Curing Behavior of Epoxy Resin Having Hydroxymethyl Group

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SYNOPSIS

A new type of epoxy resin having hydroxymethyl group was synthesized. This epoxy resin was mixed with commercial epoxy resin in various ratios. The mixed epoxy resins were cured with a mixture of 4,4′-diaminodiphenylmethane and *m*-phenylenediamine (molar ratio, 6 : 4) as a hardener. Curing behavior of the epoxy resin systems with the hardener was examined by DSC and TG-DSC, and parameters of cure reaction were obtained. Viscoelastic properties of cured resin were studied by dynamic mechanical analyzer.

It was found that the higher the amount of epoxy resin having hydroxymethyl group, the lower the activation energy (Ea) and the higher the rate constant (k) were. It was also found that the higher the amount of the epoxy resin having hydroxymethyl group, the better heat resistance the fully-cured resin had.

These results were explained as follows: Hydroxymethyl group accelerated an epoxide–amine reaction. The crosslinking density of the cured resin was increased because in the hydroxymethyl group occurred a condensation reaction above 200°C.

INTRODUCTION

Epoxy resins are widely employed as coatings, electrical or electronical materials, adhesives, and in structural applications because of their high performances, such as good mechanical, thermal, and electrical properties. Recently, since high performance epoxy resin is strict in its requirement, polyfunctional epoxy resins have been of interest and have been offered in practical fields. In particular, novolac type epoxy resins have been widely used as encapsulation materials for semiconductors because of their good heat resistance. The structure of novolac-type epoxy resins has a large influence on the properties of cured resins. So, we have studied the relationship between viscoelastic property and structure of epoxy resins prepared from novolacs.[1,2] On the other hand, resol, which is the other intermediate of phenolic resin, is barely used as a starting material for production of epoxy resins. There are only a few articles in the literature concerned with resol-type epoxy resin. One article was presented by Renner.[3] According to this report, not only phenolic hydroxy group but also hydroxymethyl group were glycidyletherified with epichlorohydrin. So, we considered that resol-type epoxy resins, having hydroxymethyl groups that had not been glycidyletherified, gave excellent performances, such as rapid curing behavior, high heat resistance, and good adhesive property. In the previous article,[4] we reported that four new epoxy resins having hydroxymethyl group were synthesized; they cured very quickly with polyamine-type hardener. In the present study, the curing behavior of two-nuclei *o*-cresol type epoxy resin, having two hydroxymethyl groups (I), and the thermal property of the cured resin were investigated. Additionally, a diglycidylether of bisphenol A (DGEBA) was mixed with (I) and was used in the same way. Curing examined by differential scanning calorimeter (DSC) and parameters of cure reaction were obtained. Properties of the cured resin were studied by dynamic mechanical analyzer.

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Journal of Applied Polymer Science, Vol. 44, 419–423 (1992)
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EXPERIMENTAL

Epoxy Resin

An epoxy resin having hydroxymethyl group and a commercial epoxy resin were used.

Bis(3-hydroxymethyl-4-glycidyloxy-5-methylphenyl)methane (I)

This epoxy resin was synthesized according to the previous article.[4]

Diglycidylether of Bisphenol A (DGEBA)

A commercial epoxy resin (Epikote 828) was used. The structure and properties of epoxy resins were shown in Table I.

Hardener

As a hardener, a mixture of 4,4′-diaminodiphenylmethane (DDM) and *m*-phenylenediamine (MPDA) (molar ratio, 6 : 4) was used.

Measurement of Curing Behavior

Epoxy resin (I) and DGEBA were mixed in various ratios and were heated to 50°C. To this mixture, the stoichiometric amount of a hardener was added and was mixed well. The sample was then examined by DSC (DSC-8230, Rigaku Denki Co.) and TG-DSC (PTC-10A, Rigaku Denki Co.) with a heating rate of 10°C/min from room temperature to 250°C under nitrogen atmosphere.

Preparation and Characterization of Cured Resin

Epoxy resin (I) and DGEBA were mixed in various ratios and were heated to 50°C. To this mixture, the stoichiometric amount of a hardener was added and mixed well. The above mixture was then poured to a preheated Teflon mold, and cured under the following conditions: 2 h at 100°C + 2 h at 150°C + 2 h at 180°C + 2 h at 200°C. Dynamic mechanical properties of cured resin were measured by a viscoelastic spectrometer (tensile-mode, VES-S type, Iwamoto Co.) at 10 Hz with a heating rate of 2°C/min.

