

Structure and Viscoelastic Properties of Epoxy Resins Prepared from Four-Nuclei Novolacs

KIICHI HASEGAWA, AKINORI FUKUDA,
and SABURO TONOGAI,

*Plastic Department of Osaka Municipal Technical Research Institute,
6-50, 1-chome Morinomiya, Joto-ku, Osaka, 536 Japan*

Synopsis

The relation between the structure and the viscoelastic properties of seven kinds of epoxy resins was studied. Seven tetraglycidylethers were synthesized from four-nuclei novolacs in which the positions of methylene linkage or number of kind of substituents were different. These epoxy compounds were cured with diaminodiphenylmethane as a hardener. From the viscoelastic properties of the fully cured resins with the hardener, characteristic properties such as glass transition temperature (T_g), average molecular weight between crosslinking points (\bar{M}_c), and front factor (ϕ) were obtained. It was concluded that higher linearity in the main chain of epoxy resins gave a cured resin with a higher T_g , a smaller \bar{M}_c , and a larger ϕ .

INTRODUCTION

Epoxy resins have been widely used as an engineering plastic because of its high performance, such as good mechanical, thermal, and electrical properties. To use epoxy resins properly, it is important to understand the relation between structures and properties of epoxy resins. Considerable amounts of researches discussed on the relation between the properties of cured epoxy resins and the structures of epoxy compounds. However, these studies were mostly made on the base of bisphenol-A type epoxy resins with various kinds of hardeners.

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 resin is largely used as on electronics encapsulation material because of its good heat resistance. Since the structures of novolac type epoxy resins have a large influence on the properties of cured epoxy resins, it is necessary to elucidate the relation between structure and properties systematically. However, there are few papers concerned with such a study. Therefore, we have studied the relation between the viscoelastic properties and structures of epoxy resins prepared from novolacs in which the positions of methylene linkage, or number and kind of substituents were different. In the previous papers,¹⁻³ we reported the relation between the structure of the epoxy resins prepared from two- or three-nuclei novolacs and the properties of the cured resin, and the conclusions were: (1) A bulky and rigid substituent such as *t*-butyl or phenyl group

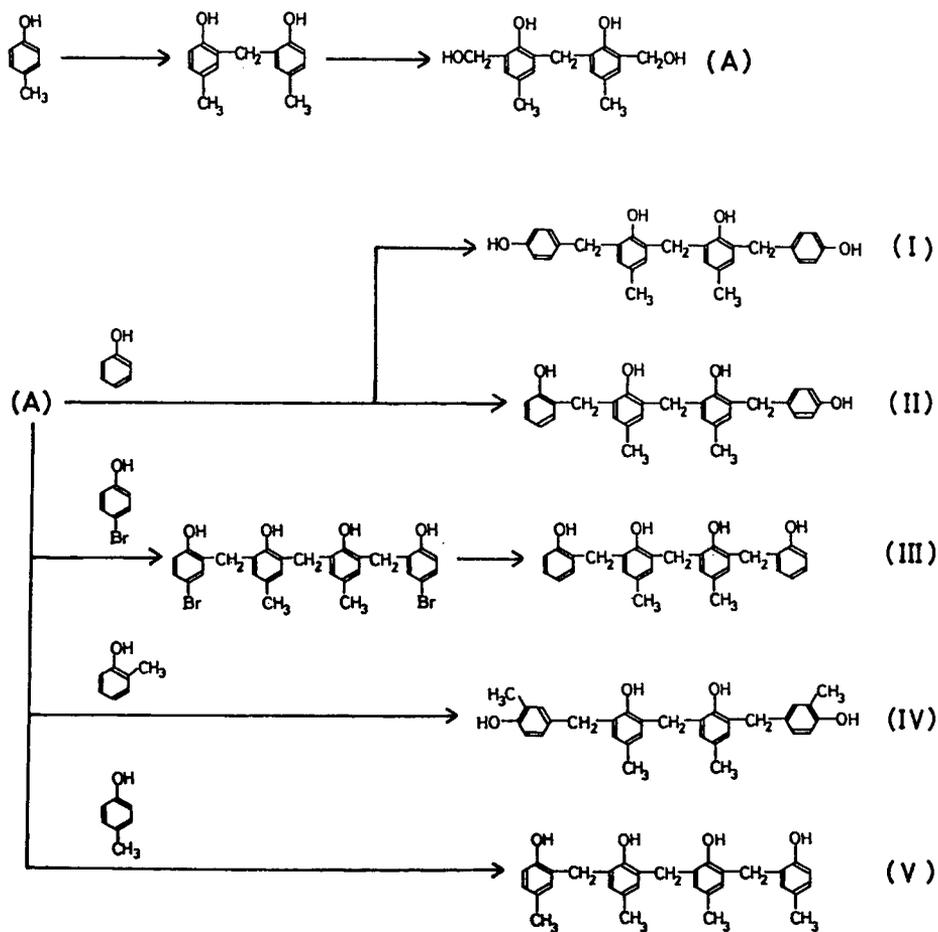
was effective for improving T_g of the cured resin, while a flexible substituent such as nonyl group reduced T_g ; (2) the values of \overline{M}_c and ϕ were more influenced by the degree of bend in the main chain than by the kind of substituents.

