

Dynamic Mechanical Properties of Nonstoichiometric, Amine-Cured Epoxy Resin

T. HIRAI* and D. E. KLINE, *Department of Material Sciences, The Pennsylvania State University, University Park, Pennsylvania 16802*

Synopsis

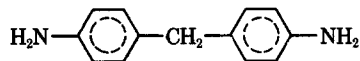
The dynamic mechanical properties of epoxy resins cured with nonstoichiometric amounts [37%–103% of stoichiometric composition (SC)] of diethylenetriamine at room temperature have been measured in the temperature range 85° to 300°K and correlated to structures of cured resins. The dynamic mechanical behavior changed above and below 62.5% of SC, at which network structures are formed. The intensities of γ - and β -peaks, $\sim 150^\circ$ and $\sim 250^\circ$ K, respectively, depend upon the concentration of DETA used. The processes of the γ - and β -peaks are discussed.

INTRODUCTION

Several low-temperature studies of the dynamic mechanical properties of epoxy resins cured with different types of amines have been reported.^{1–11} However, most of this work has been carried out using stoichiometric concentrations (SC) of amine. Up to the present, very little information has appeared in the literature for epoxy resins cured with nonstoichiometric amounts of amine.

In most of the previous studies, high-temperature curing agents have necessitated heat treatment to promote the polymerization. The heat-treating conditions, moreover, differ from experiment to experiment. Since heat treatment has a substantial effect on structural features of these polymers, it is important to examine dynamic mechanical properties (DMP) of unheated polymers with no history of heat treatment to understand the relation between dynamic mechanical properties and structural features.

Bell¹² and Murayama and Bell¹³ discussed the relation between network structure and dynamic mechanical properties of the epoxy resin cured with 94–203% of the stoichiometric composition of methylenedianiline,



a high-temperature curing agent, in the temperature range of 300–470°K.

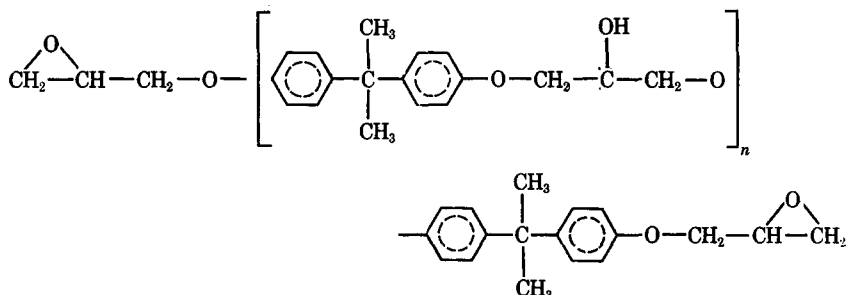
* Present address: Oarai Branch, Research Institute for Iron, Steel and Other Metals, Tohoku University, Oarai-cho, Ibaraki-ken, Japan.

The primary purpose of the present investigation is to assist in obtaining a better understanding of the relation between structural features and dynamic mechanical properties between 85° and 300°K for epoxy resins cured with nonstoichiometric amounts of amine. Samples have been prepared using nonstoichiometric amounts (37%–103%) of diethylenetriamine cured at room temperature with no subsequent heat treatment. Of particular interest in the present work are the secondary peaks appearing at about 250°K (β) and 150°K (γ).

EXPERIMENTAL

Sample Preparation

The epoxy resin used in the present experiments, diglycidyl ether of bisphenol A (Epon 828, Shell Chemical Co.), has a molecular weight between 370 and 384. The basic molecule has the following structure:



For $n = 0$, the molecular weight is 340. The epoxide equivalent was considered to be 185 in the present case. To form the cured epoxy system, this resin was combined with diethylenetriamine (DETA; a room-temperature curing agent):



A mixture of 50 cm³ of the resin and 2.5–7.0 cm³ of DETA (4.1–11.5 phr, 37%–103% of SC) was prepared and stirred for 5 min. (The abbreviation phr refers to parts per hundred parts of resin by weight.) Bubbles contained in the mixtures were removed by vacuum pumping for 15 min. The loss of DETA during the pumping process was negligible. The mixtures were then drawn into a Pyrex tube (8 mm in diameter), coated with silicone grease or petroleum jelly, and allowed to harden for about 30 days at room temperature. The hardened resins were removed from the tube and cut in lengths of \sim 11.1 cm. All samples used in this study were allowed to cure at room temperature for 1, 2, 4, 8, or 12 months.