RESULTS AND DISCUSSION

Curing Behavior

DSC scans of mixed samples of the epoxy resin systems are shown in Figure 1. The first peak is due to the heat generated by the reaction of epoxy resin and hardener. The peak temperature shifted to the lower temperature with increasing amount of (I). The second peak appeared in the systems that contained (I) more than 75%. In order to make clear the meaning of this peak, the TG-DSC curve of (I)/hardener system was measured and shown in Figure 2. It was found that the decrease of thermal gravity was about 3.2% at the second peak of DSC curve. From these results, it was considered that the second peak of DSC curves was due to the heat generated by the condensation reaction of hydroxymethyl groups with the hydrogen of aromatic ring. That is to say, the decrease of thermal gravity was due to the release of low molecular weight compounds, H_2O,

Table I Properties of Epoxy Resins

Structure	Epoxy Symbol	Epoxy Equivalent
$H_2C(-O-)HC-H_2C-O-C_6H_2(CH_3)(CH_2OH)-CH_2-C_6H_2(CH_3)(CH_2OH)-O-CH_2-CH(-O-)CH_2$ (ring substituents printed as H_3C, HO_2HC, CH_3, CH_2OH)	(I)	202 (200)[a]
$H_2C(-O-)HC-H_2C-O-C_6H_4-C(CH_3)_2-C_6H_4-O-CH_2-CH(-O-)CH_2$	DGEBA	185 (170)[a]

[a] Theoretical value.

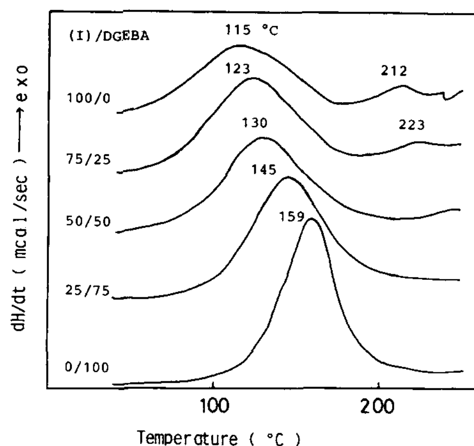

Figure 1 Curing behavior of the epoxy resin system measured by DSC.

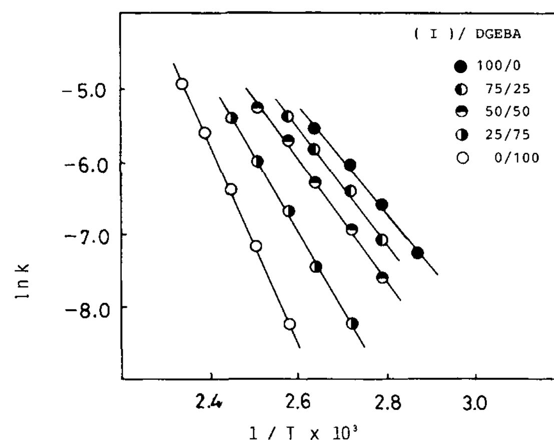

Figure 3 Arrhenius plots for epoxy resin system.

which was formed by a condensation reaction. On the other hand, crosslinking density was increased because the methylene linkage was formed by a condensation reaction. This phenomenon appeared in the temperature dispersion of the dynamic mechanical property of the cured resin.

Kinetic Parameters

Several parameters that determined the cure reaction of the epoxy resin with an amine hardener were proposed.[5,6] In this study, the rate constant (k) at different temperatures was estimated using the Barrett relation.[7] Assuming that the initial step of cure reaction follows the first order Arrhenius-type kinetics, the activation energy (Ea) can be obtained. The Barrett relation is described as:

$$k = \frac{\frac{dH}{dt}}{A - a}$$

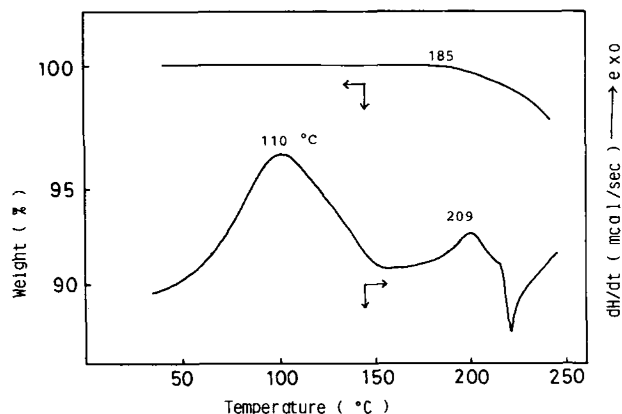

Figure 2 TG–DSC thermogram of (I)/hardener.