In the present study, the relation between the viscoelastic properties and the structures of epoxy resins prepared from four-nuclei novolacs were investigated. Additionally, two kinds of the commercial novolac type epoxy resins were used in the same way as reference resins and were compared to our prepared epoxy resins.

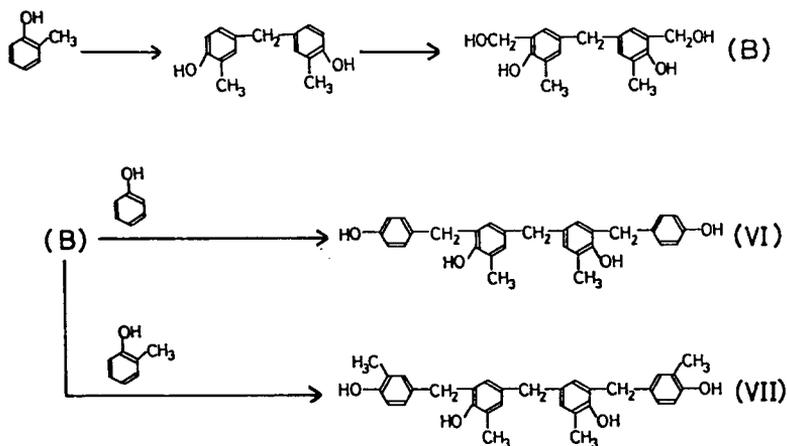
EXPERIMENTAL

Preparation of Four-Nuclei Novolacs

Seven four-nuclei novolacs (I–VII) were prepared by following routes, as shown in Schemes 1 and 2:



Scheme 1



*Bis(2-Hydroxy-3-(4-Hydroxybenzyl)-5-Methylphenyl)Methane (I) and
2,2'-Dihydroxy-3-(4-Hydroxybenzyl)-3'-(2-Hydroxybenzyl)-
5,5'-Dimethyldiphenylmethane (II)*

Compound A was reacted with the excess of phenol in an acetic acid solution in the presence of the catalytic amount of HCl. A white solid was then precipitated from the solution. After recrystallization of the precipitation, the solid was identified to be compound (II) by $^1\text{H-NMR}$ and HPLC analysis (mp = 215–217°C). The filtrate was concentrated under reduced pressure, and a white solid was obtained. This solid was characterized to be a mixture of compounds (I) and (II), of the ratio 6 : 4, by HPLC analysis. From the solid, compound (I) was separated by the extraction with a mixed solvent (1,2-dichloroethane/ CCl_4 = 95/5), and was identified by $^1\text{H-NMR}$ and HPLC analysis (mp = 187–197°C).

