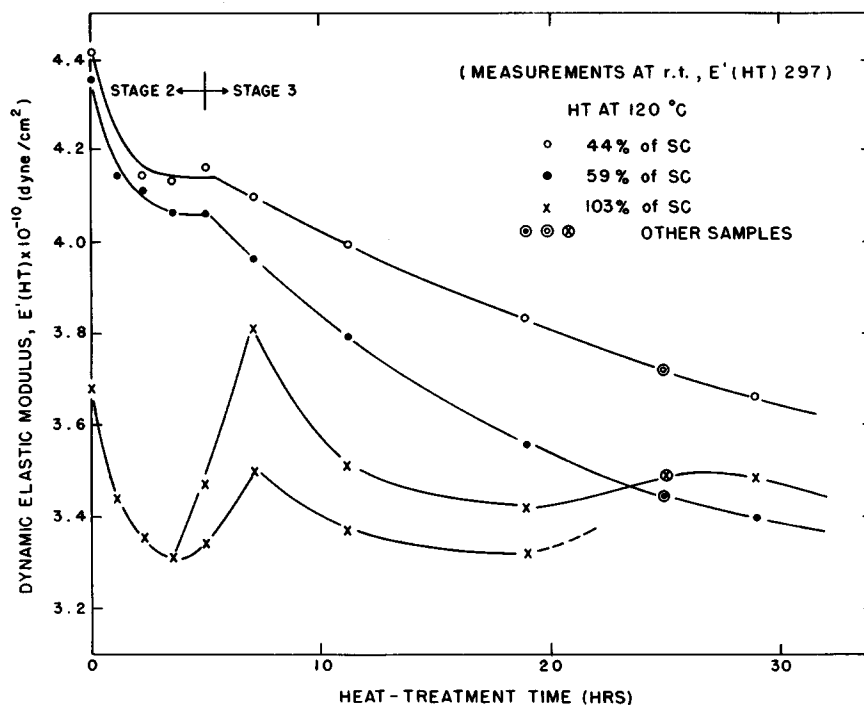

Fig. 1. Change in dynamic elastic modulus at 297°K as a function of heat treatment time (in short periods).
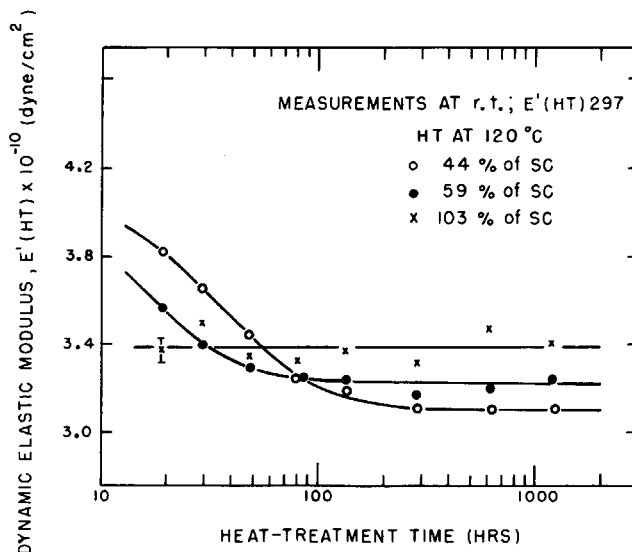
Fig. 2. Change in dynamic elastic modulus at 297°K as a function of heat treatment time (in long periods).

treatment as HT and heat-treatment time as HTT. The dynamic elastic modulus at room temperature (297°K) of heat-treated samples is designated E'(HT)297.

Figure 1 shows the dynamic elastic modulus of samples cured at room temperature for more than four months, then heat treated from 0 to 29 hr. Values for zero heat-treatment time are taken from the previous study.[1] Changes in E'(HT)297 as a function of HTT for samples with less than stoichiometric composition (44% and 59% of SC) are divided into three stages. Stage 1 takes place during the extended room-temperature cure. Stage 2 occurs with HTT from 0 to 5 hr, and stage 3, after 5 hr. For a sample prepared with 103% of SC, the HTT dependence of E'(HT)297 is complicated, as can be observed, and the samples treated for 5 to 20 hr have complex resonance curves. Values of E'(HT)297 decrease with increasing HTT up to 4 hr and are almost independent of HTT above about 20 hr or so.

