Structure and Viscoelastic Properties of Epoxy Resins Prepared from o-Cresol Novolacs

KIICHI HASEGAWA, AKINORI FUKUDA, and SABURO TONOGALI, *Plastics Department of Osaka Municipal Technical Research Institute, 6-50, 1-chome Morinomiya, Joto-ku, Osaka, 536 Japan* and KAZUO UEDE, *Research Laboratory of Koei Chemical Co., Ltd., 12-13, 2-chome Hanaten-Nishi, Joto-ku, Osaka, 536 Japan*

Synopsis

The relation between the structure and viscoelastic properties of the epoxy resins prepared from o-cresol novolacs was studied. Our model epoxy resins were two kinds of epoxy compounds synthesized from three-nuclei and four-nuclei o-cresol novolacs. In addition to these models, a commercially available o-cresol novolac-type epoxy resin was also studied. Each of the three epoxy compounds was cured with one of three kinds of novolacs, which were starting materials of the above-mentioned epoxy resins. Characteristic properties of the cured resins, such as glass transition temperature (T_g), average molecular weight between crosslinking points ($\overline{M}_c$), and front factor (ϕ) were obtained. It was concluded that the number of functional groups contained in the curing system almost dominated the viscoelastic properties of the cured resins.

INTRODUCTION

Epoxy resins have been widely used as engineering plastics. Recently, because high-performance epoxy resins are subject to strict requirements, o-cresol novolac-type epoxy resins have been used as encapsulation materials for semiconductors for their good heat resistance. Though the structure of novolac-type epoxy resins has a large influence on the properties of cured resins, the relationship between their structure and properties has not been systematically investigated. Therefore, we studied the relationship between viscoelastic property and structure of epoxy resins prepared from novolacs.[1-4] As reported previously, we studied the relationship between structure of epoxy resins prepared from four-nuclei novolacs and properties of the resins cured with diaminodiphenylmethane, and drew the conclusions that: higher linearity in the main chain of epoxy resins gave a cured resin with a smaller molecular weight between crosslinking points $\overline{M}_c$ and a larger front factor (ϕ). On the other hand, o-cresol novolacs are commonly used as hardeners for encapsulation materials for semiconductors. In the present study, we have investigated the relationship between viscoelastic properties and structure of resins which consisted of o-cresol novolac-type epoxy resins and o-cresol novolacs as hardeners. Three- and four-nuclei o-cresol novolac-type epoxy

resins were used. The hardeners used were *o*-cresol novolacs which were the starting materials of the above mentioned epoxy resins.

EXPERIMENTAL

Preparation of *o*-Cresol Novolacs

Three-nuclei and four-nuclei *o*-cresol novolacs were prepared along the following routes, as shown in Scheme 1.

2,4-Bis(3-methyl-4-hydroxybenzyl)-6-methylphenol (I). Compound A was reacted with an excess amount of *o*-cresol in acetic acid solution and in the presence of a catalytic amount of HCl. After concentrating the reaction solution in vacuum, a yellow solid was obtained. This product was identified by high-performance liquid chromatography (HPLC) analysis to be a mixture of four isomers of compound I (mp 38–42°C, (I) 66%; 2-(3-methyl-4-hydroxybenzyl)-4-(2-hydroxy-3-methylbenzyl)-6-methylphenol and 2-(2-hydroxy-3-methylbenzyl)-4-(3-methyl-4-hydroxybenzyl)-6-methylphenol 29%; 2,4-bis(2-hydroxy-3-methylbenzyl)-6-methylphenol 5%).

Bis(3-(3-methyl-4-hydroxybenzyl)-4-hydroxy-5-methylphenyl) methane (II). Compound B was reacted with an excess amount of *o*-cresol in acetic acid solution and in the presence of a catalytic amount of HCl. After concentrating the reaction solution, a pale yellow solid was obtained. This product was identified by HPLC analysis to be a mixture of three isomers of compound II (mp 60–66°C, (II) 56%; 3-(3-methyl-4-hydroxybenzyl)-3'-(2-hydroxy-3-methylbenzyl)-4,4'-dihydroxy-5,5'-dimethyldiphenylmethane 38%; bis(3-(2-hydroxy-3-methylbenzyl)-4-hydroxy-5-methylphenyl)methane 6%.

