JOURNAL OF APPLIED POLYMER SCIENCE VOL. 21, 3367-3379 (1977)

Change of Viscoelastic Properties of Epoxy Resin in the Curing Process

KATSUHITO SUZUKI and YASUSHI MIYANO, *Hitachi Research Laboratory, Hitachi Limited, Hitachi, Japan,* and TAKESHI KUNIO, *Faculty of Engineering, Keiougijuku University, Yokohama, Japan*

Synopsis

This paper is concerned with the relation between the time and temperature dependences of the flexural properties and the curing conditions for the bisphenol A-type epoxy resin with acid anhydride hardener. Relaxation moduli of epoxy resin, prepared at several curing temperatures and times, were measured in the temperature range from T_g − 70°C to T_g. The master curves of relaxation modulus for the epoxy resin could be constructed, using their thermorheological simple properties. The time–temperature shift factors of the epoxy resin could be approximately expressed by the Arrhenius equation with the activation energy 59.4 kcal/mole. independent of its curing conditions. The curing time and temperature were equivalent, that is, the short curing time at high temperature corresponded to the long curing time at low temperature. The curing time–temperature shift factor could be approximately expressed by the Arrhenius equation with the activation energy 21.3 kcal/mole, which was higher than the activation energy 14.2 kcal/mole obtained in the measurements of gel times. The increase in the values shows that the temperature dependences of reaction rates increase with progressing gelation.

INTRODUCTION

The viscoelastic behavior of amorphous polymers has been widely studied, and it has become well known that their mechanical properties are governed by the time–temperature reduced law, and that the temperature dependence of the time–temperature shift factor can be expressed by a WLF equation.[1] The authors measured the stress–strain relation of unsaturated polyester resins and found that at high crosslinking densities, the temperature dependence of the time–temperature shift factor could be expressed by an Arrhenius equation,[2] but at low crosslinking densities it could be expressed by a WLF equation.[3] The relationship between polymer structure and viscoelastic behavior, thus, has been made considerably clear.

On the other hand, very little is known about the change of the viscoelastic properties of unsaturated polyester, epoxy, and other thermosetting resins in the curing process. The purpose of the present investigation is to shed light on the time and temperature dependences of mechanical properties of the epoxy resins having different curing degrees prepared at various curing temperatures and times. When a liquid epoxy resin is cured, its viscosity starts to rise at the gel point, and the resin eventually becomes a viscoelastic solid after going through the rubber state. In this study, the process of change to the rubber state was measured by means of a Culastometer, and with regard to the viscoelastic solid,

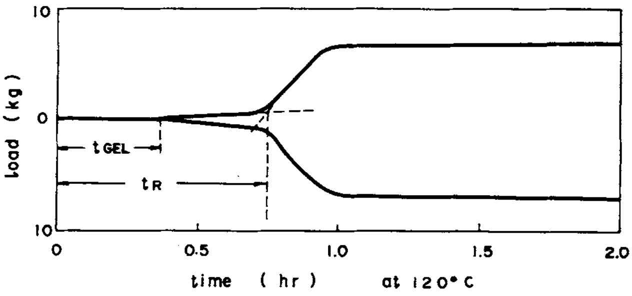


Fig. 1. Load–time curve obtained by Culastometer.

the relaxation moduli at various temperatures were measured by the flexural constant strain test.

As a result, it was revealed that the time-temperature reduced law held in this case and that the time-temperature shift factor did not depend on curing conditions of the resin and could be expressed by the same Arrhenius equation, and also that the curing time and curing temperature were equivalent.

EXPERIMENTAL

The epoxy resin was Dow Chemical DER 332; this is a diglycidyl ether of bisphenol A with a molecular weight of approximately 350. The crosslinking agent used in the curing reactions was Hitachi Chemical methyl himic anhydride (MHAcP). The catalyst was Shikoku Chemical 2-ethyl-4-methylimidazol (2E4MZ). These materials were mixed at proportions of 100 g DER 332, 103.6 g MHAcP, and 1 g 2E4MZ. Mole ratio of epoxy group/acid anhydride was 1/1.

Measurement of Gel Time and Rubber Time

Gel time t_{Gel} and rubber time t_R were measured with Japan Synthetic Rubber Culastometer II[4,5] for the samples weighing 2 g and at 0.25° torsional angle, in the temperature range from 100° to 150°C. From the load–time curve shown in Figure 1, the time when the load started rising and the time it later rose suddenly were taken, respectively, as t_{Gel} and t_R, and their relationships with curing temperature were investigated.