where A and a are the total area and the area at a particular temperature t. The plot of ln k, which was estimated using the Barrett relation against 1/T, is shown in Figure 3. The Ea and k at 100°C were obtained from regression plot (Table II). The more the amount of (I), the lower Ea and the higher k were, so it was found that the curing rate of the epoxy resin system was increased with an increase of the amount of (I). It is known that the addition of alcohol to epoxy resin accelerates the amine curing reaction.[8,9] In the present case, hydroxymethyl group in the epoxy resin not only plays the role of accelerating, but also can react itself and increase the crosslinking density of cured resin.

Dynamic Mechanical Properties of Cured Epoxy Resins

Dynamic mechanical properties are shown in Figures 4–6. In the (I)/hardener system, the resin that was cured for 2 h at 100°C had a glass transition temperature (T_g) of 144°C, but the after-cured resin didn't have clear T_g until 250°C (Fig. 4). That is to

Table II Curing and Kinetic Parameters of the Epoxy Resin System Measured by DSC

(I)/DGEBA (wt %)	*To* (°C)	*Tp* (°C)	*Ea* (kJ/mol)	$k \times 10^3$ [a] (sec^{-1})
100/0	62	115	61.9	3.01
75/25	65	123	66.5	2.12
50/50	71	130	69.9	1.29
25/75	76	145	88.3	0.363
0/100	89	159	114.2	0.0684

To: Onset temperature of curing reaction.
Tp: Peak temperature of thermogram.
[a] At 100°C.

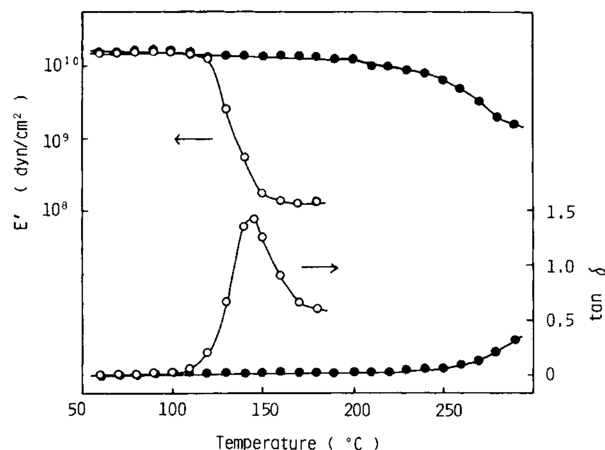

Figure 4 Temperature dependence of viscoelastic properties of cured (I)/hardener: (○) 100°C/2 h, (●) 100°C/2 h + 150°C/2 h.

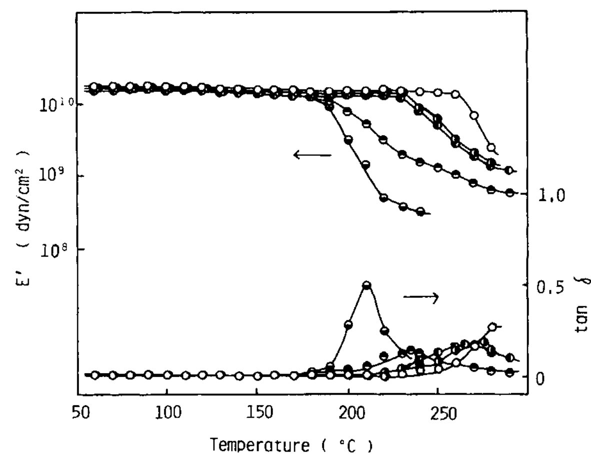

Figure 6 Temperature dependence of viscoelastic properties of fully-cured resins: Composition (wt %), (I)/ DGEBA, (○) 100/0, (◑) 75/25, (◐) 50/50, (◓) 25/75, (◒) 0/100.