As the commercially available *o*-cresol novolac, we used a raw material (OCN) of an *o*-cresol novolac-type epoxy resin (Epiclon N-660, Dainippon Ink and Chemicals, Inc.). Gel permeation chromatographs (GPC) of OCN, I, and II are shown in Figure 1. Average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) were calculated by a GPC calibration curve that was drawn on the basis of a series of *o*-cresol novolacs with known molecular weights. The *p*-/*o*- ratio of methylene linkage of OCN was measured nuclear magnetic resonance (NMR). The ratios of compounds I and II were calculated from their structures. The structures and properties of these novolacs are shown in Table I.
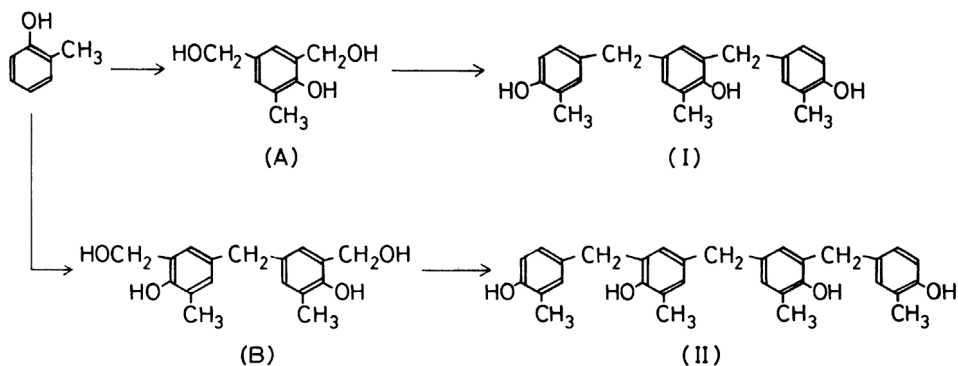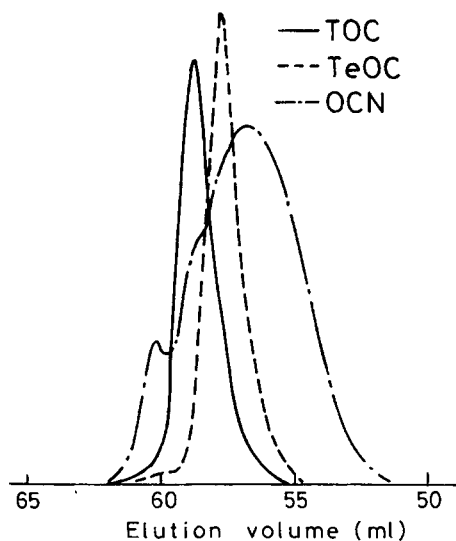

Scheme 1.

Fig. 1. GPC chromatograms of o-cresol novolacs.

TABLE I
Properties of o-Cresol Novolacs

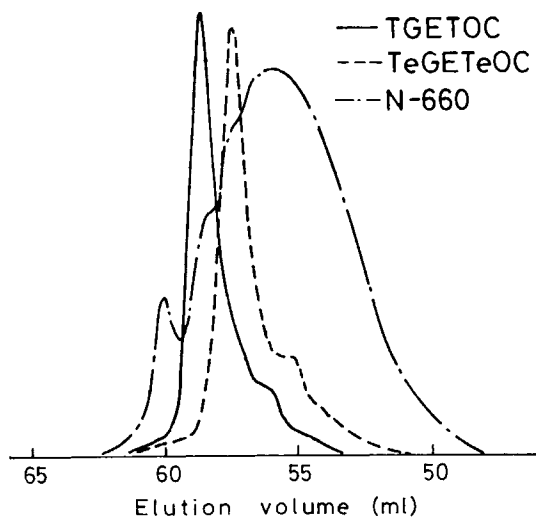| Structure	Symbol	p-/o-Ratio of methylene linkage	mp (°C)
	TOC	1.88	38–42
	TeOC	1.40	60–65
	OCN	1.83	62–64

[a] $M_n = 493$, mw = 1006 (by GPC).