Dynamic Mechanical Measurements

Measurements of the dynamic elastic modulus and the internal friction were carried out by using the apparatus developed by Kline.¹⁴ In this ap-

paratus, rod-like specimens are supported horizontally by two vertical lines. One line, coupled to a magnetostrictive transducer, drives the specimen in the fundamental transverse mode while a second line, attached to a piezoelectric crystal pickup cartridge, notes the specimen response. In the present case, the measurements were made in the temperature range of 85° to 300°K and in the frequency range of 900 to 1500 Hz. The heating rate was maintained at about 1C°/min, which is sufficient to achieve approximately uniform temperature conditions for the duration of a measurement. Temperatures were determined by a copper-Constantan thermocouple.

The dynamic elastic modulus E' (dyne/cm²) was calculated from the fundamental resonant frequency f_r (Hz) by the relation

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

where L , a , and W , respectively, are the length (cm), diameter (cm), and mass (g) of the specimen.

The internal friction Q^{-1} was determined from the relation

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

where Δf is the 3-db frequency separation at the half-power level of the amplitude-frequency curve, and f_r is the resonant frequency of the fundamental vibration mode.

RESULTS

Density

Figure 1 shows densities of epoxy resins cured with different amounts of DETA. (Density of the resin is about 1.16 g/cm³.) Densities were obtained by the mass-volume method. Results at 2, 8, and 12 months of curing are included in Figure 1. Since these data are within the experimental measurement error, it appears that the densities reach constant values after 2 months of curing.

The density of the cured resin depends on the concentration of DETA used during sample preparation. In the range of 35%–65% of SC, the density decreases as the concentration of the curing agent is increased. The density is rather constant in the range of 70%–95% of SC and then decreases rapidly above 100% of SC.

Dynamic Elastic Modulus

Values of the dynamic elastic modulus measured at room temperature, E'_{297} , are shown in Figure 2. The change in E'_{297} with amounts of DETA is divided into two regions: region I below ~60% of SC, and region II above ~60% of SC. In region I, E'_{297} is almost independent of DETA concentration. In region II, however, E'_{297} decreases with increasing amounts of DETA.

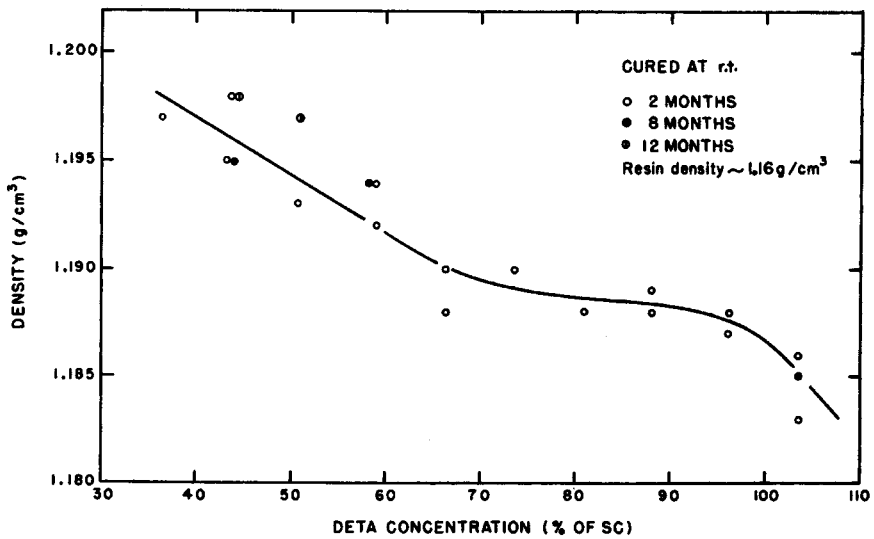


Fig. 1. Density of epoxy resins cured with different amounts of DETA.

Values of E'_{297} for samples cured 2–12 months are also shown in Figure 2. The solid and broken lines indicate results of 2 months and of above 4 months of curing, respectively. In region I, the change in E'_{297} with curing time is observed to be largely completed by 4 months. In region II, E'_{297} increases with the curing time to 6 months. At stoichiometric composition, however, E'_{297} is nearly constant after 2 months of curing. The