Bis(2-Hydroxy-3-(2-Hydroxybenzyl)-5-Methylphenyl)Methane (III)

At the first step, bis(2-hydroxy-3-(2-hydroxy-5-bromobenzyl)-5-methylphenyl)methane (III') was prepared by the reaction of compound A with the

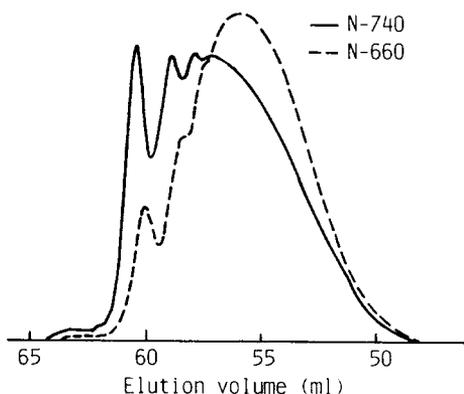
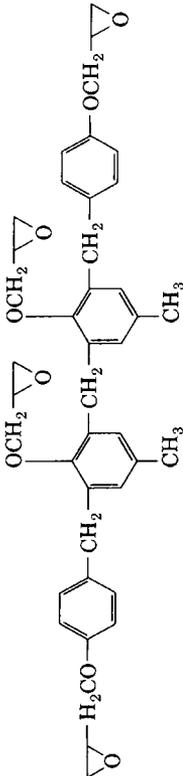
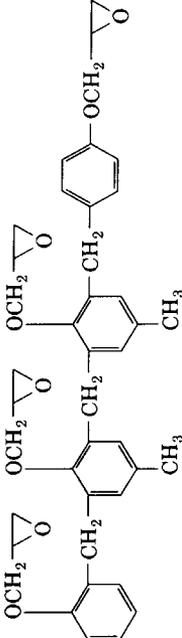
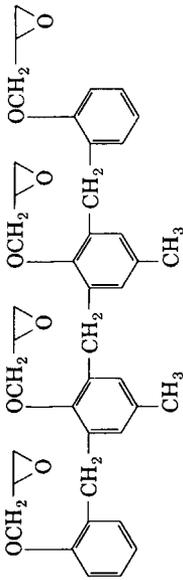
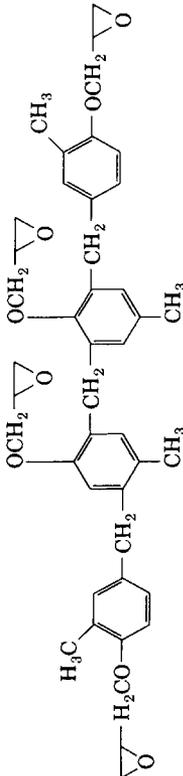


Fig. 1. GPC chromatograms of epoxy resins.

TABLE I
Properties of Epoxy Resins

Structure	Symbol	Epoxy equivalent	<i>p</i> -/ <i>o</i> - ratio of methylene linkage	mp (°C)
	TeGETeP-1(4,4')	213 (166) ^a	0.5	30
	TeGETeP-1(2,4')	194 (166) ^a	0.2	28
	TeGETeP-1(2,2')	215 (166) ^a	0	45
	TeGETeC-1(4,4')	202 (173) ^a	0.5	38

<p>Chemical structure of TeGETeC-1(2,2'): A bisphenol A-derived epoxy resin with two methyl groups and two glycidyl ether groups per phenyl ring.</p>	214 (173) ^a	0	45
<p>Chemical structure of TeGETeP-2(4,4'): A bisphenol P-derived epoxy resin with two methyl groups and two glycidyl ether groups per phenyl ring.</p>	196 (166) ^a	2	18
<p>Chemical structure of TeGETeC-2(4,4'): A bisphenol A-derived epoxy resin with two methyl groups and two glycidyl ether groups per phenyl ring.</p>	199 (173) ^a	1.4	18
<p>Chemical structure of N-740: A bisphenol A-derived epoxy resin with two glycidyl ether groups per phenyl ring.</p>	183	1.35	Semi-solid
<p>Chemical structure of N-660: A bisphenol A-derived epoxy resin with two glycidyl ether groups per phenyl ring.</p>	207	1.83	66

^aTheoretical value.

^b $\bar{M}_n = 639$, $\bar{M}_w = 1059$ (by GPC).

^c $\bar{M}_n = 848$, $\bar{M}_w = 1361$ (by GPC).

excess of *p*-bromophenol in an acetic acid solution in the presence of the catalytic amount of HCl. Secondly, compound (III') was reduced over Raney nickel.⁴ This reduced product was purified by recrystallization and was identified to be compound (III) by ¹H-NMR and HPLC analysis (mp = 186–189°C).

