Curing Behavior of Epoxy Resin Having Hydroxymethyl Group and Different Molecular Weight Distribution

K. OHTSUKA,[1]* K. HASEGAWA,[1] A. FUKUDA,[1] and K. UEDE[2]

[1]Plastics Department of Osaka Municipal Technical Research Institute, 6-50, 1-chome Morinomiya, Joto-ku, Osaka 536, Japan, and [2]Research Laboratory of Koei Chemical Co., Ltd., 12-13, 2-chome Hanaten-Nishi, Joto-ku, Osaka 536, Japan

SYNOPSIS

o-Cresol novolac-type epoxy resins having hydroxymethyl group were synthesized. These epoxy resins were cured with a mixture of 4,4′-diaminodiphenylmethane and *m*-phenylenediamine (molar ratio, 6:4) as a hardener. Effects of molecular weight distribution of epoxy resins on curing behavior were studied. Curing behavior of epoxy resins with hardener were examined by differential scanning calorimetery (DSC), and cure reaction parameters were obtained. Viscoelastic properties of the cured epoxy resins were studied by dynamic mechanical analyzer. It was found that the lower the average molecular weight of the epoxy resin, that is, the higher the concentration of hydroxymethyl group, the shorter the onset time of exothermal reaction, the higher the rate constant (k), and the lower the activation energy (E_a) were. It was also found that glass transition temperature (T_g) of fully cured epoxy resins was higher than those of fully cured general novolac-type epoxy resins.

INTRODUCTION

Novolac, which is an intermediate for phenolic resin, is an important starting material for production of epoxy resins. Novolac-type epoxy resins have been widely used as encapsulation materials for semiconductors because of their good heat resistance.

We have studied earlier the relationship between viscoelastic properties and structure of epoxy resins prepared from novolacs.[1,2] On the other hand, resol, which is the other intermediate of phenolic resin, is rarely used as a starting material for production of epoxy resins. There are only a few papers concerned with resol-type epoxy resins.[3] We have reported that four new epoxy resins having hydroxymethyl group have been synthesized and that they cured very fast with amine-type hardener.[4]

In a previous paper,[5] we reported that two-nuclei *o*-cresol-type epoxy resin having hydroxymethyl group was mixed with a commercial epoxy resin (DGEBA) and cured with an aromatic amine as a hardener, and that the higher the amount of the epoxy resin having hydroxymethyl group, the better heat resistance the fully cured resin had.

In this report, curing behavior and viscoelastic properties of *o*-cresol-type epoxy resin having hydroxymethyl group (*o*-cresol resol-type epoxy resin) were investigated. Additionally, novolac-type epoxy resins were used as reference resins and were compared to our prepared epoxy resins.

EXPERIMENTAL

Epoxy Resin

Six *o*-cresol resol-type epoxy resins (epoxy resin of o-cresol di-alchol: EOCDA) and two o-cresol novolac-type epoxy resins (epoxy resin of o-cresol novlac: EOCN) were synthesized.

Bis-(3-hydroxymethyl-4-glycidyloxy-5-methylphenyl) methane (EOCDA-1): This epoxy resin was synthesized according to the previous paper.[5]

EOCDA-2-6: First, *o*-cresol novolac was synthesized by a conventional method. Then, five kinds of *o*-cresol novolac were prepared by fractional precipitation (methanol–water) of the above *o*-cresol novolac. Second, the fractionated novolacs were hy-

* To whom correspondence should be addressed.

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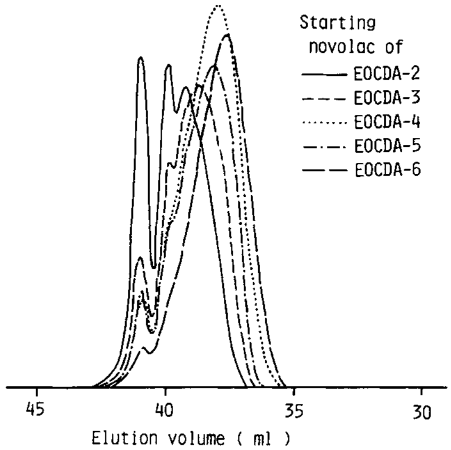


Figure 1 GPC chromatograms of *o*-cresol novolacs.

droxymethylated by formaldehyde in the presence of NaOH. Finally, those *o*-cresol resols were glycidyletherified by epichlorohydrin.

EOCN-1-2: *o*-cresol novolacs were synthesized by a conventional method. Then the *o*-cresol novolacs were glycidyletherified by epichlorohidrin.

Diglycidylether of bisphenol A (DGEBA): A commercial epoxy resin (Epikote 828) was used.

