

Viscoelastic Changes of Epoxy Resin-Acid Anhydride System During Curing

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Synopsis

The changed viscoelastic properties of the epoxy resin-acid anhydride system, Epikote 834-HHPA, are followed to the gel point at 130, 140, and 150°C with a dynamic viscoelastometer. The viscosity increases with curing time through two inflections designated A and B. The point A is interpreted (from the reference to the chemical changes reported in the previous paper) as the termination of the initial stage of this curing reaction, and point B coincides with the gel point determined by the torsion method. The resonance frequency remains constant value up to the point B, followed by a rapid increase. The extents of reaction for epoxide, anhydride, and initial OH are 15, 45.8, and 100% at the point A; 27.8, 63.7, and 100% at the point B, respectively. The apparent activation energies for viscosity are 7.5 kcal/mole for the resin mixture before curing, 10.5 kcal/mole for point A, 48.8 kcal/mole for point B (gel point). The overall apparent activation energies of this curing reaction are obtained from the Arrhenius plots for the curing time required for the resin mixture to reach the state of the points A and B; these values were 8.9 kcal/mole for point A and 16.2 kcal/mole for point B.

INTRODUCTION

As reported in a previous paper,¹ the course of curing of the uncatalyzed epoxy resin-acid anhydride system is divided into three stages on the basis of chemical changes: the initial stage is characterized by rapid increase of monoester; the second stage by increase of diester and gelation; and the last stage by increase in ether bonds. In this case, diester and ether bonds act as crosslinks.

The purpose of this paper is to report on a study of the correlation between the chemical changes and viscoelastic behavior. The viscoelastic behavior of the reacting system was followed by a dynamic mechanical method under isothermal conditions from the start of reaction to the gel point. Noteworthy characteristic points in this interval were taken as the termination of the initial stage and the gel point. Additional problems are as follows: (1) how the termination of the initial stage is reflected in changes in viscosity; (2) how the gel point determined by the torsion method is observed in viscoelastic behavior; and (3) to what extent chemical changes are observed at the gel point. Also, the changes in the apparent activation energy of viscosity during the curing were obtained, it being assumed that the characteristic point found in viscoelastic data at

different curing temperatures arises from the same mechanism; these data are useful for discussing the molding method and conditions in practice. In addition, the overall apparent activation energies of curing reaction were obtained for two characteristic points, the termination of the initial stage and the gel point, and compared with the value reported by other workers.^{2,3}

EXPERIMENTAL

Reagents

Epikote 834 (Shell Chemical Company) was used as the epoxy resin and hexahydrophthalic anhydride (HHPA) (Allied Chemical and Dye Corporation) was used as the crosslinking agent. The resin is a condensation product of bisphenol A and epichlorhydrin, so the reactive functional groups are terminal epoxy groups and pendant hydroxyl groups.

The reagents used here were the same materials as used in the previous study¹ concerning chemical changes. Epikote 834 had an epoxy value (determined¹ by the HCl-pyridine method) of 0.389 equiv/100 g resin and an OH value (from the epoxy value and esterification data) of 0.119 equiv/100 g resin.

Analysis of hexahydrophthalic anhydride by the method of Smith⁴ showed acid anhydride, 97.4; free acid, 1.3%; other, 1.3%.

The reagents were mixed in such a ratio that the molar ratio of epoxide to anhydride was about 1 to 0.9. Analysis results of the resin mixture by the method described in the previous paper showed epoxide, 0.253 (equiv/100 g resin mixture and acid anhydride, 0.221 equiv/100 g resin mixture.

Measurement

The dynamic mechanical behavior for the cured epoxy resin has been studied by Kaeble,⁵ Kline,⁶ Shitō,⁷ and Satō,⁷ and Kwei,⁸ the changes in the dynamic mechanical behavior during the curing course have been studied by Kline,⁹ Lewis and Gillham,¹⁰ Lewis,¹¹ and Jenkins and Karre.¹²

In this report, the changes in the viscosity and resonance frequency of the curing resin were followed continually with a Rion Corporation dynamic viscoelastometer, Model V-1201.¹³ This apparatus is shown schematically in Figure 1. The frequency was about 1.1 keps. The viscosity measured here was the apparent viscosity η_p . The apparatus was calibrated over the range from unity to 5.9×10^5 cP-g/cm³ by use of water and six kinds of silicon oil whose viscosity was determined with a Hoeppler viscometer.