say, T_g shifted to the higher temperature region by the after-curing. Storage modulus (E') of the after-cured resin retained the value of 10^{10} dyn/cm^2 until 250°C. Therefore, it was concluded that the cross-linking density increased as a result of the after-curing. On the other hand, in the DGEBA/hardener system, the resin that was cured for 2 h at 100°C had a T_g of 185°C (Fig. 5), which was higher than that of the (I)/hardener system. However, after-cured resin had a T_g of 192°C, which was only 7°C higher than that of the cured resin for 2 h at 100°C. From these results, it was considered that the epoxy resin having hydroxymethyl group could cure by the two kinds of reactions; one is the epoxide-amine addition reaction and the other is the condensation reaction. In Figure 6, the temperature dependence of viscoelastic properties of fully-cured resins that had various compositions were shown. The higher the amount of (I), the higher the T_g. In Table III, the viscoelastic parameters of cured resins were summarized. The higher the amount of (I), the lower the T_g of resins that were cured for 2 h at 100°C. On the other hand, the higher the amount of (I), the higher the T_g of the fully-cured resin. The E' at 250°C of the (I)/DGEBA mixture showed values of above 10^9 dyn/cm^2, but that of the DGEBA system showed a value of 10^8 dyn/cm^2. That is to say, the addition of (I) to DGEBA increases the heat resistance of the cured resin. These results were considered to be due to the increase of the cross-linking density of the cured resin by the condensation reaction of the hydroxymethyl group.

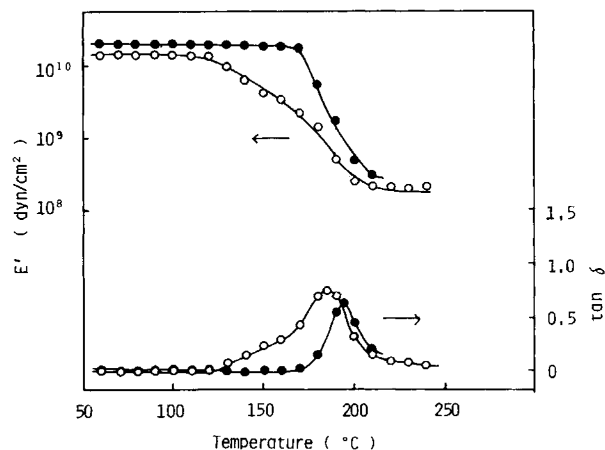

Figure 5 Temperature dependence of viscoelastic properties of cured DGEBA/hardener: (○) 100°C/2 h, (●) 100°C/2 h + 150°C/2 h.

CONCLUSIONS

Epoxy resin having the hydroxymethyl group was mixed with the commercial resin in various ratios. Aromatic amine was used as a hardener. Curing behavior of the epoxy resin systems and the dynamic mechanical properties of the cured resins were studied. Curing rate of the resin system increased with an increase in the amount of the epoxy resin having the hydroxymethyl group. Also, the higher the amount of the epoxy resin having the hydroxymethyl group, the better the heat resistance of the fully-cured resin, because in the hydroxymethyl group occurred a condensation reaction at high temperature,

Table III Viscoelastic Parameters of Cured Epoxy Resin

(I)/DGEBA (wt %)	T_g (°C)	E′ (dyn/cm^2) At 25°C	At 200°C	At 250°C
100/0	288 (144)[a]	2.59×10^{10}	1.91×10^{10}	1.46×10^{19}
75/25	277 (149)[a]	2.42×10^{10}	1.32×10^{10}	7.66×10^{9}
50/50	266 (160)[a]	2.60×10^{10}	1.57×10^{10}	7.00×10^{9}
25/75	233 (172)[a]	1.74×10^{10}	8.79×10^{9}	1.20×10^{9}
0/100	209 (185)[a]	1.94×10^{10}	5.20×10^{9}	5.14×10^{8} [b]

Cure condition: 100°C/2 h + 150°C/2 h + 180°C/2 h + 200°C/2 h.
[a] Cured at 100°C/2 h.
[b] At 241°C.

and crosslinking density was increased. It was concluded that the addition of the epoxy resin having the hydroxymethyl group to the commercial epoxy resin improved the properties of the commercial epoxy resin.

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Received June 25, 1990
Accepted March 20, 1991