Epoxy equivalents of the obtained epoxy resins were determined by a tetraethylammoniumbromide-perchloric acid method (ISO-3001), using a potentiometric meter. Gel permeation chromatograms (GPC) of the fractionated *o*-cresol novolacs are shown in Figure 1, and the average molecular weight ($\bar{M}_n$ and $\bar{M}_w$) of the obtained *o*-cresol novolacs were calculated by use of GPC calibration curve that was made on the base of a series of *o*-cresol novolacs with a known molecular weight. The $—CH_2OH/—CH_3$ ratios of EOCDA were measured by ^{1}H-NMR. The T_g of the obtained epoxy resins was measured by differential scanning calorimetery (DSC) (DSC 120, Seiko Instruments Inc.). The structures and properties of these epoxy resins are shown in Tables I and II.

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 and the stoichiometric amount of a hardener were dissolved in CH_2Cl_2, and this mixture was dried under reduced pressure. Then the sample was examined by DSC (DSC-8230, 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

A mixture of epoxy resin and DGEBA (weight ratio, 8:2) was heated to 100°C. To this mixture, the stoichiometric amount of hardener was added and was well mixed. This mixture was poured into a preheated Teflon mold, and cured under the following conditions: 2 h at 100°C plus 1 h at 120°C plus 1 h

Table I Structures of Epoxy Resins

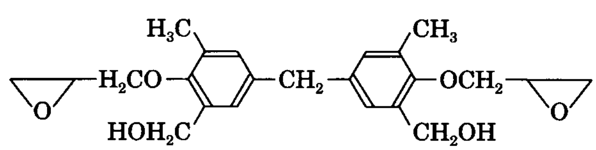
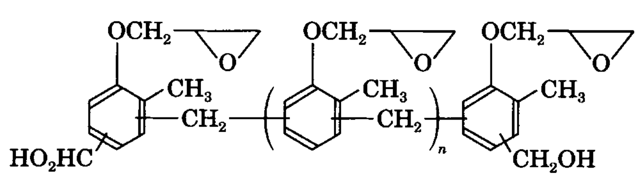
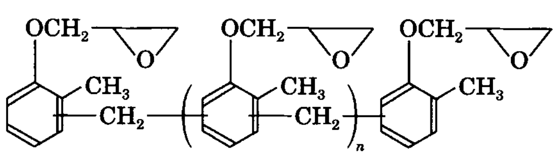
Symbol	Structure
EOCDA-1	
EOCDA-2-6	
EOCN-1-2	

Table II Properties of Epoxy Resins

Symbol	$\bar{M}_n$	$\bar{M}_w$ (of novolac)[a]	$\bar{M}_w/\bar{M}_n$	—CH_2OH[b] / —CH_3	Epoxy eq.	T_g[c] (°C)
EOCDA-1		M_w = 228		0.97	218	−3.2
EOCDA-2	380	450	1.18	0.36	236	5.8
EOCDA-3	470	560	1.19	0.27	228	18.0
EOCDA-4	520	640	1.23	0.26	221	20.0
EOCDA-5	540	700	1.30	0.18	212	20.5
EOCDA-6	650	820	1.26	0.15	209	22.8
EOCN-1	350	460	1.31	—	188	−5.5
EOCN-2	540	750	1.39	—	191	16.4

[a] By GPC.
[b] By ^{1}H-NMR.
[c] By DSC.

at 140°C plus 1 h at 160°C plus 1 h at 180°C plus 1 h at 200°C plus 1 h at 220°C plus 1 h at 240°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

Properties of Epoxy Resin

In Figure 1 gel permeation chromatograms of *o*-cresol novolacs, starting materials of EOCDA, are shown. Structures and properties of epoxy resins are given in Tables I and II. In Table II it was found that the higher the average molecular weight, the lower the —CH_2OH/—CH_3 ratios were. This is because the *o*-cresol resol-type epoxy resins had two terminal hydroxymethyl groups. Further, it was shown that the higher the average molecular weight, the higher the T_g was, and that T_g of resol-type epoxy resins was higher than that of novolac-type epoxy resins, which had similar average molecular weight.

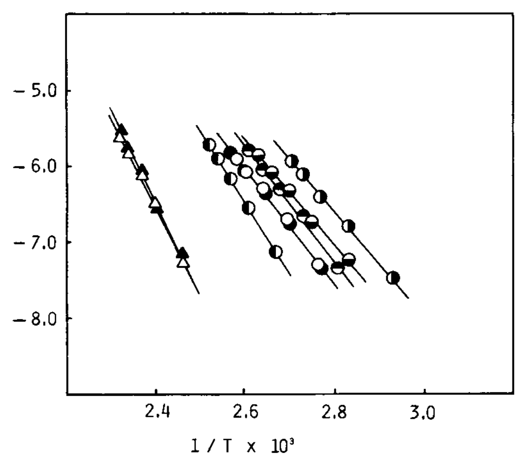


Figure 2 Arrhenius plots for epoxy resins/hardener: (◑) EOCDA-1; (⊖) EOCDA-2; (◓) EOCDA-3; (○) EOCDA-4; (●) EOCDA-5; (◐) EOCDA-6; (△) EOCN-1; (▲) EOCN-2.