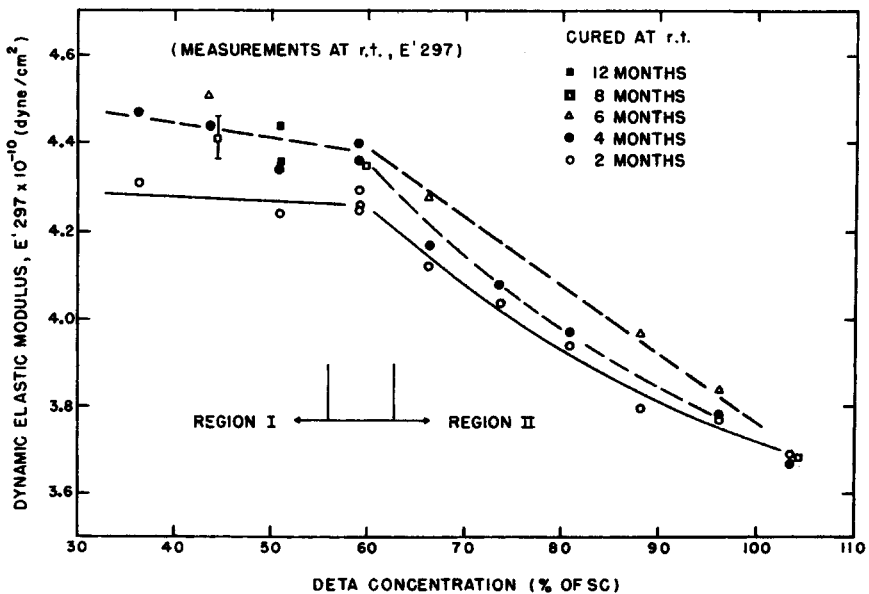


Fig. 2. Dynamic elastic modulus at room temperature, E'_{297} , of epoxy resins cured with different amounts of DETA.

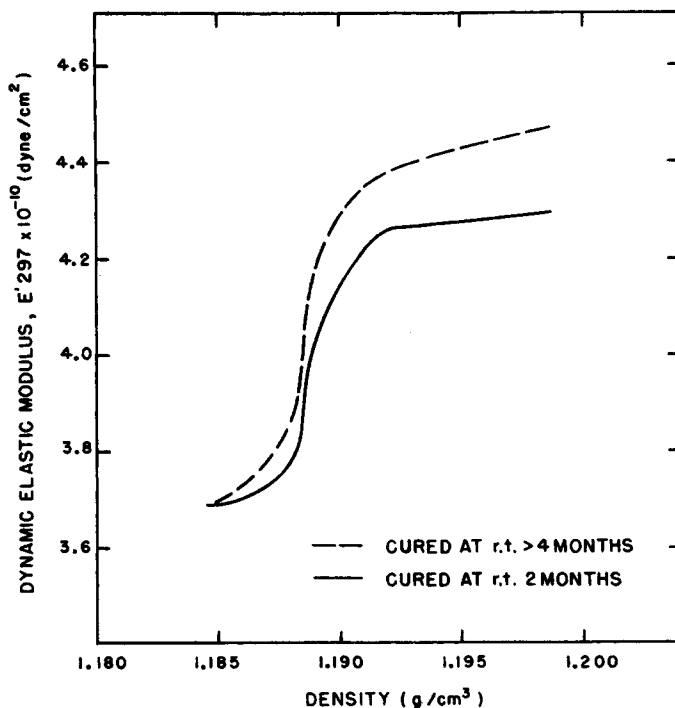


Fig. 3. Relation between dynamic elastic modulus and density.

relation between E'_{297} and the density, obtained from Figure 1 and 2 is given in Figure 3. To make a composite with a relatively higher elastic modulus compared to the density, a reasonable choice of a matrix for composite materials is a resin with density in the range of 1.192–1.194 g/cm³. This resin is prepared by combining 5.8–6.6 phr DETA (52%–59% of SC) with Epon 828.

Internal Friction

Figure 4 shows values of the internal friction measured at room temperature, Q^{-1}_{297} . Values of Q^{-1}_{297} are subject to considerable experimental error. After 2 months of curing time, Q^{-1}_{297} is independent of the curing period.

The relation between Q^{-1}_{297} and DETA concentration is similar to the results obtained for E' (see Fig. 2), in that there are two regions with a transition point occurring at about 60% of SC (Fig. 4). In region I, Q^{-1}_{297} is almost independent of DETA concentration and resonance curves are relatively sharp, indicating relatively low damping, while in region II, resonance curves become broad and Q^{-1}_{297} increases with increasing DETA. These results indicate that relaxation mechanisms are altered in region I as compared to region II and that cured epoxy resins in regions I and II have different structural features.