Fig. 2.   GPC chromatograms of epoxy resins.

TABLE II
Properties of Epoxy Resins

Structure	Symbol	Epoxy equivalent	mp (°C)
	TGETOC	$190_{(172)}$[a]	Semisolid
	TeGETeOC	$199_{(173)}$[a]	18
	N-660	207	66

[a] Theoretical value.
[b] $\overline{M}_n = 848$, $\overline{M}_w = 1361$ (by GPC).

Synthesis of Epoxy Compounds

The glycidylethers of novolacs (I and II) were synthesized by a conventional method.[5] Epoxide equivalent of the obtained epoxy resin was determined by the tetraethylammoniumbromide-perchloric-acid method (ISO-3001), using a potentiometer. A commercially available o-cresol novolac-type epoxy resin (Epiclon N-660) was also used in this study. GPC chromatograms of the three epoxy resins are shown in Figure 2. The average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) of N-660 were calculated by the GPC calibration curve that was drawn on the basis of a series of epoxy compounds with known molecular weights. The structures and properties of these epoxy resins are shown in Table II. The average number of functional groups of the commercially available epoxy resin was calculated by the ratio of number-average molecular weight to epoxy equivalent weight. This value was found to be 4.10 for N-660.

Preparation of Cured Resin

As hardeners, synthesized three- and four-nuclei o-cresol novolacs (TOC and TeOC) and a commercially available o-cresol novolac (OCN) were used, respectively. A mixture of the epoxy resin and the stoichiometric amount of the novolac was heated to 140°C and well mixed. To this mixture 1 phr of 2-ethyl-4-methylimidazole (2E4MZ) was added as catalyst. The mixture was well mixed, poured to a preheated Teflon mold, and cured under the following conditions: 2 h at 140°C + 2 h at 160°C + 2 h at 180°C + 2 h at 200°C. By combining the three kinds of epoxy resins with the three kinds of novolacs, nine kinds of cured resins were prepared.

Measurement

Dynamic mechanical properties of cured resin were measured by a viscoelastic spectrometer (tensile-mode, type VES-S, Iwamoto Co.) at 10 Hz and a heating rate or 2°C/min. Coefficients of linear expansion were measured by a thermal mechanical analyzer (type TMA-30, Shimazu Co.) at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of Cured Epoxy Resins

The dynamic mechanical properties are shown in Figure 3–5. Their modulus-temperature curves showed three distinct regions, which are typical for crosslinked systems, namely, a glassy region, a transition region, and a rubbery region. The peak temperature of tan δ was considered as the glass transition temperature.[6] The degree of crosslinks of a polymer network is usually described by the parameter $\overline{M}_c$, the average molecular weight between crosslinking points. The value of $\overline{M}_c$ was estimated using the equation of state for rubber elasticity [Eq. (1)].[7]

$$\overline{M}_c = 3\phi \, dRT/E' \tag{1}$$

where ϕ is the front factor, d is the density of the network at an absolute
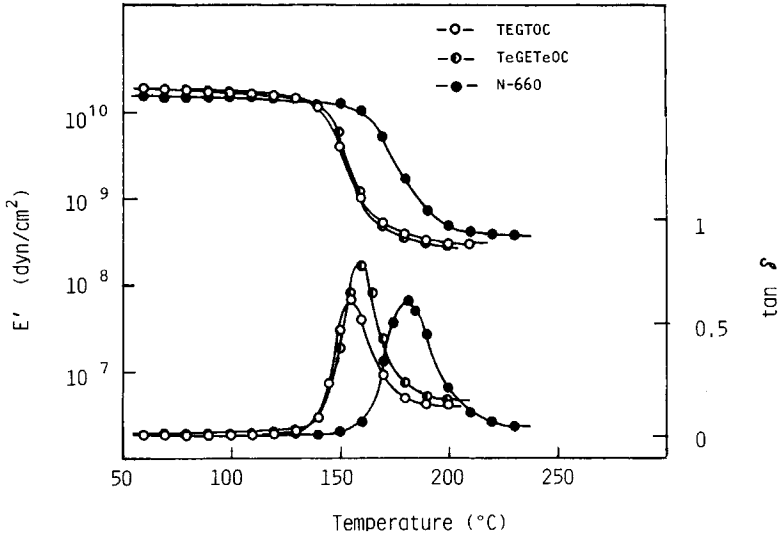
Fig. 3.　Dynamic mechanical properties of epoxy resins cured with TOC.