Bis(2-Hydroxy-3-(3-Methyl-4-Hydroxybenzyl)-5-Methylphenyl)Methane
(IV)

Compound (IV) was prepared by the reaction of compound A and *o*-cresol under the same method as described in compound (I). The product was purified by recrystallization and identified to be compound (IV) by ¹H-NMR and HPLC analysis (mp = 151–154°C).

Bis(2-Hydroxy-3-(2-Hydroxy-5-Methylbenzyl)-5-Methylphenyl)Methane
(V)

By the reaction of compound A with the excess of *p*-cresol in an acetic acid solution in the presence of the catalytic amount of HCl, compound (V) was prepared in the same way as compound (IV) (mp = 186–187°C).

Bis(4-Hydroxy-3-(4-Hydroxybenzyl)-5-Methylphenyl)Methane (VI)

By the reaction of compound B with the excess of phenol in an acetic acid solution in the presence of the catalytic amount of HCl, compound (VI) was prepared in the same way as compound (IV) (mp = 166–172°C).

Bis(4-Hydroxy-3-(3-Methyl-4-Hydroxybenzyl)-5-Methylphenyl)Methane
(VII)

Compound B was reacted with the excess of *o*-cresol in an acetic acid solution in the presence of the catalytic amount of HCl. After concentrating the reaction solution, a pale yellow solid was obtained. This product was identified to be the mixture of three isomers of compound (VII) by HPLC analysis (mp = 60–65°C; (VII), 56%; 3-(3-methyl-4-hydroxybenzyl)-3'-(2-hydroxy-3-methyl-benzyl)-4,4'-dihydroxy-5,5'-dimethyldiphenylmethane, 38%; bis(3-(2-hydroxy-3-methylbenzyl)-4-hydroxy-5-methylphenyl)methane, 6%).

Synthesis of Epoxy Compounds

The tetraglycidylethers of four-nuclei novolacs were synthesized by a conventional method.⁵ Epoxide equivalent of the obtained epoxy resins was determined by the tetraethylammoniumbromide–perchloric acid method (ISO-3001), using a potentiometric meter. In addition to the synthesized epoxy resins, two commercial epoxy resins (Epiclone N-740, phenolnovolac-type, and Epiclone N-660, *o*-cresolnovolac-type, Dainippon Ink and Chemicals) were used in this study. GPC chromatograms of the two commercial epoxy resins are shown in Figure 1, and average molecular weights (\overline{M}_n and \overline{M}_w) were calculated by use of GPC calibration curve that was made on the base of a series of epoxy compounds with a known molecular weight. The *p*-/*o*- ratios

of methylene linkage of the two commercial epoxy resins were measured by NMR method. These ratios of the other epoxy compounds were calculated from their structures. The structures and properties of these epoxy resins are shown in Table I. The average number of functional groups of the commercial epoxy resins was calculated by the ratio of number-average molecular weight to epoxy equivalent weight. This value was 3.49 for N-740 and 4.10 for N-660.

Hardener and Curing Conditions

As a hardener, commercial 4,4'-diaminodiphenylmethane (DDM) was used without further purification. The mixture of epoxy resins and the stoichiometric amount of DDM was heated to 120°C, well mixed, and transferred to a preheated Teflon mold. The mixture was then cured under these conditions: 4 h at 120°C + 1 h at 140°C + 1 h at 160°C + 1 h at 180°C + 1 h at 200°C + 1 h at 220°C + 1 h at 240°C.

Measurement

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. Coefficients of linear expansion were measured by a thermal mechanical analyzer (TMA-30 type, Shimadzu Co.) with a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of Cured Epoxy Resins

The dynamic mechanical properties are shown in Figures 2–5. The modulus-temperature curves showed clearly three regions, which are typical for