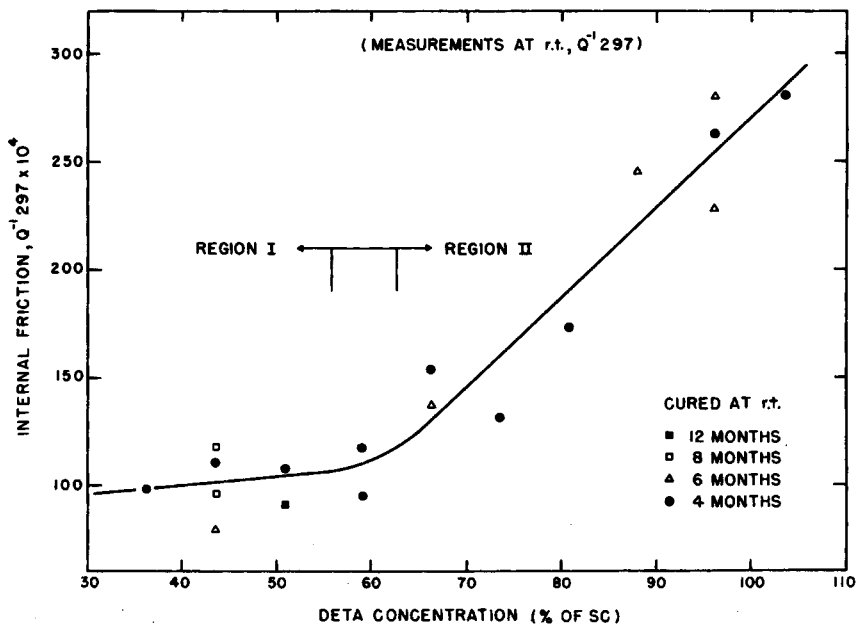


Fig. 4. Internal friction at room temperature, $Q^{-1} 297$, of epoxy resins cured with different amounts of DETA.

Temperature Dependence of E' and Q^{-1}

Figures 5 and 6 show typical results of the temperature dependence of E' and Q^{-1} over the temperature range of 85° to 300°K. These results are for samples cured for 4 months. As shown in Figure 5, E' decreases with increasing temperature for each of the four samples studied. For 37% and 59% of SC, the slope of the E' -versus-temperature curve decreases with temperature, while the two curves for the samples prepared with high DETA concentration are more complex. At 85°K, all samples have a E'_{85} value of 7.64×10^{10} dyn 2 /cm 2 (Fig. 7A). With increasing DETA concentration, E' increases at the intermediate temperatures of 150°–200°K, but E' decreases at room temperature as shown in Figure 2.

Resonance curves are sharp and symmetric at low temperatures, but become broad with reduced symmetry with increasing temperature. In some cases, complex resonance curves were obtained at intermediate temperatures.

In Figure 6, the two secondary peaks appearing at about 150° and 250°K are shown. The intensity of these peaks is found to depend on the DETA concentration. As the DETA concentration is increased, the γ -peak at $\sim 150^\circ$ K decreases, and the β -peak at $\sim 250^\circ$ K increases (Figs. 8 and 9).

With increasing DETA concentration, Q^{-1} decreases slightly at 85°K (Fig. 7) and increases at room temperature (Fig. 4).

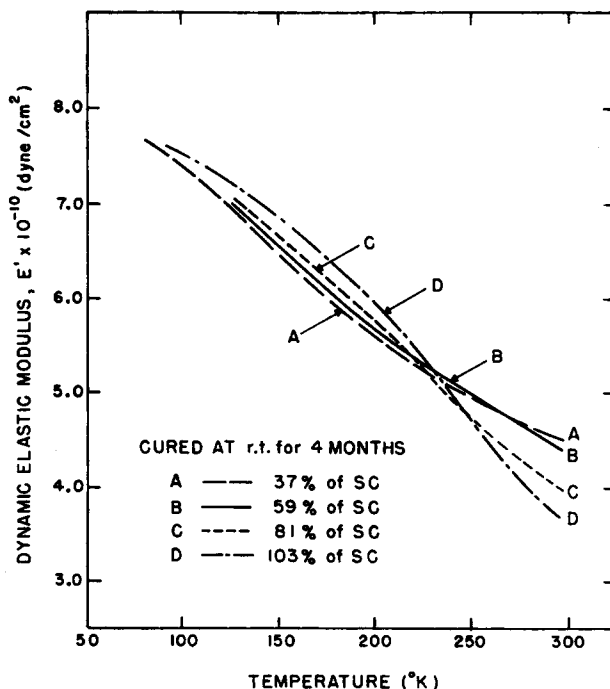


Fig. 5. Temperature dependence of dynamic elastic modulus of epoxy resins cured with different amounts of DETA.

DISCUSSION

Cuthrell^{15,16} examined macrostructures of epoxy resins and reported that several epoxy resins appeared to be two-phase systems composed of floccular aggregates and an interstitial fluid. Structures and properties of the floccules and the interstitial fluid were considered to vary with curing conditions, especially with the amount of curing agent.