temperature T, R is the gas constant, and E' is the storage modulus of the network at the temperature T.

The experimental $\overline{M}_c$ value, $\overline{M}_c(E')$, was calculated by Eq. (1), with ϕ assumed to be unity.[8] A method for estimating $\overline{M}_c$ of polyfunctional epoxy resin/amine system was reported by Lau.[9] We applied this method to our systems.[4] The theoretical $\overline{M}_c$ was calculated by Eq. (2).

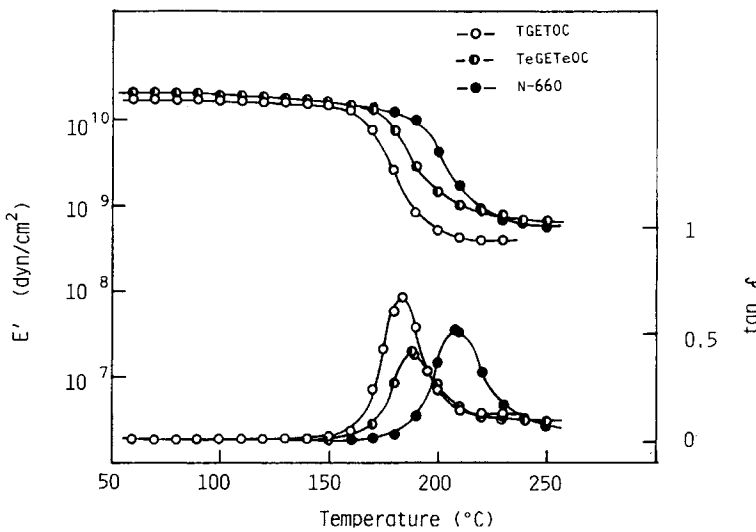$$\overline{M}_c = 2(aM_A + bM_B)/3(Aa + Bb) \tag{2}$$

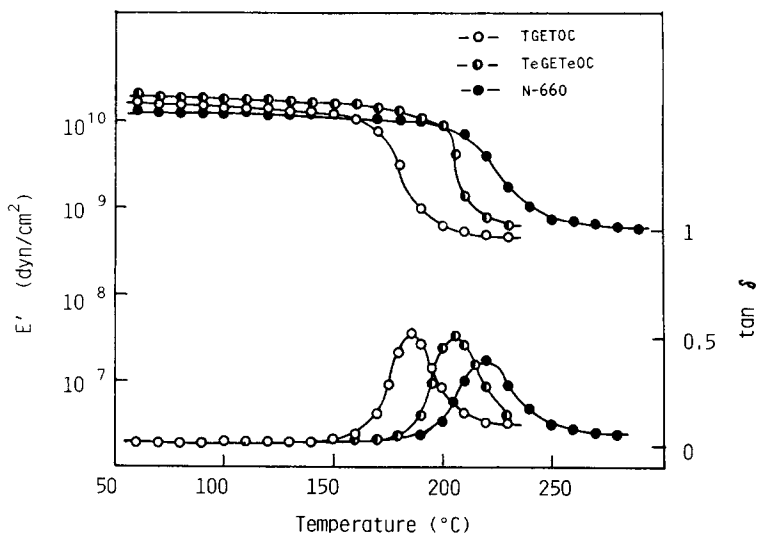Fig. 4.　Dynamic mechanical properties of epoxy resins cured with TeOC.