As shown in Figures 1 and 2, the rate of change of E'(HT)297 with HTT is slow during stage 3 for low DETA concentrations. Within experimental fluctuations, Figure 2 shows that time-independent values of E'(HT)297 are obtained after about 200 hr for 44% of SC ($\sim$3.10$\times$10^{10} dynes/cm^2), about 70 hr for 59% of SC ($\sim$3.17$\times$10^{10} dynes/cm^2) and about 20 hr for 103% of SC ($\sim$3.38$\times$10^{10} dynes/cm^2). These results indicate that heat-treatment effects depend on the percentage of DETA in the mixture.

Density and Dynamic Elastic Modulus of Heat-Treated Resins

Figure 3 shows the influence of HTT and composition on the density of the cured resin. For a HTT of 25 hr, the density is nearly independent
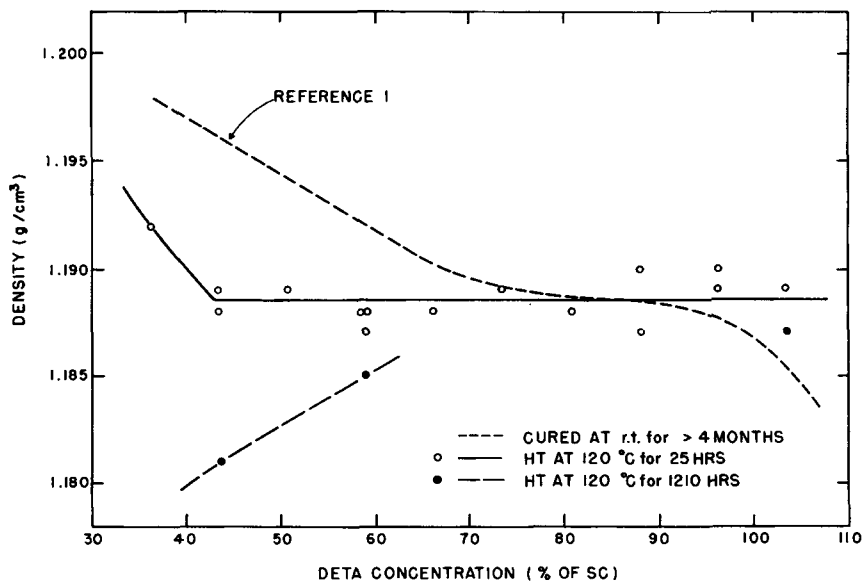
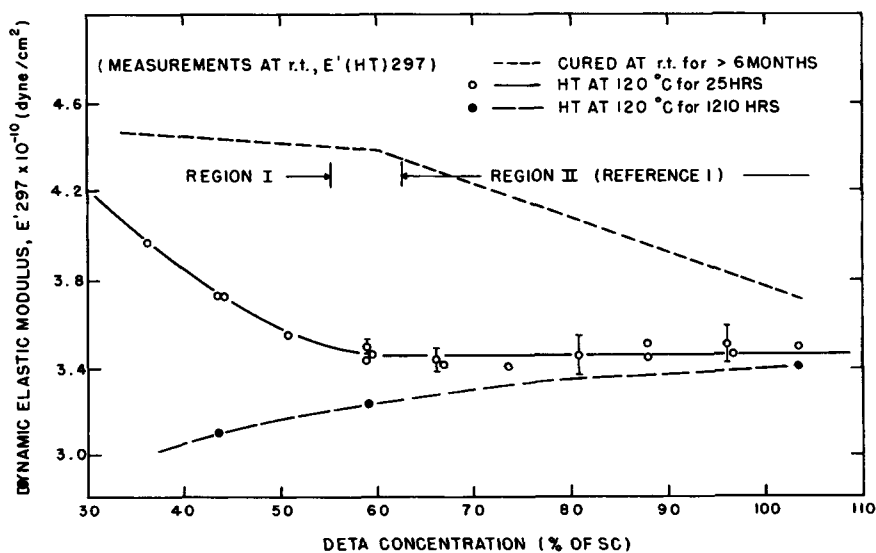Fig. 3. Relation between density and DETA concentration.