Measurement of Relaxation Modulus

Preparation of Test Pieces. Originally, it was planned to prepare the test pieces at 100°–150°C, the same curing temperature as in the Culastometer, but the resin was heated by the curing reaction heat and could not be kept at constant temperature. Therefore, first the resin was precured for 6 hr at 80°C, where very little heat generation at curing was observed, and then cured at 100°–150°C. First, the precuring was performed by pouring liquid resin into a mold of 130 × 140 × 5 mm inside dimensions held at 80°C in an air oven for 6 hr. This 6 hr for precuring is equivalent to twice the estimated gel time at 80°C. The precured

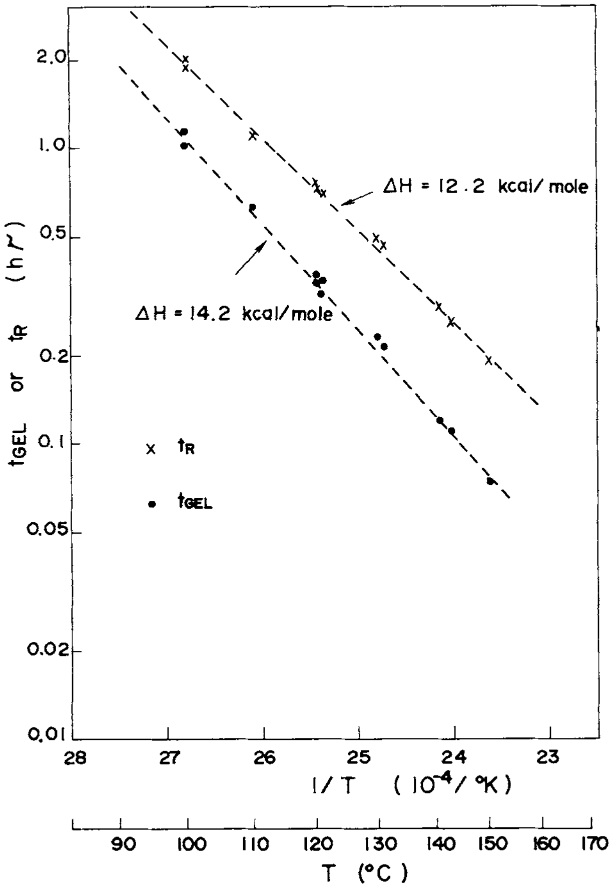


Fig. 2. Arrhenius plot of gel time t_{Gel} and rubber time t_R.

resin plate was then cured for the specified time by inserting it between two steel plates previously maintained at 100°–150°C in an air oven.

By temperature measurements with a thermocouple buried in the precured resin plate, it was confirmed that the resin temperature rose to 150°C within 6 min and that no particular heat generation occurred thereafter. Curing time was taken at 2–16 times the t_R at each curing temperature. From the resin plate thus prepared, test pieces 10 mm wide, 130 mm long, and 5 mm thick were taken and subjected to measurement of relaxation modulus.

Measurement of Relaxation Modulus. Relaxation modulus was measured in a three-point flexural test at a constant strain rate,[6] with an Autograph IS-20T (a product of Shimazu Seisakusho Ltd.). The temperature dependence of the relaxation modulus was measured in the temperature range from $T_g - 70°C$ to T_g, below the curing temperature. A deformation speed of 5 mm/min, for a span of 100 mm, was taken as standard. For test pieces of the lowest or highest curing degree, that is, for those cured at 100°C-4 hr and 150°C-2.56 hr, the time dependence of relaxation modulus was examined in greater detail by varying the deformation speed from 0.05, 0.5, 5, to 50 mm/min.