The temperature of the curing resin sample was measured directly with the thermocouple immersed in it and regulated within $\pm 0.2^\circ\text{C}$ to obtain isothermal runs.

A glass rod of 1 mm diameter was immersed on the sample for determining the gel point. The gel point was determined by a torsion method

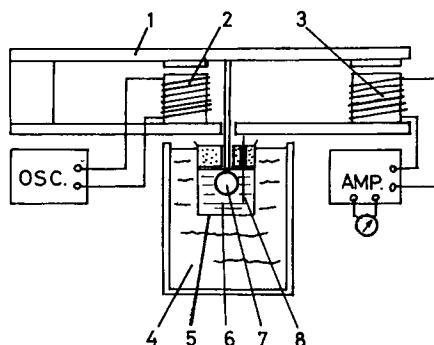


Fig. 1. Schematic of dynamic viscoelastomer;⁵ (1) vibrating plate; (2) vibrating coil; (3) induction coil; (4) oil bath; (5) 300-ml beaker; (6) sample (about 200 ml); (7) vibrating disk, 20 mm diameter, 2 mm thickness; (8) glass rod, 1 mm diameter.

by which the glass rod was wrenched at an angle of 90° in the sample and let go, the gel point being considered to have been reached if the glass rod returned to the initial position.

The measurements were made for curing temperatures of about 130, 140, and 150°C . The resin and crosslinking agent were warmed to the curing temperature before being blended together, to effect good mixing and accuracy of curing time. Once the resin and crosslinking agent were thoroughly mixed, the mixture was cast into a beaker set in the apparatus. The curing time was taken as the time after mixing of the resin and crosslinking agent.

RESULTS AND DISCUSSION

Changes in Viscosity and Resonance Frequency

Figures 2, 3, and 4 show the data for changes in the apparent viscosity $\eta\rho$ and resonance frequency ν with curing time at curing temperatures of 131, 139.5, and 150.5°C , respectively. The broken line in each figure shows the changing rate of the logarithm of apparent viscosity as a function of time, $\partial(\log \eta\rho)/\partial t$.

The $\eta\rho$ curve increases through the two inflections designated A and B, as illustrated also from the fact that the $\partial(\log \eta\rho)/\partial t$ curve goes through a broad minimum A and a sharp maximum B. The ν curve is found to be almost constant up to point B, followed by a rapid increase. The point B coincides with the gel point determined by the glass rod method described above.

Correlations with Chemical Changes

Table I shows the chemical contents of the resin mixtures cured at 131°C for 0, 200, and 495 min., where a curing time of 200 min corresponds to point A, and 495 min to point B. These data are from Figure 5 of the previous study,¹ where the contents of epoxide, anhydride, and monoester

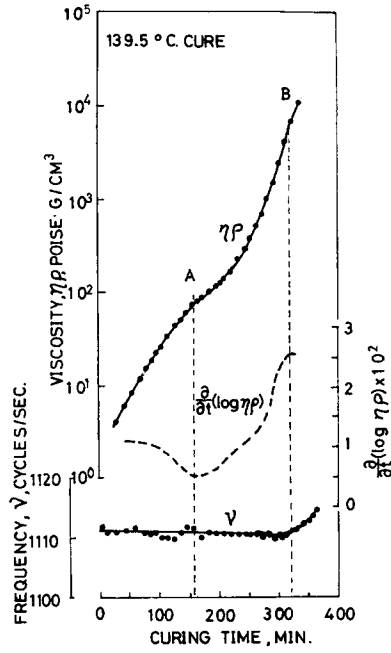


Fig. 2. Viscosity and resonance frequency as a function of curing time at curing temperature of 131°C.

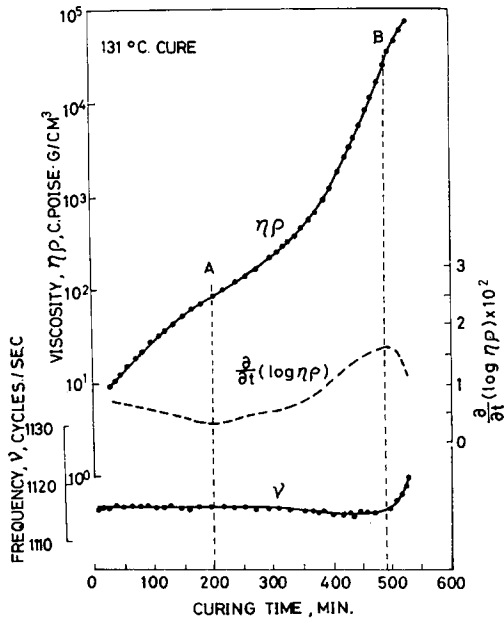


Fig. 3. Viscosity and resonance frequency as a function of curing time at curing temperature of 139.5°C.