Fig. 4. Relation between dynamic elastic modulus at 297°K and DETA concentration.

of the amount of DETA above 44% of SC. On the other hand, the density increases with increasing DETA concentration for a HTT of 1210 hr.

Values of E'(HT)297 are shown in Figure 4. The curves are divided into two regions, as in the preceding study.[1] The transition between the regions occurs at about 60% SC, where the slope of the curve for the room temperature-cured resin changes abruptly. A transition is also evident at
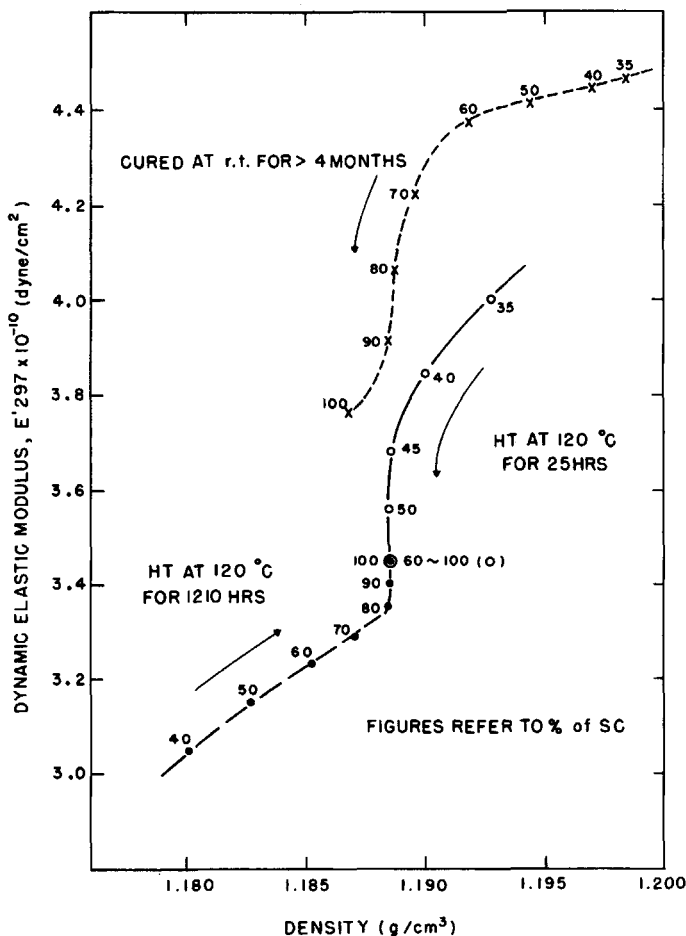
Fig. 5. Relation between dynamic elastic modulus and density.

the same DETA concentration in resin heat treated for 25 hr; as the amount of DETA is increased, $E'(HT)297$ decreases in region I, but is nearly constant ($\sim 3.45 \times 10^{10}$ dynes/cm^2) in region II. For a HTT of 1210 hr, $E'(HT)297$ appears to increase slightly with increasing DETA concentration, with no obvious demarcation into two regions.

The relations between $E'(HT)297$ and the density, obtained from Figures 3 and 4, are given in Figure 5, in which DETA concentration (% of SC) is indicated for each point. For a HTT of 25 hr, $E'(HT)297$ and the density decrease with increasing DETA until 45% of SC is reached. In the range of 45–60% of SC, the density is constant and $E'(HT)297$ decreases with increasing DETA concentration. Above 60% of SC, the density and $E'(HT)297$ are independent of DETA concentration (data not shown in Figure 5). In contrast with this, for a HTT of 1210 hr, the density and $E'(HT)297$ increase with increasing DETA concentration.

Also one can observe that for 90% of SC, the density is almost unaffected while the dynamic elastic modulus decreases from 3.9×10^{10} to 3.4×10^{10} dynes/cm^2 ($\sim$13%) with heat treatment. For 40% of SC, the density decreases from 1.197 to 1.180 g/cm^3, and the dynamic elastic modulus, from 4.45×10^{-10} to 3.05×10^{10} dynes/cm^2 ($\sim$31%). These results again imply that the change in structural features with heat treatment depends on the amount of DETA.