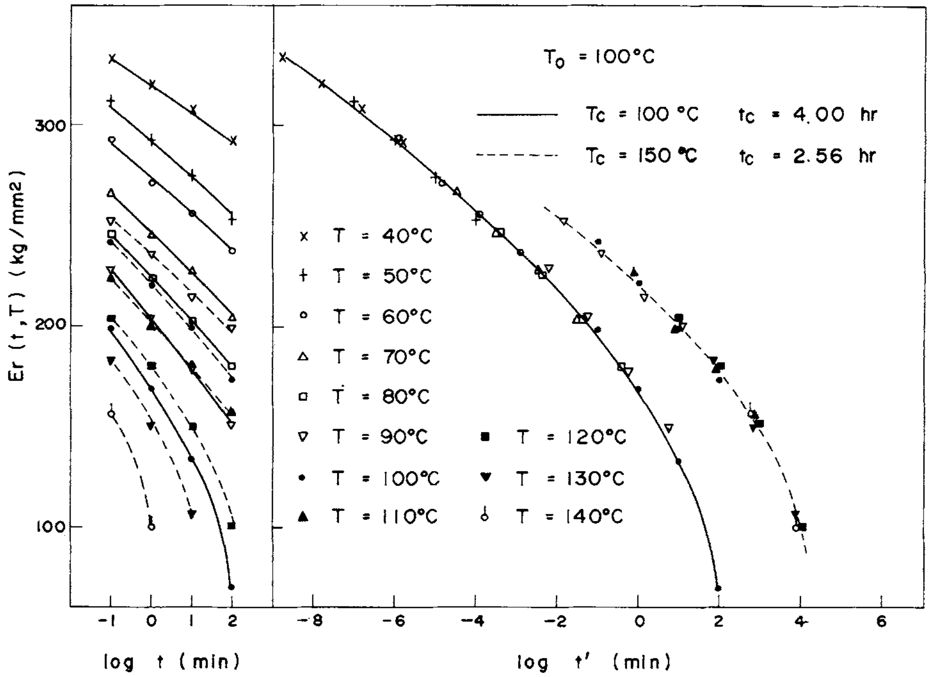


Fig. 3. Master curve of relaxation modulus.

RESULTS AND DISCUSSION

Curing Temperature Dependence of Gel Time and Rubber Time

The gel time t_{Gel} and rubber time t_R are presented in Figure 2, which shows that both t_{Gel} and t_R, within the curing temperature range of 100°–150°C, can be expressed by the Arrhenius equation.

$$\log \frac{t_1}{t_2} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1}$$

where $t = t_{\mathrm{Gel}}$ or t_R, in hr, ΔH = activation energy, in kcal/mole, R = gas constant, 1.69×10^{-3} kcal/deg °C·mole, and T = curing temperature, in °K.

Also from Figure 2, the activation energy ΔH of reaction was calculated to be 14.2 kcal/mole for t_{Gel} and 12.2 kcal/mole for t_R. These values agree approximately with 14 kcal/mole activation energy obtained by Tanaka et al. from measurements of gel time, chemical composition, and viscosity, with regard to a bisphenol A-type epoxy resin and acid anhydride hardener.[7] Also with various combinations of other epoxy resins and hardeners, the activation energy required for the curing reaction is reported to be 8–17 kcal/mole.[8] Therefore, the results obtained here seem to be reasonable.

Relationship of Relaxation Modulus to Curing Temperature and Curing Time

In Figure 3, the experimental relaxation curves for samples cured at 100 °C·4 hr and 150°C·2.56 hr are shown on the left, and the master curves at the reference

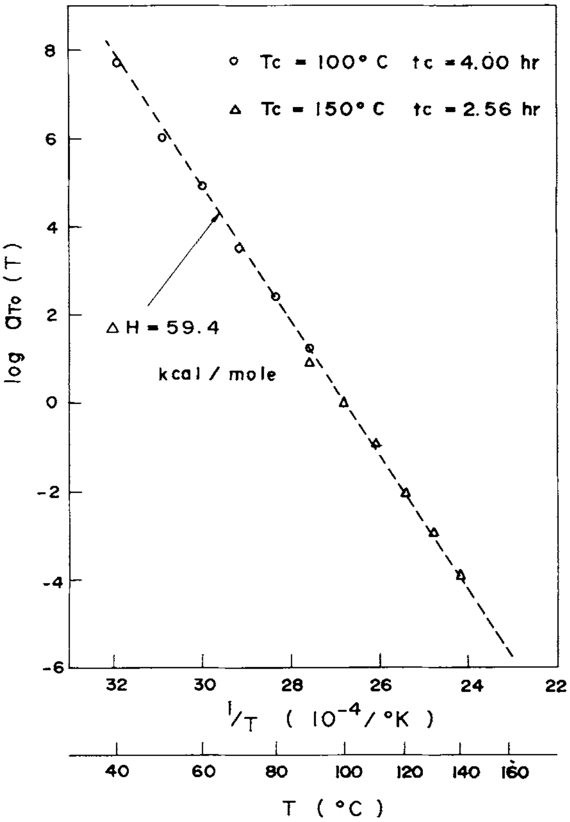


Fig. 4. Arrhenius plot of shift factor $a_{T_0}(T)$

temperature T_0 = 100°C are shown on the right. For both samples, smooth superimposed curves were obtained, and the time–temperature reduced law held. The relationship between temperature and time–temperature shift factor $a_{T_0}(T)$ is shown in Figure 4. The $a_{T_0}(T)$ for samples prepared at 100°C·4 hr and 150°C·2.56 hr agreed with each other and could be expressed by an Arrhenius equation irrespective of curing conditions. The activation energy was calculated to be 59.4 kcal/mole, which approximated the value obtained with unsaturated polyester resins.[3]

Figure 5 shows the relationship between temperature and relaxation modulus at time t = 1 min for samples prepared for various curing times at curing temperatures of 100°, 120°, and 150°C. It is seen that relaxation modulus increases as curing time lengthens.