DETA possesses five active hydrogens available for crosslinking, while Epon 828 contains two epoxides per molecule. For the reaction of epoxy resins with room-temperature curing agents such as butylamine ($\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$)^{17,18} or ethylenediamine ($\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2$),¹⁸ the reaction rate of the epoxides with a primary amine is approximately twice that of the epoxides with a secondary amine.^{17,18} Shechter, Wynstra, and Kurkijy¹⁹ reported that the two reactions occurred simultaneously and that, after 6 hr at 50°C, 100% of the primary amine and 95% of the secondary amine were consumed. On the other hand, for high-temperature curing agents such as methylenedianiline, the primary amine groups were completely consumed and half the epoxy groups remained after curing at 80°C.¹² Moreover, it is reported that the hydroxyl groups do not contribute to opening epoxides at room temperature.¹⁹ For the samples cured with nonstoichiometric amounts of DETA (a room-temperature curing agent) as in the present experiments, the results dis-

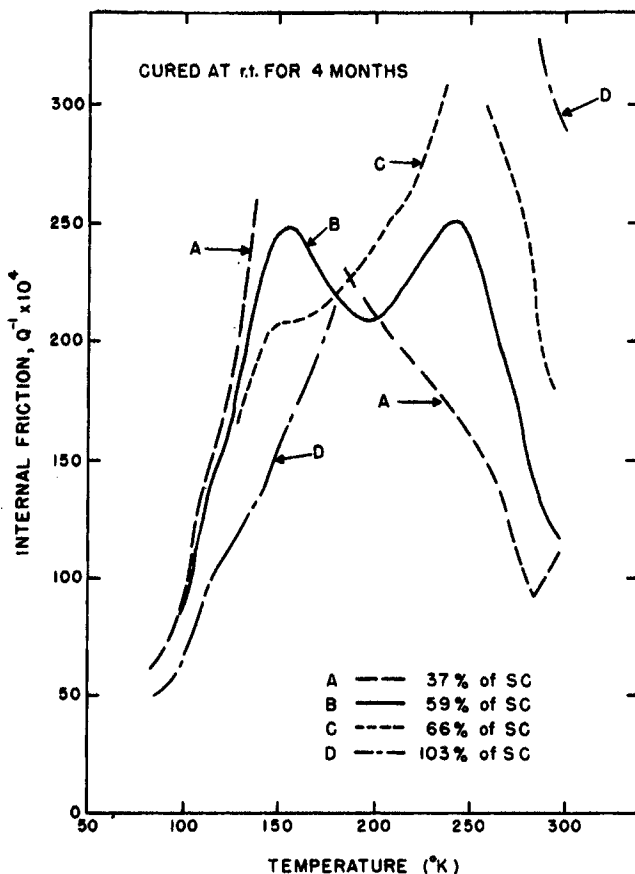


Fig. 6. Temperature dependence of internal friction of epoxy resins cured with different amounts of DETA.

cussed above might suggest that, for sufficiently long curing periods, almost all of the amines were consumed at room temperature.

The densities of Epon 828 and DETA are 1.16 and 0.95 g/cm³, respectively, and the density of solid products from the mixture of Epon 828 and DETA is higher than that of each component. Densities increase with decreasing amount of DETA, as shown in Figure 1. This implies that, for the epoxy resins cured with less than 50% of SC, a packing of the product composed of the unit is impregnated with unreacted epoxy molecules. Figure 10 shows the effect of curing time at room temperature E'_{297} for three samples prepared with different DETA concentrations.

Lewis and Gillham²⁰ examined the dynamic shear modulus (torsion pendulum) of an epoxy resin prepared with 10 phr of DETA (90% of SC) and cured at 25°C. They found that the rigidity becomes constant after about seven days. Jenkins and Karre²¹ reported that the mechanical vibrating-reed property reached a constant value after 4–5 hr at 20°C for