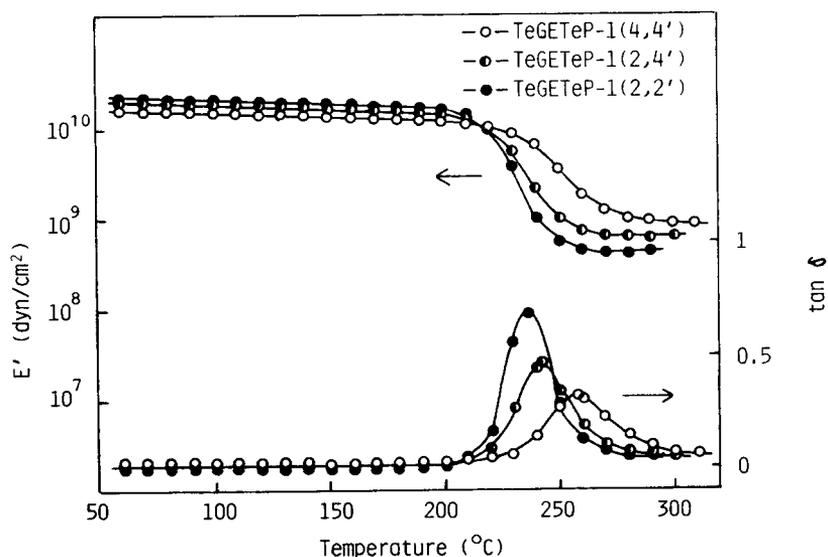


Fig. 2. Dynamic mechanical properties of epoxy resins cured with DDM.

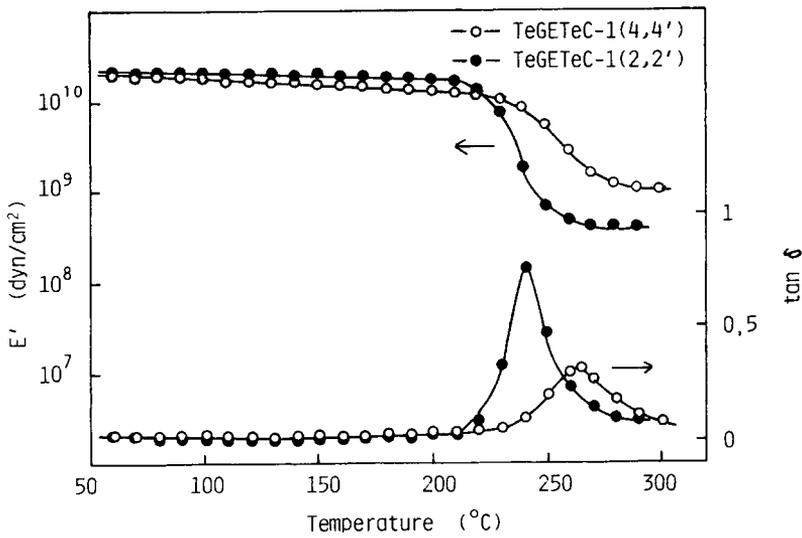


Fig. 3. Dynamic mechanical properties of epoxy resins cured with DDM.

highly crosslinked systems, i.e., a glassy region, a transition region, and a rubbery region. The peak temperature of $\tan \delta$ 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 can be calculated using the equation of state for rubber elasticity⁷

$$\overline{M}_c = 3\phi dRT/E' \quad (1)$$

where ϕ is the front factor, d is the density of the network at an absolute

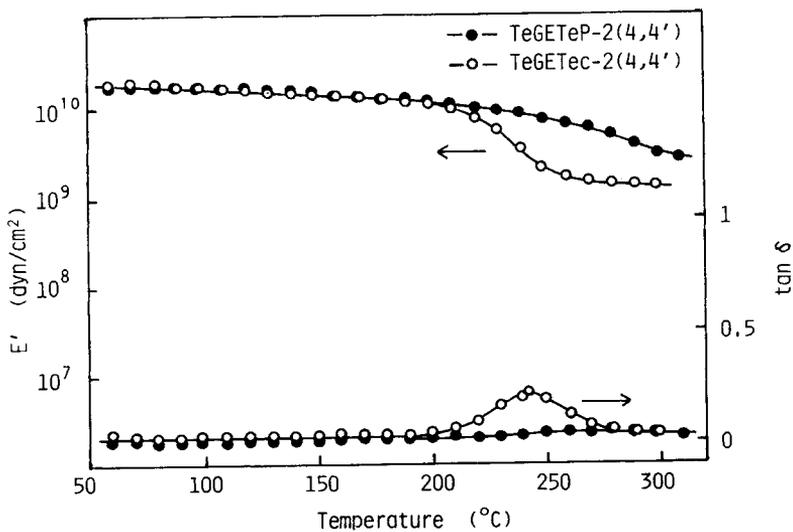


Fig. 4. Dynamic mechanical properties of epoxy resins cured with DDM.