Figure 6 shows the relationship of temperature and relaxation modulus at t = 1 min for samples prepared at 100°–150°C curing temperature and a curing time twice the t_R. It is seen that in the lower temperature region, the relaxation moduli agree with each other regardless of curing conditions but that in the higher temperature region, the relaxation moduli are higher for samples with higher curing temperatures.

Figure 7 shows the relationship between time and relaxation modulus at reference temperature T_0 = 100°C for samples used in Figure 5. It is seen that the longer the curing time, the higher the relaxation modulus. Figure 8 indicates

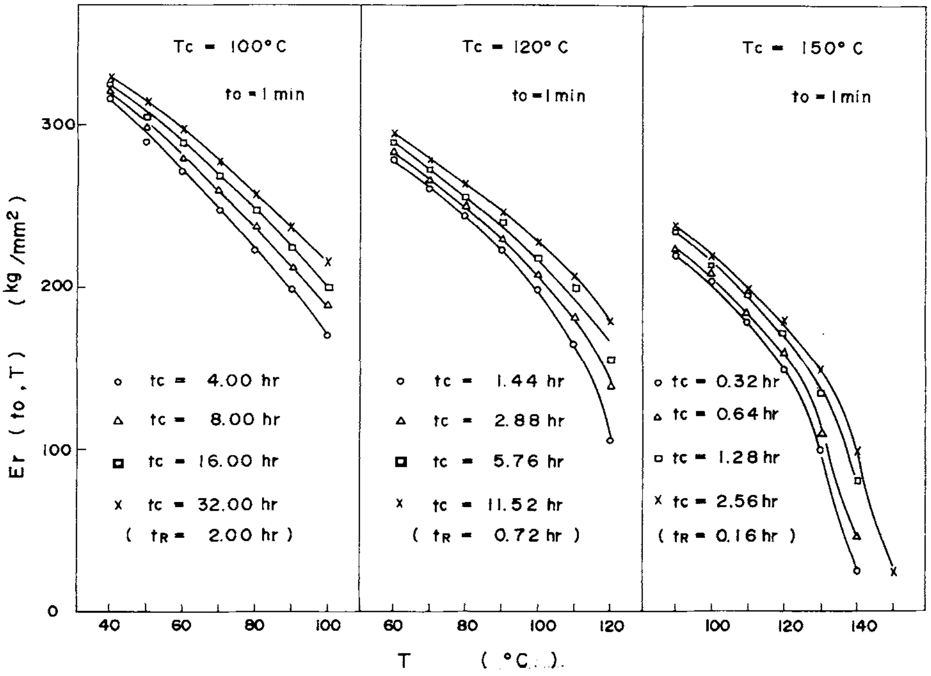


Fig. 5. Temperature dependence of relaxation modulus of resins cured under several conditions.

the relationship of relaxation modulus to time for samples used in Figure 6. As in the case of Figure 6, the relaxation moduli tend to agree in the short time region regardless of curing conditions, but in the long time region, they become higher for samples with higher curing temperatures.

As mentioned above, the time and temperature dependences of relaxation modulus have been made clear for samples prepared at various curing temperatures and times. Using relaxation modulus as a yardstick, the correlation between curing temperature and time will be discussed, so as to find, for example, the length of curing time at 150°C that corresponds to 4 hr at 100°C.

In Figure 3, the master curves for two samples prepared under different curing conditions are somewhat different and cannot be superposed by shifting along the horizontal axis. This presumably suggests that the form of a master curve differs depending on the combination of curing temperature and time, and consequently that curing temperature and time must be considered separately. Therefore, on the relaxation modulus–time curve with curing time as the parameter as shown in Figure 7, the point at which the 100°C-4 hr cured sample shows a relaxation modulus of 200 kg/mm^2 was taken as a reference, and it was attempted to superpose, by shifting along the horizontal axis, the points of other samples where they show a relaxation modulus of 200 kg/mm^2. The quantity of shift here is $(\log t' - \log t_0') = \log t'/t_0' = \log Cd$, where Cd means the curing degree of each sample against the 100°C-4 hr cured sample as the reference, and it is the relaxation time–curing time shift factor.

Figure 9 indicates the relationship between curing degree C_d and curing time. The point A corresponds to the value of 100°C-4 hr cured sample as the reference.