Effects of Heat Treatment on the Temperature Dependence of the Dynamic Elastic Modulus and the Internal Friction

Figure 6 shows the temperature dependence of the dynamic elastic modulus on the samples of 44%, 59%, and 103% of SC, cured at room temperature for four months (dotted lines) and then heat treated for 25 hr (solid lines) and 1210 hr (broken lines). The temperature dependence of the dynamic elastic modulus varies gradually with the amount of heat treatment for low DETA concentrations. For 103% of SC, samples with
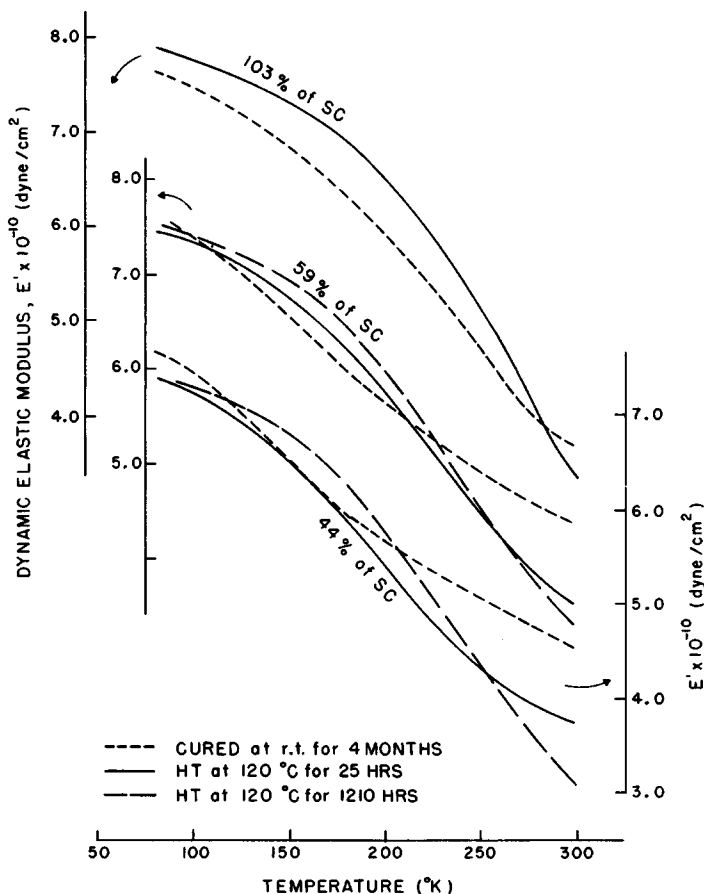

Fig. 6. Typical results of temperature dependence of dynamic elastic modulus.
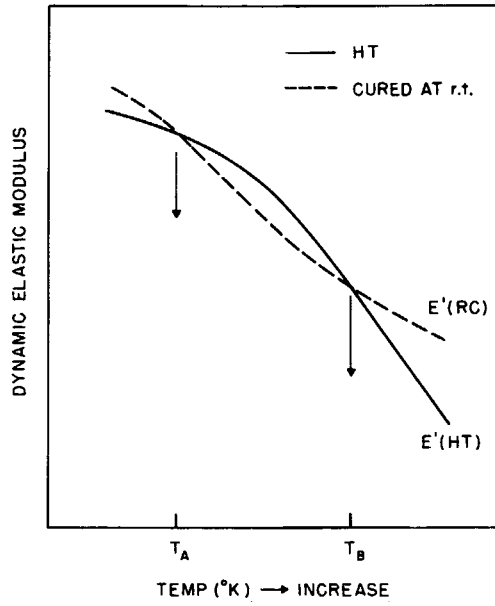
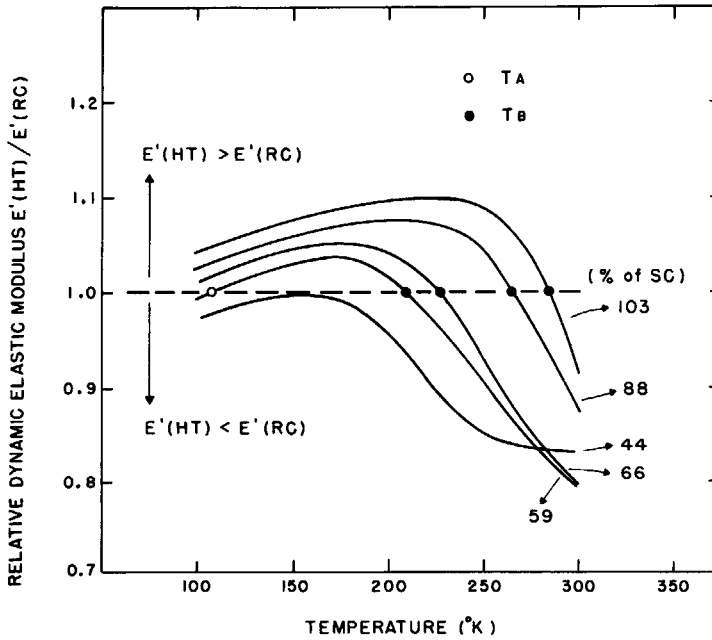Fig. 7. Change in temperature dependence of dynamic elastic modulus with heat treatment.