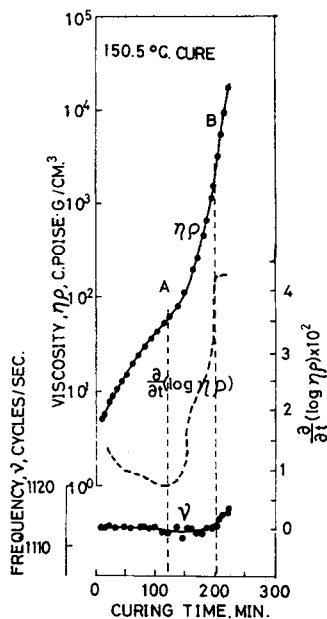


Fig. 4. Viscosity and resonance frequency as a function of curing time at curing temperature of 150.5°C.

were determined directly by chemical analysis, and that of diester, ether, and OH was calculated from these by means of the following relations:^{1,2}

$$\text{Anhydride} + \text{Monoester} + \text{Diester} = \text{Initial anhydride content}$$

$$\text{Epoxide} + \text{Diester} + \text{Ether} = \text{Initial epoxide content}$$

$$\text{Hydroxyl} + \text{Monoester} = \text{Initial hydroxyl content}$$

As shown in Figure 5 and Table I, all of the initial OH is converted to monoester with anhydride in the first 200 min. Accordingly, it is believed that the point A shows the termination of the initial stage of the epoxy resin-acid anhydride curing course.

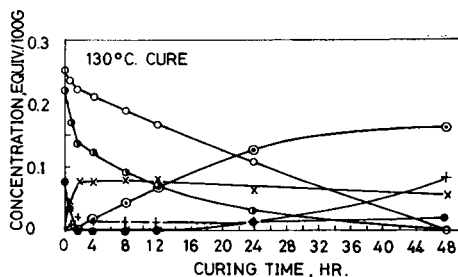


Fig. 5. Chemical changes with curing times: (O) epoxide; (●) acid anhydride; (⊙) alcoholic OH; (⊙) diester; (X) monoester; (+) ether bond.

TABLE I
Chemical Composition of Resin Mixtures (Curing Temperature 131°C)

Curing time, min	Chemical contents, equiv/100 g resin mixture					
	Epoxide	Anhydride	Mono-ester	Diester	Ether	OH
0	0.253	0.221	—	—	—	0.077
200	0.214 (15.4%) ^a	0.125 (43.4%) ^a	0.090	0.015	0.025	0 (100%) ^a
495	0.183 (27.7%) ^a	0.08 (63.8%) ^a	0.08	0.058	0.020	0 (100%) ^a

^a Parenthetical values are extent of reaction.

For bisphenol-type epoxy resin, the total concentration of reactive functional group is given by (epoxide \times 2) + (initial OH \times 1) so the extent of reaction of the functional group is calculated as 26.6% for point A and 37.2% for point B (gel point). On the other hand, for acid anhydride, the total concentration of reactive functional group is given by (anhydride \times 2), so the extent of reaction of the functional group is calculated as 43.4% for point A and 63.8% for point B (gel point).

For the systems Epikote 828-HHPA and Epikote 1001-HHPA with triethanolamine catalyst, Tanaka and Kakiuchi^{3,14} reported that epoxide and anhydride were consumed at approximately the same rate; the extent of reaction of the anhydride functional group was observed to be 50–70% at the gel point, a value in good agreement with the calculated one obtained from their equations derived by means of Flory's method.¹⁵

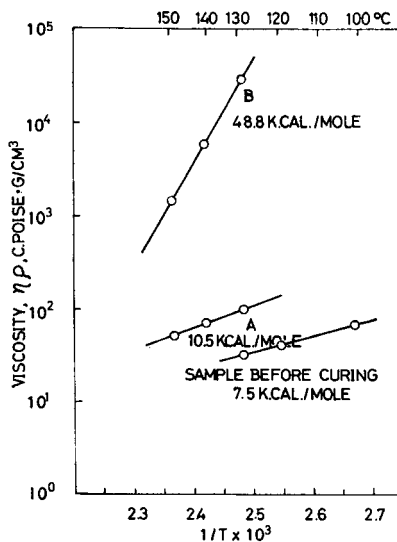


Fig. 6. Viscosity vs. reciprocal absolute temperature for resin mixture before curing, at point A, and point B.