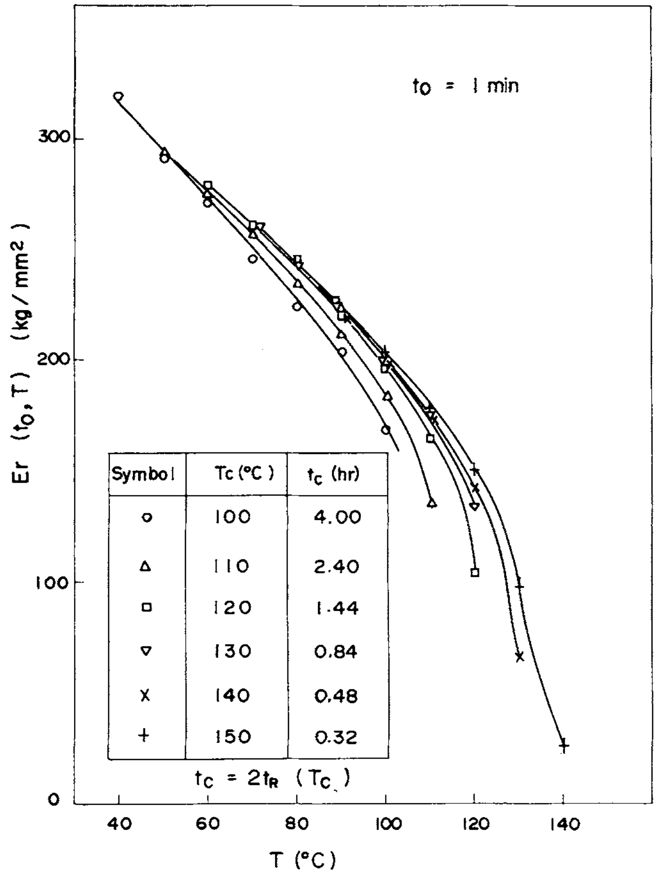


Fig. 6. Temperature dependence of relaxation modulus of resins cured under several conditions.

In Figure 9, the samples cured at 110°, 130°, and 140°C have only one C_d point respectively, because they were prepared under one curing condition.

To standardize the data of Figure 9, an attempt to superpose them by shifting along the horizontal axis was made. This operation corresponds to a conversion of curing time to temperature, which means that the state of a sample cured at a high temperature for a short time corresponds to that of a sample cured at a low temperature for a long time. In other words, the time–temperature reduced law recognized for the viscoelastic phenomena is extended to the reduction of time and temperature in chemical reactions.

Figure 10 presents a C_d master curve where 100°C curing temperature is used as the reference. The relationship between temperature and curing time–temperature shift factor $b_{T_0}(T)$ used in drawing this master curve is shown in Figure 11. It could be expressed by an Arrhenius equation with activation energy 21.3 kcal/mole.

Figure 11 also gives the $a_{T_0}(T)$ and the $c_{T_0}(T)$, obtained from time–temperature reduction of relaxation modulus and from gel time at 100°C as the reference, respectively. In Figure 11, the 21.3 kcal/mole activation energy obtained

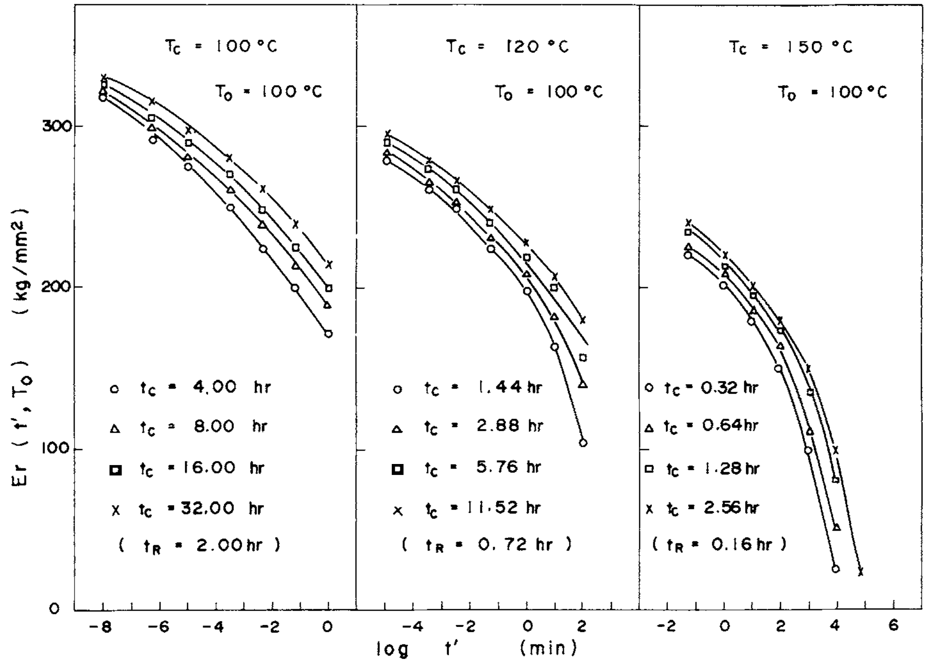


Fig. 7. Time dependence of relaxation modulus of resins cured under several conditions.