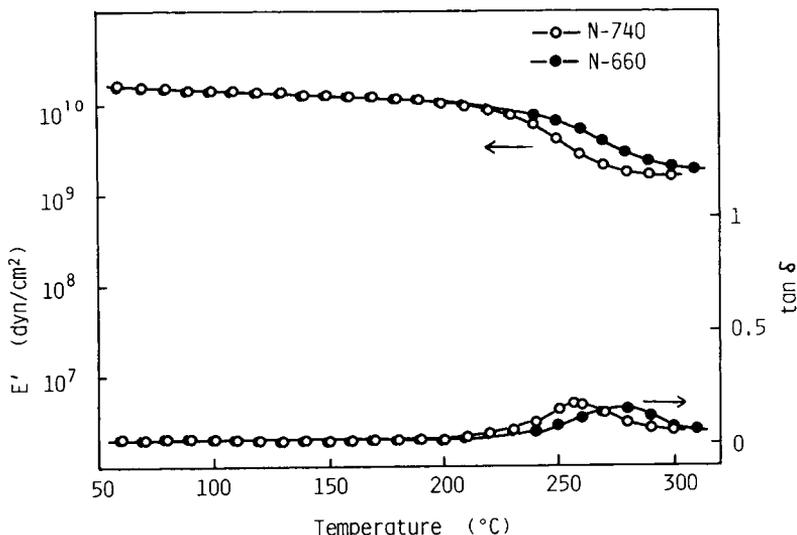


Fig. 5. Dynamic mechanical properties of epoxy resins cured with DDM.

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

Equation (1) is suitable to the polymer network that has a rubbery plateau region. As the polymer network systems that were prepared in this study were highly crosslinked, the magnitude of the rubbery plateau modulus of some network systems was too high to use the word "rubbery." The application of eq. (1) to these systems may be beyond the applicable range of eq. (1) on the basis of rubbery elasticity. But there is no good method to compare the degree of crosslinks of highly crosslinked polymers. On the other hand, some studies⁸⁻¹⁰ about the highly crosslinking systems had been done, with the result that the rubber elasticity theory was useful in discussing the degree of crosslinks. So, to compare the properties of highly crosslinked polymers, eq. (1) was adapted to the polymers for convenience.

The experimental \bar{M}_c value, $\bar{M}_c(E')$, was calculated by eq. (1), where ϕ was assumed to be unity.¹¹ A method for estimating \bar{M}_c of polyfunctional epoxy resin/amine system was reported by Lau and Hodd.¹² The theoretical \bar{M}_c was calculated by

$$\bar{M}_c = NW/C. \quad (2)$$

where N is Avogadro's number, W is the total weight of a single network molecule, given by eq. (3), and C is the total number of molecular chains between crosslink or junction points, given by eq. (4). We designate this \bar{M}_c by $\bar{M}_c(s)$, where s means "stoichiometry":

$$W = aM_A + bM_B \quad (3)$$

where a = moles of amine, M_A = molecular weight of amine, b = moles of epoxy resin, M_B = molecular weight of epoxy resin,

$$C = \frac{3}{2}(Aa + Bb)N \quad (4)$$

A = number of crosslink points formed from an amine molecule = (number of active hydrogens - 2), and B = number of crosslink points formed from an epoxy resin molecule = (number of functional groups - 2). The factor $3/2$ arises because three chains originate from each junction and each chain terminates at two junction points.

An apparent front factor, ϕ_a ,¹³ is expressed by

$$\phi_a = \overline{M}_c(s) / \overline{M}_c(E') \quad (5)$$

The front factor was usually smaller than unity,¹³ but in our study the calculated ϕ_a was larger than unity in major cases. This result should come from the fact that the adaption of eq. (1) to the highly crosslinking systems was over the applicability of the rubber elasticity theory.

The respective viscoelastic parameters of cured resins were tabulated in Table II.

Glass Transition Temperature

Glass transition temperature (T_g) of four-nuclei epoxy resin systems were 241–281°C, which were higher than those of three-nuclei epoxy resin systems³ (181–253°C). This tendency was dependent on the number of functional groups of epoxy compound.