Fig. 8. Typical results of temperature dependence of relative modulus, $E'(\mathrm{HT})/E'(\mathrm{RC})$.
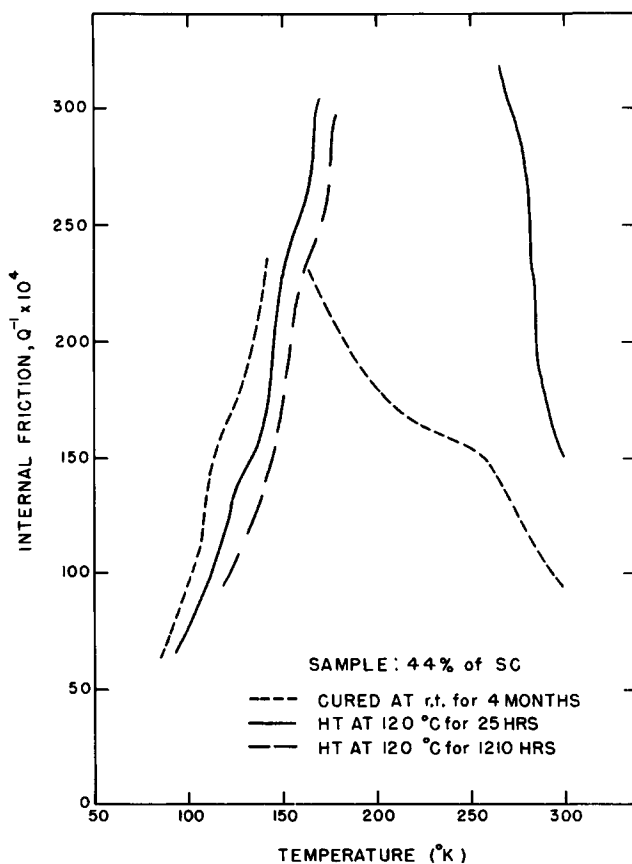
Fig. 9. Internal friction of a sample cured with 44% of SC of DETA as a function of temperature.

HTT of 25 hr and 1210 hr show the same temperature dependence. This implies that there is no unusual change in structural features with a HTT greater than 25 hr for a sample with 103% of SC.

As shown in Figure 7, the curves of the temperature dependence before and after heat treatment intersect each other at two temperatures T_A and T_B. In the temperature range of $T < T_A$ and $T > T_B$, $E'(\mathrm{HT})$ is smaller than $E'(\mathrm{RC})$, while at $T_A < T < T_B$, $E'(\mathrm{HT})$ is larger than $E'(\mathrm{RC})$. Changes in E' with heat treatment can be represented by the ratio of $E'(\mathrm{HT})$ to $E'(\mathrm{RC})$. The temperature dependence of $E'(\mathrm{HT})/E'(\mathrm{RC})$ for a HTT of 25 hr is shown in Figure 8. It is noted that T_A and T_B tend to shift to lower and higher temperatures, respectively, with increasing DETA concentration. For room temperature modulus values (in the vicinity of $300°\mathrm{K}$), heat treatment decreases the dynamic elastic modulus, especially in the range of 59% to 66% of SC.