Kinetic Parameters

Several parameters that determine cure reaction of epoxy resin with an amine hardener have been proposed.[6,7] In this study the rate constant k at different temperatures was estimated using the Barrett relation,[8] assuming that the initial step of cure reaction follows the first-order Arrhenius-type kinetics. The plot of ln k, which was estimated using the Barrett relation, against $1/T$ is shown in Figure 2. E_a and k at 100°C were obtained from a regression plot (Table III). It was found that the higher the amount of hydroxymethyl group, the lower the onset temperature and the peak temperature of exothermal

Table III Curing Behavior of Epoxy Resins with a Hardener[a]

Symbol	Onset Temp. (°C)	Peak Temp. (°C)	$k \times 10^3$ [b] (sec^{-1})	E_a (kcal/mol)
EOCDA-1	19.0	120.0	3.13	13.5
EOCDA-2	31.0	126.5	2.05	13.9
EOCDA-3	48.5	132.0	1.81	15.2
EOCDA-4	51.0	134.5	1.31	15.2
EOCDA-5	52.0	145.5	1.30	15.0
EOCDA-6	65.0	143.5	0.746	18.4
EOCN-1	94.5	169.0	0.0540	23.8
EOCN-2	98.5	170.5	0.0536	23.2

[a] By DSC.
[b] At 100°C.

Table IV Viscoelastic Parameters of Cured Epoxy Resins[a]

Symbol	T_g (°C)	At 30°C	E' (dyn/cm^2) at 200°C	At 250°C
EOCDA-1	>300 (198[b])	2.22×10^{10}	1.41×10^{10}	1.24×10^{10}
EOCDA-2	285 (228[b])	2.22×10^{10}	1.79×10^{10}	1.33×10^{10}
EOCDA-3	285 (212[b])	2.21×10^{10}	1.79×10^{10}	1.28×10^{10}
EOCDA-4	>300 (229[b])	2.21×10^{10}	1.40×10^{10}	1.17×10^{10}
EOCDA-5	>300 (226[b])	2.06×10^{10}	1.26×10^{10}	9.55×10^{9}
EOCDA-6	>300 (245[b])	2.29×10^{10}	1.70×10^{10}	1.44×10^{10}
EOCN-1	230 (219[b])	2.13×10^{10}	1.02×10^{10}	1.15×10^{9}
EOCN-2	289 (260[b])	2.27×10^{10}	1.37×10^{10}	9.12×10^{9}

[a] EOCDA, EOCN/DGEBA = 80/20. Cure condition: 100°C/2 h + 120°C/1 h + 140°C/1 h + 160°C/1 h + 180°C/1 h + 200°C/1 h + 220°C/1 h + 240°C/1 h.
[b] Cured at 100°C/2 h.

reaction, the higher k, and the lower E_a were. At 100°C, k of EOCDAs was 10 times more than that of EOCNs. For example, comparing EOCDA-5 with EOCN-2, which had similar average molecular weight, k of EOCDA-5, having the $-CH_2OH/-CH_3$ ratio of 0.18, was about 24 times as large as that of EOCN-2. These results indicated that the hydroxymethyl groups of the resol-type epoxy resin accelerated the epoxide-amine reaction.

Dynamic Mechanical Properties of Cured Epoxy Resins

Viscoelastic properties of cured epoxy resin are shown in Table IV. In the EOCDA series, the effect of after-cure was extremely large. That is, T_g of the after-cured EOCDAs shifted considerably to the higher temperature region, compared to that of EOCNs, and was higher than that of EOCNs.

Epoxy resins having hydroxymethyl group can cure by two kinds of reaction, epoxide-amine addition and condensation reaction of hydroxymethyl group at high temperature. So these results were considered to be due to the increase of crosslinking density of cured resin by condensation reaction of hydroxymethyl group during after-curing.

There was no obvious difference between E' at 250°C of the after-cured EOCDAs and those of the after-cured EOCNs. T_g and E' of the after-cured EOCDAs were not much influenced by the average molecular weight of the starting novolac.

CONCLUSION

o-Cresol novolac-type epoxy resins having hydroxymethyl group and different molecular weight distribution were cured with aromatic amine as a hardener. Curing behavior of epoxy resins and dynamic mechanical properties of the cured resins were studied. It was found that curing rate of the resol-type epoxy resins was more than 10 times as large as that of novolac-type epoxy resins. It was also found that curing rate of resol-type epoxy resins increased with an increase in the concentration of hydroxymethyl group. Furthermore, T_g of the after-cured resol-type epoxy resins was higher than that of after-cured novolac-type epoxy resins. It was considered that hydroxymethyl groups of the resol-type epoxy resins accelerated the epoxide-amine reaction and self-condensed at high temperature to increase the crosslinking density.

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