In the three systems of TeGETeP-1, T_g became higher in the order, 2,2'-, 2,4'-, and 4,4'-. That is to say, the higher linearity in the main chain of epoxy resins gave a cured resin with a higher T_g .¹⁴ In the systems of TeGETeC-1, the same tendency as described above was also found. The TeGETeP-2(4,4') system had the highest T_g of 281°C. T_g became higher in 5–7°C when the methyl group was introduced, as seen from two examples, TeGETeC-1(4,4') vs. TeGETeP-1(4,4') and TeGETeC-1(2,2') vs. TeGETeP-1(2,2'). In the commercial epoxy resins, N-660 system gave a higher T_g than N-740 system. This result was due to N-660 containing less amounts of low molecular weight compounds (two- or three-nuclei compounds) than N-740, and *p*-/*o*- ratio of N-660 was larger than that of N-740.

Storage Modulus (E')

There was no significant difference in the storage modulus (E') at a glassy state, but there was a large difference at a rubbery state. In the systems of TeGETeP-1, E' at a rubbery state became higher in the order, 2,2'-, 2,4'-, and 4,4', and this order was the same as that of T_g described above. The same tendency was found in the TeGETeC-1 system. It was concluded that the higher linearity in the main chain of epoxy resins gave a cured resin with a higher E' at a rubbery state.

$\overline{M}_c(E')$ and ϕ_a

Both $\overline{M}_c(E')$ and ϕ_a were in a wide range of values due to the structures of epoxy resins. In the previous paper,³ we reported that the three-nuclei type epoxy resin with largely bent main chain had a larger $\overline{M}_c(E')$ and a smaller ϕ_a . The same tendency was found in this study. That is to say, an epoxy resin

TABLE II
Viscoelastic Parameters of Epoxy Resins Cured with DDM

Epoxy resin	T_g (°C)	E' (dyn/cm ²)		d (g/cm ³)		$\bar{M}_c(E')$	$\bar{M}_c(s)$	ϕ_a
		At 20°C	At $T_g + 40^\circ\text{C}$	At 20°C	At $T_g + 40^\circ\text{C}$			
TeGE/TeP-1(4,4')	258	1.77×10^{10}	9.34×10^8	1.173	1.065	162	175	1.08
TeGE/TeP-1(2,4')	241	2.14×10^{10}	6.55×10^8	1.210	1.112	235	162	0.69
TeGE/TeP-1(2,2')	236	2.29×10^{10}	4.33×10^8	1.188	1.088	344	176	0.51
TeGE/TeC-1(4,4')	265	2.11×10^{10}	1.05×10^9	1.172	1.060	146	168	1.15
TeGE/TeC-1(2,2')	241	2.11×10^{10}	3.99×10^8	1.174	1.083	375	176	0.47
TeGE/TeP-2(4,4')	281	1.94×10^{10}	2.07×10^9	1.203	1.087	78	164	2.10
TeGE/TeC-2(4,4')	243	1.72×10^{10}	1.34×10^9	1.200	1.096	113	166	1.47
N-740	257	1.79×10^{10}	1.60×10^9	1.230	1.131	100	167	1.67
N-660	277	1.70×10^{10}	1.76×10^9	1.167	1.064	89	169	1.90

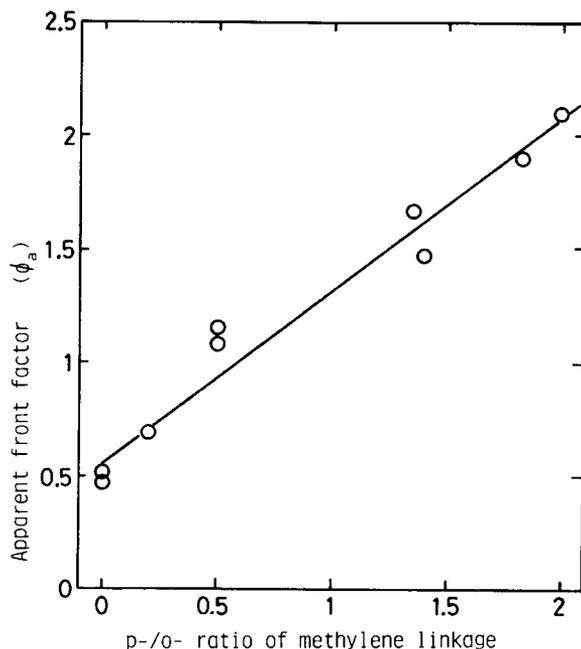


Fig. 6. Correlation between ϕ_a and p -/ o - ratio of methylene linkage.