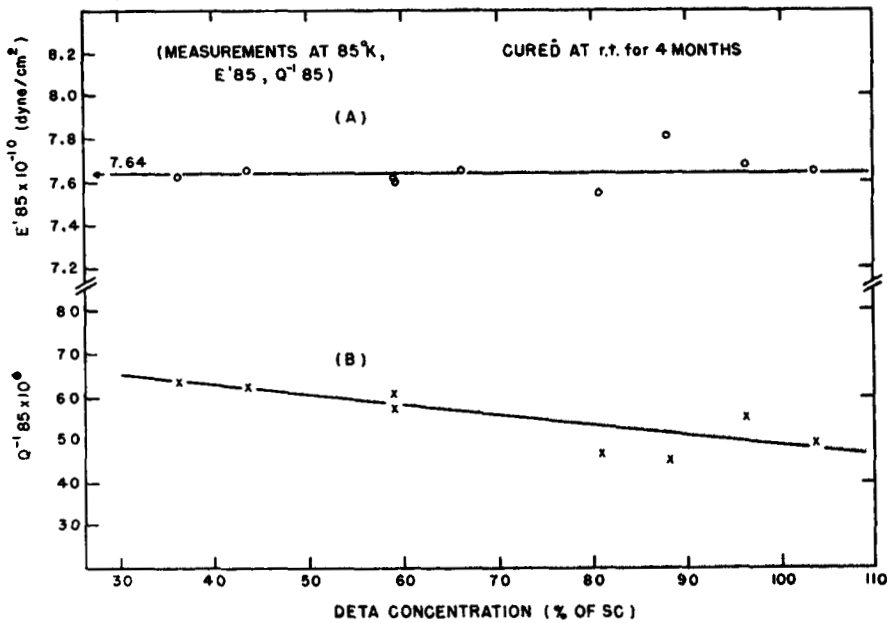


Fig. 7. Dynamic elastic modulus and internal friction at 85° K (E'_{85} , and Q^{-1}_{85}) of epoxy resins cured with different amounts of DETA.

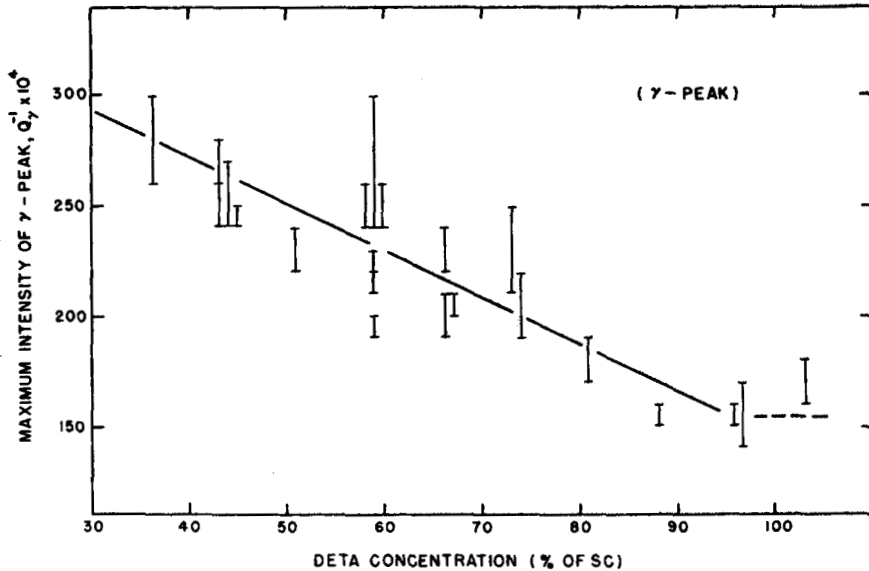


Fig. 8. Relation between maximum intensity of γ -peak and DETA concentration.

the same resin combined with 10 phr of DETA. Figure 10 shows that E'_{297} remains constant during the curing period of 2-8 months for samples prepared with near SC. At SC the rate of polymerization is relatively fast, and all epoxides are opened in a short period. This appears to lead

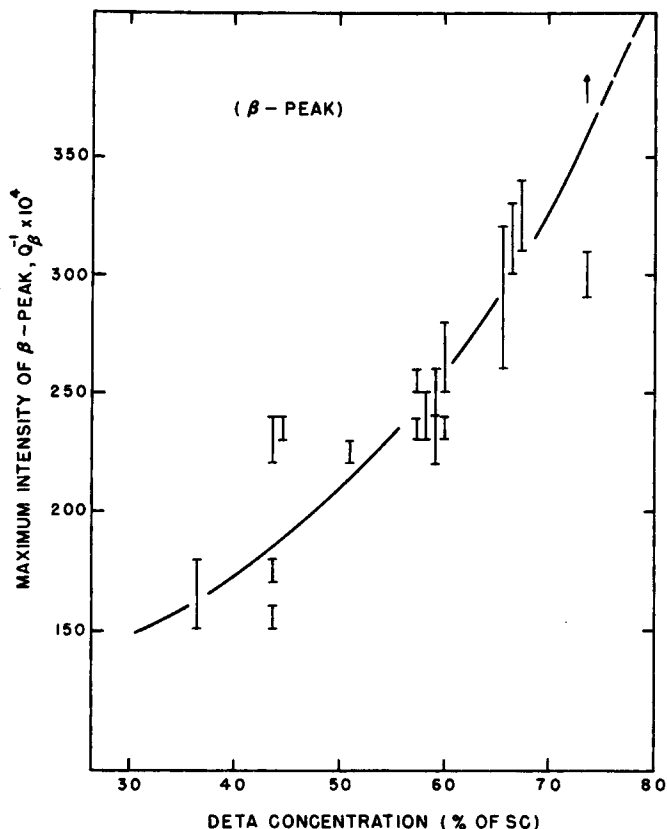
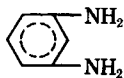