Our experimental results give the different data from theirs, except for the extent of reaction of the anhydride functional group at the gel point. The differences are attributed to the presence of catalyst.

Apparent Activation Energy for Viscosity

Figure 6 shows plots of apparent viscosity versus reciprocal absolute temperature for the resin mixture before curing, for point A, and for the point B. In this figure plots for the resin mixture before curing were obtained at lower temperatures (100, 120, and 130°C) to eliminate errors due to curing.

The apparent activation energies for viscosity obtained are 7.5 kcal/mole for the resin mixture before curing, 10.5 kcal/mole for point A, and 48.8 kcal/mole for point B (gel point).

Overall Apparent Activation Energy of Polymerization

Figure 7 shows Arrhenius plots for the curing time required by the resin mixture to reach the states represented by the points A and B. The activation energies are 8.9 and 16.2 kcal/mole, respectively, for points A and B. These activation energies represent the overall apparent activation energies of polymerization as reported by Gough and Smith.¹⁶ Therefore the value, 8.9 kcal/mole, is connected with the initial stage of the curing course, and the value 16.2 kcal/mole with the gel point.

For the initial stage of the curing the main reaction is monoester formation between acid anhydride and OH group of the epoxy resin, as described in the previous paper.¹ Fisch et al.² obtained the heat of reaction for the monoester formation as 7.5 kcal/mole from the temperature dependence of the equilibrium constant of the glyceryl ditolyl ether-phthalic anhydride reaction system. Kannebley¹⁷ obtained the activation energy as 10.85 kcal/mole from the temperature dependence of the reaction rate constant for the cyclohexanol-HHPA reaction system. In his study, measurements

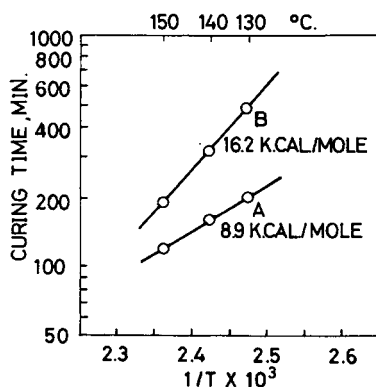


Fig. 7. Curing time vs. reciprocal absolute temperature.

were made at such low temperatures that side reactions were avoided; and an excess of cyclohexanol (about 40 times molar) was used, so that the reaction was pseudomonomolecular. Thus, the values, both 7.5 and 10.85 kcal/mole, were obtained for model reaction systems for monoester formation in the absence of epoxide. On the other hand, the value of 8.9 kcal/mole of this paper is obtained for an actual curing system with epoxide, and so this value involves to some extent the activation energy for diester formation and etherification as illustrated in Figure 5 and Table I.

Concerning the gel point, Tanaka and Kakiuchi³ obtained apparent activation energies for the curing in Epikote 828-HHPA and Epikote 1001-HHPA systems with triethanolamine as 14.1 and 14.4 kcal/mole, respectively. These values were obtained from the temperature dependence of the time it took the extent of reaction to reach the value for the gel point and a convenient value, such as 20, 30, or 40%. Our experimental results, give a larger value, i.e., 16.2 kcal/mole. The difference is attributed to the presence of catalyst. On the other hand, the gelatin is considered to be caused by increase of diester, and so the overall apparent activation energy for the gel point may be related to the activation energy for diester formation. Kannebly¹⁷ obtained an activation energy of 17.85 kcal/mole for the system, low molecular epoxy resin-benzyl monoester of HHPA. In this case, measurements were made at the low temperatures to avoid side reactions, and an excess of epoxide (about 40 molar) was used; thus the reaction was pseudo-monomolecular. Our experimental results, give a smaller value (16.2 kcal/mole) than Kannebly's value (17.85 kcal/mole). The differences are considered to be caused by the fact that the value obtained here is the overall apparent activation energy, and so the value involves the activation energy for the simultaneous monoester formation.

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