with a smaller ratio of p -/ o - gave a larger $\overline{M}_c(E')$ and a smaller ϕ_a . A nearly linear relation was obtained when ϕ_a was plotted against the ratio of p -/ o -, as shown in Figure 6. We can predict ϕ_a from the p -/ o - ratio of methylene linkage for a novolac-type epoxy resin by using the relation. On the other hand, from Table II it was concluded that the introduction of a methyl group had little influence on the $\overline{M}_c(E')$ and ϕ_a .

Thermal Mechanical Analysis (TMA)

The results of TMA measurement of cured resins were tabulated in Table III. However, T_g measured by TMA was lower 50–60°C than that measured

TABLE III
Thermal Expansion Properties of Epoxy Resins Cured with DDM

Epoxy resin	T_g (°C)	Coefficient of linear expansion (K^{-1})	
		Before T_g	After T_g
TeGETeP-1(4,4')	193	7.85×10^{-5}	1.85×10^{-4}
TeGETeP-1(2,4')	188	7.14×10^{-5}	1.81×10^{-4}
TeGETeP-1(2,2')	175	6.73×10^{-5}	1.94×10^{-4}
TeGETeC-1(4,4')	202	7.57×10^{-5}	2.00×10^{-4}
TeGETeC-1(2,2')	189	6.60×10^{-5}	1.76×10^{-4}
TeGETeP-2(4,4')	220	7.34×10^{-5}	2.01×10^{-4}
TeGETeC-2(4,4')	183	7.73×10^{-5}	1.81×10^{-4}
N-740	197	7.99×10^{-5}	1.44×10^{-4}
N-660	204	7.40×10^{-5}	1.59×10^{-4}

by VES (viscoelastic spectroscopy).³ The relation between T_g and the structure of epoxy resins showed the same tendency as that measured by VES. The coefficient of linear expansion (β) was shown in the two regions, i.e., before T_g and after T_g . In this study, β took the value of $6.6\text{--}8.0 \times 10^{-5}$ (K^{-1}) before T_g and $1.4\text{--}2.0 \times 10^{-4}$ (K^{-1}) after T_g . The effect of structures on the β was not clear. However, in the three systems of TeGETeP-1, β in a glassy state became larger in the order, 2,2', 2,4', and 4,4', and the order was reversed to the order of E' in a glassy state. The epoxy resin system with a larger E' had a smaller β .

CONCLUSION

The relation between the structures and the viscoelastic properties of epoxy resins prepared from four-nuclei novolacs was studied. T_g was closely related to the structures of epoxy resins, that is to say, a higher *p*-/*o*- ratio of methylene linkage gave a cured resin with a higher T_g . Furthermore, when a methyl group was introduced to the benzene ring, T_g was somewhat increased. It was found that $\overline{M}_c(E')$ and ϕ_a were closely related to the structures of epoxy resins, that is, higher *p*-/*o*- ratio of methylene linkage gave a cured resin with a smaller $\overline{M}_c(E')$ and a larger ϕ_a .

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. S. R. Finn and J. W. G. Musty, *J. Appl. Chem.*, **2**, 88 (1952).
5. J. M. Goppel, U.S. Pat. 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. D. Katz and A. V. Tobolsky, *Polymer*, **4**, 417 (1963).
9. D. Katz and A. V. Tobolsky, *J. Polym. Sci.*, A, **2**, 1587 (1964).
10. D. Katz and A. V. Tobolsky, *J. Polym. Sci.*, A, **2**, 1595 (1964).
11. T. Kamon, K. Saito, Y. Miwa, and K. Saeki, *Kobunshi Ronbunshu*, **30**, 279 (1973).
12. C. H. Lau and K. A. Hodd, *Br. Polym. J.*, **18**, 316 (1986).
13. T. Takahama and P. H. Gail, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 453 (1982).
14. N. Hata and J. Kumanotani, *J. Appl. Polym. Sci.*, **15**, 2371 (1971).

Received June 2, 1988

Accepted June 23, 1988