Figure 9 shows the effect of heat treatment on the temperature dependence of the internal friction of a sample with 44% of SC. The γ-peak at
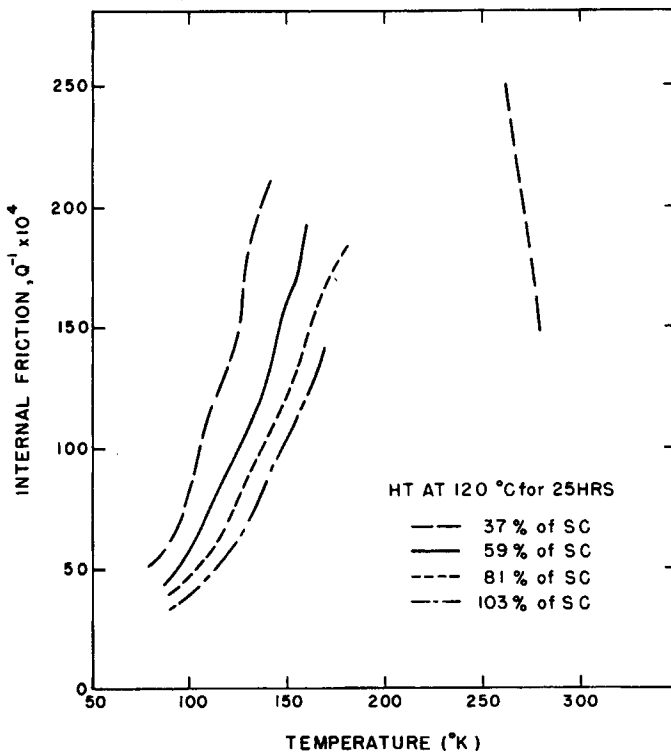
Fig. 10. Internal friction of heat treated samples as a function of temperature.

about 150°K and the β-peak at about 250°K, which were observed in samples cured at room temperature, seem to merge into a single peak as a result of the heat treatment. The intensity of Q^{-1} is markedly increased by heat treatment and becomes too high to measure between about 170° and 260°K. Typical results for a HTT of 25 hr are included in Figure 10 as a function of SC. Although the peak heights could not be measured, the maxima appear to shift to higher temperatures with increasing DETA concentration.

After heat treatment at 120°C, the dynamic mechanical properties could have been measured at temperatures up to this value. However, to study the effects of the heat treatment, the dynamic mechanical properties of heat-treated samples must be compared with those of samples cured at room temperature. Obviously, room temperature-cured samples cannot be tested above room temperature without converting them into partially heat-treated samples, so the comparison cannot be made at higher temperatures.

Another reason for not testing above room temperature is the absence of a classical reversible primary glass transition. A crosslinked epoxy network has such a high effective molecular weight that its primary glass transition occurs in the temperature range where thermal degradation begins. Kreah-

ling and Kline[4] observed an α-peak at 440°K; but after heating to 470°K, their samples showed a 6% decrease in specific heat. This is not typical of the behavior to be expected from further crosslinking; it may indicate the onset of network breakup. Fortunately, the β- and γ-peaks occurring below room temperature are sensitive indicators of structural changes; it is not necessary to observe an α-peak.

DISCUSSION

General Effects of Heat Treatment

Dammont and Kwei[8] prepared resin samples from mixtures of several kinds of epoxy resins and stoichiometric amounts of ethylenediamine and xylylenediamine, which are room-temperature curing agents. They found no detectable change in the infrared spectra between the samples cured at room temperature for 4–5 hr and then heated at 65°C for 24 hr as compared to the samples supplemented by a postcure of 5 hr at 95°C.

In the case of stoichiometric composition, polymerization reactions seem to end within relatively short periods. Infrared analysis of stoichiometric epoxy/DETA confirms this; all epoxide groups disappear during the six-day room-temperature cure. Figure 1 indicates that further changes occur with a few hours of heat treatment at 120°C, with final stabilization after 20 hr or more.