Fig. 9. Relation between maximum intensity of β -peak and DETA concentration.

to disordered structures and low densities. Data for nonstoichiometric cases (Fig. 10) show that when there is an excess of epoxides, the curing rate becomes slower.

The end of region I and the beginning of region II correspond to $\sim 60\%$ of SC. Figure 1 indicates that the packing of the species products is disordered with increasing the amounts of DETA in region I and is independent of DETA concentration in region II. From Figures 1, 2, and 4, it seems that E' and Q^{-1} are not greatly affected by the change in packing density in region I but do depend on the bonding and that network bonding appears in region II where E' decreases and Q^{-1} increases with increasing concentration of DETA.

As shown in Figure 5, E' increases near 150° – 200° K and decreases at room temperature as the amount of DETA is increased. Similar results are observed² for Epon 828 cured with metaphenylenediamine:



However, these phenomena are unexplained.

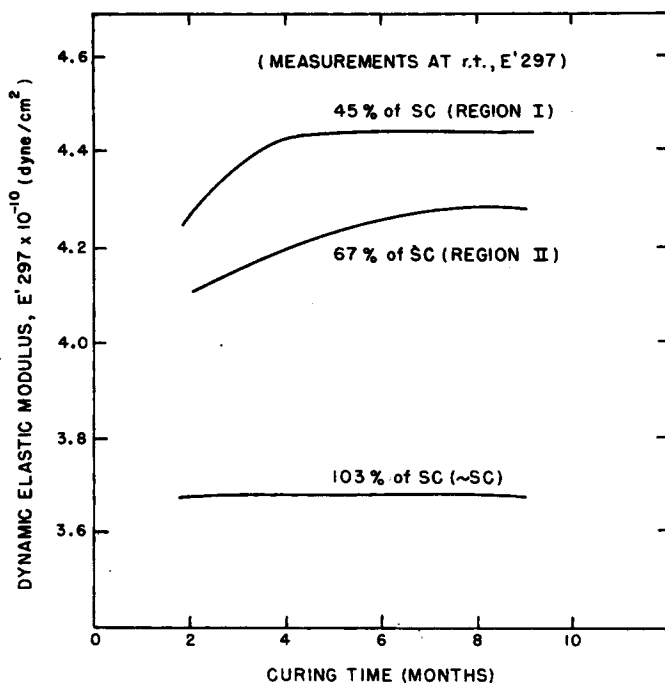


Fig. 10. Effect of curing time at room temperature on dynamic elastic modulus.

Figure 6, 8, and 9 indicate that intensities of β - and γ -peaks depend on the amount of DETA. The γ -peak predominates for low DETA concentrations (region I), while in region II the β -peak is predominant. In the transition zone between regions I and II, the intensity of the β -peak is approximately equal to that of the γ -peak.

Experimental data have been reported which indicate that the β -peak appears at various temperatures between 210° and 250°K.^{1,11} This range of temperatures has been at least partially attributed to a difference in frequencies used in the various reports.¹¹ Since the temperature at which the β -peak appears seems to be nearly independent of both the curing agent and raw epoxy resin, the presence of the β -peak is apparently associated with only the epoxide-amine reactants or products. These may include (1) unreacted epoxides, (2) epoxy molecules with one reacted oxirane ring, (3) opened (reacted) epoxides, (4) reacted epoxy molecules, and (5) hydroxyl groups.

The relative concentrations of the components in a specimen may be related to the heights of the damping peaks; i.e., the greater the concentration of a product, the larger its damping peak.²² The β -peak, whose intensity increases with DETA concentration (Fig. 9), may be correlated to the concentration of opened epoxides, reacted epoxy molecules, or hydroxyl groups. As shown in Figures 6 and 9, however, the β -peak is observed on samples below 50% of SC. Thus, it is suggested that the β -peak is not related to completely reacted epoxy molecules. In measure-

ments of the dynamic mechanical properties of a glass-fiber braid impregnated with a reacting mixture of the same epoxy resin and 10 phr DETA (90% of SC), Lewis²³ found that gelation occurred when about 40% of the epoxide groups were converted. He also found by infrared analysis that only 80% were converted during room-temperature cure of this 90% SC formulation, with the remaining 20% converted by subsequent heat treatment. Some of the samples described here were also heat treated; results of the heat treatment, revealed by changes in the intensity of the β -peak and by infrared analysis, will be reported separately.