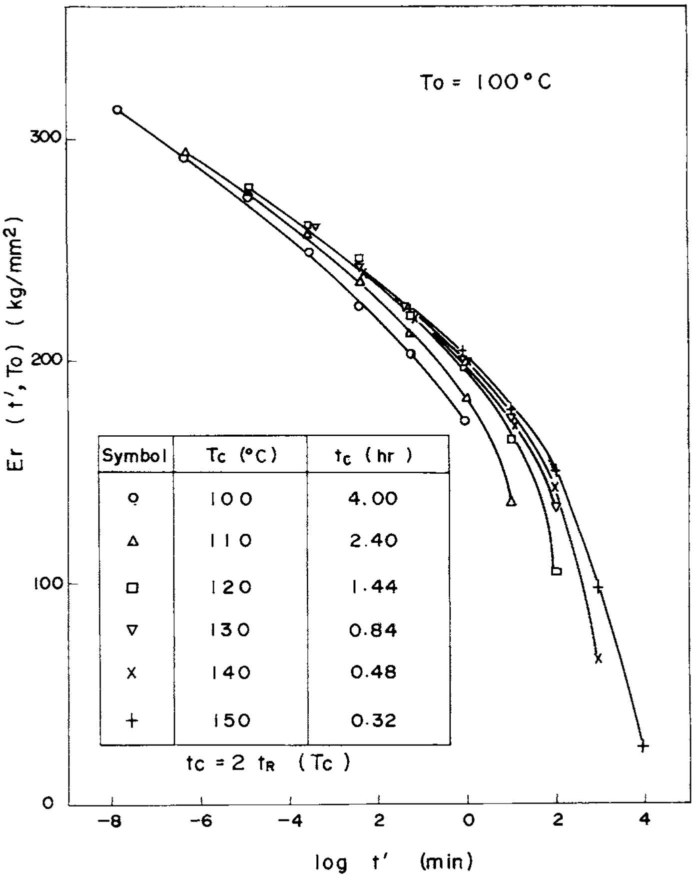
from the curing degree lies between the 14.2 kcal/mole from the gel time and the 59.4 kcal/mole from the relaxation modulus.

As mentioned above, it has been made clear that the activation energy based on the relaxation process below T_g was constant irrespective of curing conditions, and that the activation energy of curing reaction obtained from the curing degree with relaxation modulus as the yardstick was larger than the value obtained from the gel time. These results will be discussed in relation to other physical values.

Table I gives the specific volume, T_g, heat distortion temperature *HDT*, and infrared absorbance of the samples used for the measurement of the relaxation modulus. These values were measured in order to estimate the curing states of samples from characteristics other than mechanical properties.

First, the degree of chemical reaction in the resin will be discussed in terms of epoxy group content. In the 80°C-6 hr precuring, about 80% of the epoxy groups have undergone reaction. At the subsequent 100°–150°C curing, the degree of reaction rises to a maximum of 90%. This means that, as far as epoxy group content is concerned, there is not much difference among the resins with various curing degrees used in the present study. This, presumably, is why the activation energy based on the relaxation process below T_g was constant irrespective of the curing conditions of the samples.

Next, specific volume at 23°C will be discussed. After the precuring at 80°C-6 hr, the specific volume has decreased by 3.3%, but after the subsequent 100°–150°C curing, the value has increased. In the 150°C-2.56 hr cured sample, the specific volume has increased by 0.9% over that of the 80°C-6 hr precured sample.



Symbol	Tc (°C)	tc (hr)
o	100	4.00
△	110	2.40
□	120	1.44
▽	130	0.84
x	140	0.48
+	150	0.32

Fig. 8. Time dependence of relaxation modulus of resins cured under several conditions.