Fava and Horsfield[9] examined the relation of electrical resistivity and HTT for an anhydride-cured Epikote 828 epoxy resin during heat treatments at 170° and 200°C. They reported that resistance changed after 10 hr at 170°C, although infrared measurements and mechanical properties were found to show no changes after only 1 hr. This implies that structural features can continue to change with heat treatment for rather long times. Similar behavior may occur with stoichiometric composition of resins used in the present experiments.

As summarized in reference 1, the reaction of Epon 828 with DETA proceeds by epoxides reacting with (i) primary amines, (ii) secondary amines, and (iii) at elevated temperatures, hydroxyl groups. Changes in the dynamic elastic modulus with HTT are shown in Figure 11. At stage 1 (room temperature), resins are cured by the reactions of (i) and (ii).

At stage 2, reaction (iii) occurs.[1] Below a stoichiometric concentration, the room temperature–cured resins probably contain unreacted epoxides at the end of reactions (i) and (ii). Since at stage 2 another new hydroxyl group is produced by each reaction of an epoxide with a hydroxyl group, it is assumed that reaction (iii) can continue until all unreacted epoxides are completely opened if there is sufficient chain mobility. For 100% of SC, reaction (iii) does not occur at any appreciable rate. However, from the experimental results of the temperature dependence of the internal friction on 103% of SC, which showed the γ-peak,[1] it seems that, following reactions (i) and (ii) at room temperature, small amounts of unreacted epoxides probably remain in the resins since traces of the γ-peak remain.
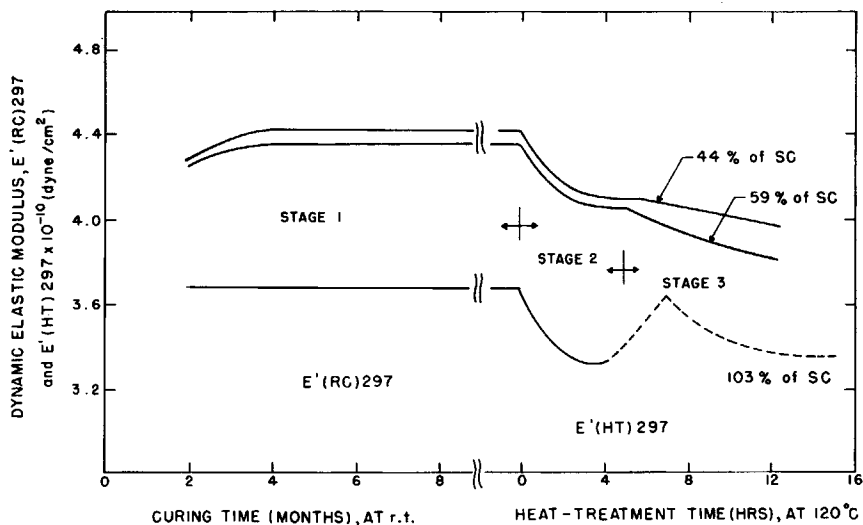
Fig. 11. Changes in dynamic elastic modulus at 297°K as a function of curing time and heat treatment time.

Reaction (iii) may also occur at elevated temperatures for a stoichiometric concentration.

At stage 2, the density is nearly constant, but E'(HT)297 decreases rapidly with HTT. There are no detectable changes in the density. At stage 3 (greater than a HTT of 5 hr), E'(HT)297 and the density decrease gradually with HTT during a long period for low DETA concentrations (density data not presented). These results show that structures of these cured resins change while in a solid state. For 103% of SC, E'(HT)297 shows complex behavior, and the density does not change with HTT. In this case, it is assumed that the movement of reaction species is more difficult because of the network structures already formed.