Fig. 5. Dynamic mechanical properties of epoxy resins cured with OCN.

where a = moles of hardener, M_A = molecular weight of hardener, b = moles of epoxy resin, M_B = molecular weight of epoxy resin, A = number of crosslink points formed from a hardener molecule, B = number of crosslink points formed from an epoxy resin molecule.

We designate this $\overline{M}_c$ as $\overline{M}_c(s)$. An apparent front factor, ϕ_a,[10] is expressed by Eq. (3).

$$\phi_a = \overline{M}_c(s)/\overline{M}_c(E')$$ (3)

Respective viscoelastic parameters of the cured resins are tabulated in Table III.

Glass Transition Temperature

In the cured epoxy resin systems with the same hardener, T_g for TGETOC, TeGETeOC, and N-660 were found to increase in the order mentioned. And, in the systems with the same epoxy resins, T_g for TOC, TeOC, and OCN was found to increase in the order mentioned. Comparing T_g with the number of functional groups, the T_g of the systems with four functional resins was higher than that of the systems with three functional resins. These results mean that T_g was affected mainly by the number of functional groups. For N-660 or OCN systems, the average number of functional groups of these resins was about 4.1 and T_g was higher in these systems than in the systems with four functional groups. These results were attributed to the finding that GPC chromatograms representing N-660 and OCN contained significant amounts of higher molecular weight compounds than TeOC and TeGETeOC, that is, these compounds comprise significant amounts of compounds having more than four functional groups.

TABLE III
Viscoelastic Parameters of Cured Epoxy Resins

Epoxy resin	Hardener	T_g (°C)	E' (dyn/cm^2)		d (g/cm^3)		$\overline{M}_c(E')$	$\overline{M}_c(s)$	ϕ_a
			At 20°C	At T_g + 40°C	At 20°C	At T_g + 40°C			
TGETOC	TOC	158	1.72×10^{10}	2.63×10^8	1.193	1.125	502	306	0.61
TeGETeOC	TOC	160	2.08×10^{10}	2.96×10^8	1.197	1.131	450	253	0.56
N-660	TOC	182	1.62×10^{10}	3.83×10^8	1.193	1.121	362	254	0.70
TGETOC	TeOC	184	1.99×10^{10}	4.01×10^8	1.190	1.118	348	246	0.71
TeGETeOC	TeOC	188	1.85×10^{10}	4.54×10^8	1.210	1.141	314	211	0.67
N-660	TeOC	209	1.87×10^{10}	5.77×10^8	1.190	1.113	251	214	0.85
TGETOC	OCN	187	1.57×10^{10}	4.88×10^8	1.164	1.092	279	236	0.85
TeGETeOC	OCN	206	2.06×10^{10}	6.13×10^8	1.157	1.087	229	207	0.90
N-660	OCN	219	1.41×10^{10}	6.82×10^8	1.145	1.068	207	211	1.02

Storage Modulus (E')

There was no clear relation between the storage modulus (E') at a glassy state and the functionality of resin system, but the N-660 or OCN systems gave relatively small values. On the other hand, in systems with the same hardener, TGETOC, TeGETeOC, and N-660 gave higher values of E' at a rubbery state in the order mentioned. In the systems with the same epoxy resins, TOC, TeOC, and OCN gave higher values of E' at a rubbery state in the order mentioned. This tendency is identical to that of T_g. These results were considered to be due to the difference in the number of functional groups between the systems, that is, the difference in crosslinking density between the systems.

$\overline{M}_c(E')$ and ϕ_a

The value of $\overline{M}_c(E')$ in Table III decreased with increasing number of functional groups of both epoxy resins and hardeners. This result demonstrates that the crosslinking density of cured resin increased with an increase in the number of functional groups of the systems.

On the other hand, the value of ϕ_a increased with increasing numbers of functional groups of both epoxy resins and hardeners. However, in TOC and TeOC systems, the value of ϕ_a of TGETOC system, a trifunctional epoxy resin system, was higher than that of the TeGETeOC system, a tetrafunctional epoxy resin system. In the previous report,[4] it was stated that the lower the p-/o- ratio of methylene linkage epoxy resins the smaller ϕ_a they gave. In this study, p-/o- ratio of methylene linkage of TeGETeOC was smaller than that of TGETOC. From these results, it was concluded that ϕ_a depended both on the crosslinking density and on the degree of bend in the main chain.