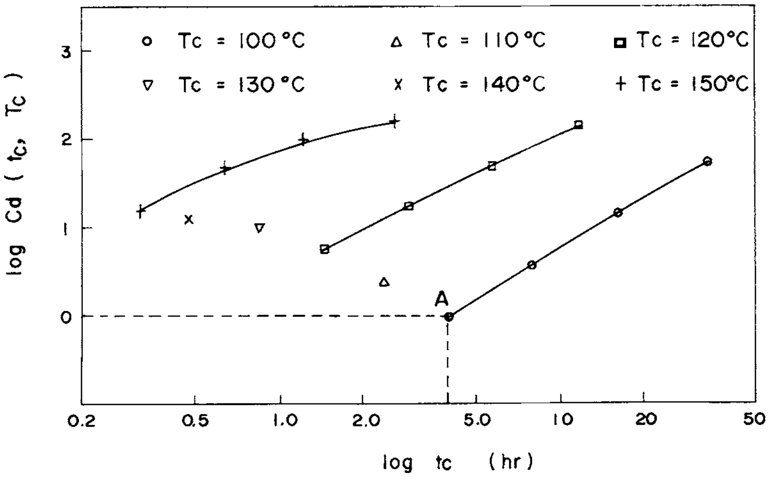


Fig. 9. Relationship between curing time and curing degree.

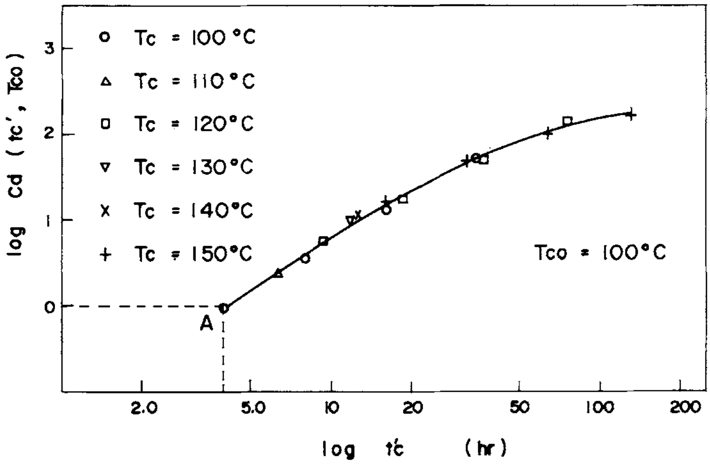


Fig. 10. Master curve of curing degree.

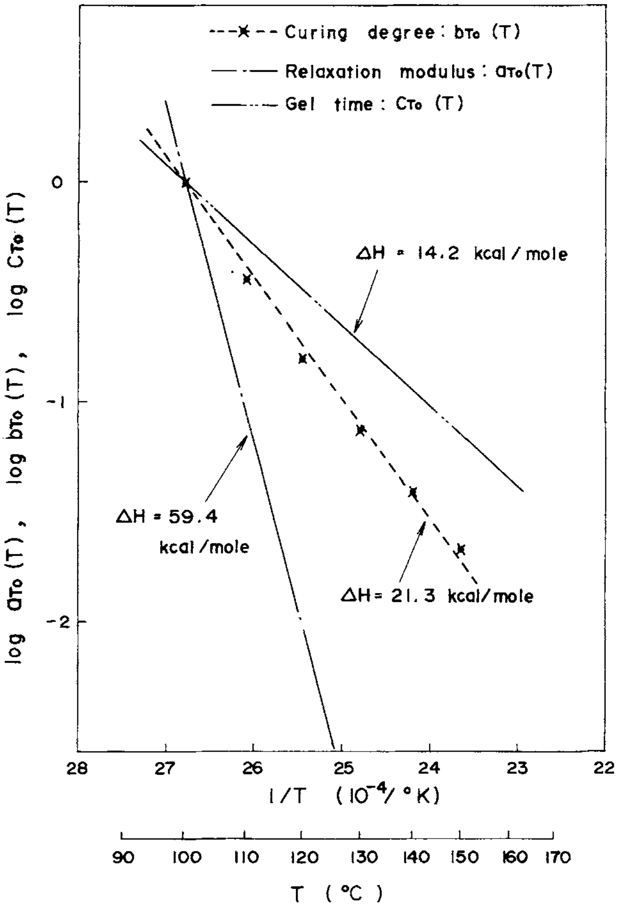


Fig. 11. Arrhenius plot of shift factor.