Heat-Treatment Effects on Temperature Dependence of the Dynamic Mechanical Properties

Kreahling and Kline[4] measured dynamic mechanical properties of X22 (diglycidyl ether of bisphenol A; Shell Development Co.) cured with metaphenylenediamine (mPDA; a high-temperature curing agent) for 24 hr at 72°C and supplemented by heat treatments of 24 hr at 102° and 127°C. Their data, involving specimens with a stoichiometric concentration of mPDA, showed that following heat treatment the dynamic modulus increased at 85°K and through the medium temperatures of 150°–200°K, but decreased at room temperature. The change in the temperature dependence of the dyanmic elastic modulus with heat treatment was systematically clarified in the present experiments, as shown in Figure 6. For 103% of SC, samples with HTT of 25 and 1210 hr both show essentially the same temperature dependence of the dynamic elastic modulus. How-

ever, data for mPDA by Kreahling and Kline,[4] with HTT of 24 hr at 102°
and 127°C, show different behavior one from another. These data imply
that the sample heat treated at 102°C is not completely cured. This
sample has a β-peak at ∼250°K, as noted below. Several results indicate
that the effect of heat treatment on the dynamic elastic modulus differs in
each sample below and above about 60–70% of SC. Some of the signif-
icance of this was discussed earlier.[1]

Kreahling and Kline[4] examined the effect of heat treatment on the in-
ternal friction of an epoxy resin cured with a stoichiometric concentration
of mPDA and reported that the temperature of the β-peak (∼250°K),
observed on the sample heated at 102°C for 24 hr, shifted to ∼270°K on
the sample heated at 127°C for 24 hr. They related the β-peak to chain
segments produced from opened epoxy rings; however, they gave no com-
ments on the shift of the β-peak from 250 to 270°K with the heat treatment.

Patterson-Jones and Smith[6] investigated the thermal degradation of the
system of epoxy resins and diaminodiphenylmethane

$$(H_2N\!-\!\langle\bigcirc\rangle\!-\!CH_2\!-\!\langle\bigcirc\rangle\!-\!NH_2),$$
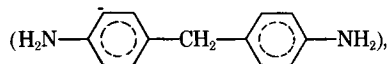
and resported that the β-peak was associated with the hydroxyl group (from
dielectric measurements). They also reported that the temperature of the
β-peak shifted to higher temperatures and the intensity of the β-peak in-
creased with increasing concentration of hydroxyl groups.

As discussed in reference 1, intensities of the γ- (∼150°K) and β-
(∼250°K) peaks were increased with increasing the number of probable
reaction products related to each peak. From the previous paper,[1] it was
suggested that the γ-peak could be accounted for by the unreacted epoxides.
For a HTT of 25 hr, the γ-peak should disappear, since unreacted epoxides
are completely opened by reaction (iii). As shown in Figures 9 and 10,
the γ-peak was not observed in this case. This indicates that the interpre-
tation on the γ-peak is reasonable.

The β-peak was related to the opened epoxide or the hydroxyl group.[1]
It might be expected that the origin of this peak could be determined from
the intensity as a function of DETA concentration in heat-treated speci-
mens. However, the intensity of the β-peak could not be determined
(Fig. 10) because complete peaks were not obtained in the present experi-
ments.

It should be noted that these peaks are changed only in intensities by
heat treatment. As shown in Figures 9 and 10, however, the temperature
of the Q^{-1} peak for a HTT of 25 hr appears to be at about 200°K (not
250°K) for 37% of SC and shifts to higher temperatures with increasing
DETA concentration and with heat treatment. This may imply that
these peaks in the heat-treated samples are not the same β-peaks, so they
will be called β'-peaks. The peak of Q^{-1} at ∼270°K reported by Kreah-
ling and Kline[4] seems to be this β'-peak. Lewis and Nielsen[10] observed a
broad secondary transition peak at about 230°K, using a torsion pen-

dulum, on Epon 828 cured with triethylenetetramine and diluted with 5% phenyl glycidyl ether, which was cured for 24 hr at 25°C and heat treated at 60°C for 3 hr, 100°C for 6 hr, and 140°C for 4 hr. The difference in the temperature of the peaks between 230°K (by Lewis and Nielsen) and 270°K (by Kreahling and Kline and in the present experiments) may be attributed to the different frequencies and methods used in their experiments.[11] From their results mentioned above and the present results, it can be concluded that the β'-peak is shifted from $\sim$200°K (37% of SC) to $\sim$270°K (100% of SC) by heat treatment.

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