Thermal Mechanical Analysis

The results of thermal mechanical analysis (TMA) measurement on cured resins were tablulated in Table IV. Although T_g measured on TMA was 20–40°C lower than that measured on viscoelastic spectroscopy (VES), the relation between T_g and structure of both epoxy resins and hardeners showed the same tendency as that measured on VES.

TABLE IV
Thermal Expansion Properties of Cured Epoxy Resins

Epoxy resin	Hardener	T_g (°C)	Coefficient of linear expansion (K^{-1})	
			Before T_g	After T_g
TGETOC	TOC	132	7.44×10^{-5}	1.79×10^{-4}
TeGETeOC	TOC	137	6.97×10^{-5}	1.74×10^{-4}
N-660	TOC	147	7.07×10^{-5}	1.63×10^{-4}
TGETOC	TeOC	149	6.43×10^{-5}	1.69×10^{-4}
TeGETeOC	TeOC	164	6.31×10^{-5}	1.67×10^{-4}
N-660	TeOC	166	6.47×10^{-5}	1.60×10^{-4}
TGETOC	OCN	158	7.18×10^{-5}	1.69×10^{-4}
TeGETeOC	OCN	168	6.07×10^{-5}	1.56×10^{-4}
N-660	OCN	174	7.10×10^{-5}	1.48×10^{-4}

The coefficient of linear expansion (β) was shown in the two regions, namely, before and after T_g. In this study, β took the value of 6.0–7.5 $\times$ 10^{-5} (K^{-1}) before T_g and 1.4–1.8 $\times$ 10^{-4} (K^{-1}) after T_g. In a rubbery state, β became smaller in the order of increasing T_g. This result showed that the higher the crosslinking density of cured resins, the smaller β they gave in the rubbery state.

CONCLUSION

The relation between structure and viscoelastic properties of the epoxy resins prepared from three-nuclei, four-nuclei, and conventional o-cresol novolacs was studied. As hardeners, the above mentioned o-cresol novolacs were used. T_g of cured resins was closely related to the number of functional groups of both epoxy resins and hardeners. That is, the larger the number of functional groups of an epoxy-resin/hardener system, the higher T_g the cured resins gave. It was concluded that the system with higher T_g had smaller $M_c(E')$ and larger ϕ_a. The effect of p-/o- ratio of methylene linkage on the viscoelastic properties of the cured resins was not clear, but the tendency that higher p-/o- ratios gave cured resins with larger ϕ_a was observed in some systems.

References

1. K. Hasegawa, A. Fukuda, S. Tonogai, and H. Horiuchi, *Kobunshi Ronbunshu*, **40**, 321 (1983).

2. K. Hasegawa, A. Fukuda, S. Tonogai, and H. Horiuchi, *Kobunshi Ronbunshu*, **41**, 575 (1984).

3. K. Hasegawa, A. Fukuda, and S. Tonogai, *Kobunshi Ronbunshu*, **43**, 529 (1986).

4. K. Hasegawa, A. Fukuda, and S. Tonogai, *J. Appl. Polym. Sci.*, **37**, 3423 (1989).

5. J. M. Goppel, US Patent, 2801227 (1957).

6. T. K. Kwei, *J. Polym. Sci.*, A-2, **4**, 943 (1966).

7. T. Murayama and J. P. Bell, *J. Polym. Sci.*, A-2, **8**, 437 (1970).

8. T. Kamon, S. Saito, Y. Miwa, and K. Saeki, *Kobunshi Ronbunshu*, **30**, 279 (1973).

9. C. H. Lau and K. A. Hodd, *Br. Polym. J.*, **18**, 316 (1986).

10. T. Takahama and P. H. Gail, *J. Polym. Sci.: Polym. Lett. Ed.*, **20**, 453 (1982).