TABLE I
Properties of the Samples

Sample		Specific volume at 23° C, cc/g	T_g, °C	*HDT*,[a] °C	Infrared absorbance $\frac{\text{epoxide at 915 cm}^{-1}}{\text{phenyl at 1500 cm}^{-1}}$
No.	Cure schedule, °C/hr				
1	non cure	0.8358	—	—	1.41
2	80/6	0.8084	78	72	0.30
3–1	80/6 + 100/4	0.8136	112	109	0.26
3–2	80/6 + 100/8	0.8137	119	114	0.25
3–3	80/6 + 100/16	0.8142	123	119	0.24
3–4	80/6 + 100/32	0.8143	125	120	0.23
4	80/6 + 110/2.4	0.8145	123	118	—
5–1	80/6 + 120/1.44	0.8153	128	120	—
5–2	80/6 + 120/2.88	0.8155	129	126	—
5–3	80/6 + 120/5.76	0.8160	131	129	—
5–4	80/6 + 120/11.52	0.8168	136	135	0.20
6	80/6 + 130/0.84	0.8166	136	125	—
7	80/6 + 140/0.48	0.8169	136	130	—
8–1	80/6 + 150/0.32	0.8179	135	130	0.18
8–2	80/6 + 150/0.64	0.8183	143	137	0.17
8–3	80/6 + 150/1.28	0.8183	150	143	0.14
8–4	80/6 + 150/2.56	0.8198	155	151	0.14

[a] Heat distortion temperature; ASTM D-648-55T, fiber stress 18.56 kg/cm^2.

Meanwhile, both T_g and *HDT* rose with an increase in curing time, and sometimes there were cases when T_g was higher than curing temperature. From these facts, it may be deduced that, in the sample epoxy resins used, about 50% of the epoxy groups reacted to form a crosslinked structure and reduce the volume, before reaching the gel point, but in the reaction thereafter, the volume slightly increased while the crosslinking density increased. Thus, after the gel point, the molecular movement presumably was impeded by the increase in viscosity, and the temperature dependence of the reaction velocity had changed, so that presumably the activation energy after the gel point obtained from the curing degree was larger than that obtained from the gel time.

The activation energy based on the relaxation process and that obtained from the curing degree are fundamentally different, because the former is based on molecular movement and the latter on chemical reaction. In the latter case, however, the reaction should also take place after the reactive points approach each other. From the viewpoint of molecular mobility, therefore, the activation energy due to the relaxation process is also related to reaction. This point requires further investigation.

CONCLUSIONS

With a system consisting of a bisphenol A-type epoxy resin and an acid anhydride hardener, the gel times and relaxation moduli of samples prepared at various curing times and temperatures were examined. The results are summarized as follows:

(1) Activation energy of reaction obtained from gel time was 14.2 kcal/mole, which was close to similar values reported in the literature.

(2) For relaxation moduli of samples of different crosslinking densities prepared under various curing conditions, the time–temperature reduced law held within the temperature range from $T_g - 70°C$ to T_g. The time–temperature shift factor was not dependent on curing conditions and could be approximated by an Arrhenius equation with an activation energy of 59.4 kcal/mole.

(3) As a yardstick of curing degree of cured resin, a relaxation time–curing time shift factor C_d was introduced from a relaxation modulus–time curve with curing time as the parameter; and further, the curing temperature–curing time shift factor was obtained from a C_d–curing time curve with curing temperature as the parameter. With this, it was shown that curing temperature and curing time could be reduced.

(4) It was found that curing temperature–curing time shift factor in paragraph (3) above could be approximated by an Arrhenius equation with an activation energy of 21.3 kcal/mole. This value represented the activation energy of curing reaction after gelation, when relaxation modulus was used as a yardstick. The value was larger than that obtained from the gel time in paragraph (1) above. This is presumably because, with progress of the reaction, viscosity rises and molecular movement is impeded, and thus reaction velocity becomes more dependent on temperature.

The authors wish to express their sincere gratitude to Dr. N. Shito, Hatachi Research Laboratory, Hitachi, Ltd., for his valuable advice and suggestions, and also to Mr. N. Shibata at the same laboratory for his cooperation in the experiments.

References

1. J. D. Ferry, *Viscoelastic Properties of Polymers,* Wiley, New York, 1961, p. 215.
2. M. Kitoh, Y. Miyano, and K. Suzuki, *Kobunshi Ronbunshu,* **32,** 55 (1975).
3. M. Kitoh and K Suzuki, *Kobunshi Ronbunshu,* **32,** 147 (1975).
4. Japan Synthetic Rubber Co., Ltd., *Jpn. Plast.,* **7,** 46 (1973).
5. M. Umeno, *Goseijushi,* **17,** 8 (1971).
6. M. L. Williams, *A.I.A.A. J.,* **2,** 785 (1964).
7. Y. Tanaka and H. Kakiuchi, *J. Appl. Polym. Sci.,* **7,** 1063 (1963).
8. W. G. Potter, *Epoxide Resins,* Plastics Institute, London, 1970, p. 56.

Received September 10, 1976
Revised October 22, 1976