Dammont and Kwei¹⁰ and Delatycki, Shaw, and Williams¹¹ observed the γ -peak ($\sim 150^\circ\text{K}$) on samples prepared by reactions of a diglycidyl ether of bisphenol A and aliphatic amines [$\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NH}_2$; $n = 2-12$]. Delatycki et al.¹¹ suggested that the magnitude (intensity) of the γ -peak increases with the length of the diamine molecule. However, the γ -peak obtained in their work was very weak and not well defined. On the other hand, Kreaehling and Kline² observed the γ -peak on the low-amine-concentration samples prepared from X22 (diglycidyl ether of bisphenol A; Shell Development Co.) and *m*PPDA. They ascribed the γ -peak to the resin with one end reacted. In the present experiments, the intensity of the γ -peak increases with decreasing amounts of DETA in the range of 37%–103% of SC (Fig. 8). This result seems to imply that the γ -peak is probably associated with unreacted epoxide.

In principle the γ -peak should not be observed for samples of stoichiometric composition, because there may be no unreacted epoxides. Actually, Figure 6 shows that a very weak peak is present. For stoichiometric composition, the cured resin may contain small amounts of unreacted epoxides in the structures because of the fast curing reaction and their complex structures. Moreover, for some cases involving diamines^{10,11} at stoichiometric composition, samples may contain unreacted epoxides because of the relatively low mobility of the diamine molecule in the gel and solid states. For the case cited, the amount of unreacted epoxides increases with increasing length of a diamine molecule which tends to produce a stronger γ -peak.

The authors are grateful to Dr. R. Kammereck and J. R. Jenness, Jr., for discussions and comments. This research was supported in part by the U.S. Atomic Energy Commission, Contract AT(30-1)-1710.

References

1. D. E. Kline, *J. Polym. Sci.*, **47**, 237 (1960).
2. R. P. Kreaehling and D. E. Kline, *J. Appl. Polym. Sci.*, **13**, 2411 (1969).
3. D. H. Kaelble, *SPE J.*, **15**, 1071 (1959).
4. D. E. Kline and J. A. Sauer, *SPE Trans.*, **2**, 1 (1962).
5. C. A. May and F. E. Weir, *SPE Trans.*, **2**, 207 (1962).
6. F. R. Dammont and T. K. Kwei, *J. Polym. Sci. A-2*, **5**, 761 (1967).
7. R. K. Jenkins, *J. Appl. Polym. Sci.*, **11**, 171 (1967).
8. J. C. Patterson-Jones and D. A. Smith, *J. Appl. Polym. Sci.*, **12**, 1601 (1968).
9. H. Van Hoorn, *J. Appl. Polym. Sci.*, **12**, 871 (1968).

10. F. R. Dammont and T. K. Kwei, *J. Polym. Sci. A-2*, **6**, 457 (1968).
11. O. Delatycki, J. C. Shaw, and J. G. Williams, *J. Polym. Sci. A-2*, **7**, 753 (1969).
12. J. P. Bell, *J. Polym. Sci. A-2*, **8**, 417 (1970).
13. T. Murayama and J. P. Bell, *J. Polym. Sci. A-2*, **8**, 437 (1970).
14. D. E. Kline, *J. Polym. Sci.*, **22**, 449 (1956).
15. R. E. Cuthrell, *J. Appl. Polym. Sci.*, **11**, 949 (1967).
16. R. E. Cuthrell, *J. Appl. Polym. Sci.*, **12**, 1263 (1968).
17. J. F. Harrod, *J. Appl. Polym. Sci.*, **6**, S 63 (1962).
18. T. Kakurai and T. Noguchi, *Kogyo Kagaku Zasshi*, **64**, 398 (1961).
19. L. Shechter, J. Wynstra, and R. P. Kurkijy, *Ind. Eng. Chem.*, **48**, 94 (1956).
20. A. F. Lewis and J. K. Gillham, *J. Appl. Polym. Sci.*, **11**, 422 (1962).
21. R. Jenkins and L. Karre, *J. Appl. Polym. Sci.*, **10**, 303 (1966).
22. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962.
23. A. F. Lewis, *SPE Trans.*, **3**, 201 (1963).

Received March 8, 1972

Revised June 21, 1972