

Mechanical relaxation mechanism of epoxide resins cured with diamines

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The mechanism of mechanical relaxation, which is observed between 50° and 90°C in epoxide resins cured with aromatic and alicyclic diamines, has been investigated by comparing dynamic mechanical properties and chemical structures of these networks. This relaxation is denoted here as the α' relaxation. The occurrence of the α' relaxation depends on the existence of *p*-phenylene groups, and is independent of the degree of cure in the cured epoxide resins. Moreover, the intensity of the α' relaxation increases linearly with increasing the concentration of *p*-phenylene groups in the networks. From these results, it is concluded that the α' relaxation of the cured epoxide resins is attributed to the motion of *p*-phenylene groups in the network structures.

(Keywords: epoxide resin; dynamic mechanical properties; relaxation mechanism; network structure)

INTRODUCTION

The low-temperature relaxations denoted here as the β and γ relaxations are observed in networks prepared from various epoxide resins and curing agents at about -50° and -130°C, respectively¹⁻¹⁶.

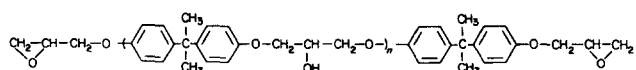
In the previous papers¹⁷⁻²⁰, we suggested that the β relaxation is interpreted as the sum of the relaxation of mobile groups, such as hydroxyether portion, and that of the other network portion, and the γ relaxation as the motion of a poly(methylene) or a poly(ethylene glycol) sequence consisting of at least six atoms. It has been reported, however, by Kline²¹ and Pogany²² that the cured epoxide resins have another mechanical relaxation at 50° to 90°C, other than the β and γ relaxations. The relaxation is denoted here as the α' relaxation. The mechanism of the α' relaxation has not been studied sufficiently.

In the present paper, the relation between the behaviour of the α' relaxation and the chemical structures of the network systems consisting of various epoxide resins and curing agents is investigated in detail. The mechanism of the α' relaxation for the cured epoxide resins is also pursued.

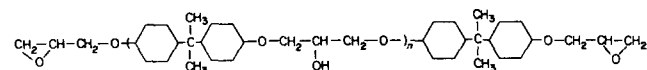
EXPERIMENTAL

Materials

The epoxide resins used were liquid bisphenol-A type epoxide resin (Epikote 828, epoxide eq.:190 ± 5)

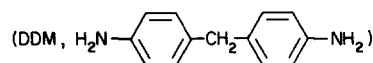


and liquid hydrogenated bisphenol-A type resin (Adek-aresin EP-4080, epoxide eq.:245 ± 10).

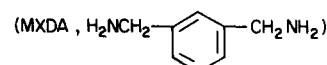


These resins are abbreviated as the aromatic and alicyclic epoxide resins, respectively. G.p.c. curves of the aromatic and alicyclic resins are shown in *Figure 1*. The former mainly consists of monomer and the latter is mixture of 49% of monomer and 51% of dimer. Though the aromatic and alicyclic epoxide resins have the different molecular weight, these resins were used without further purification because the recrystallization and the reduced pressure distillation of the alicyclic resins are very difficult.

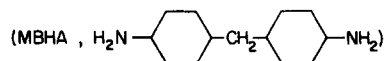
Two aromatic and two alicyclic diamines were used as curing agents, i.e. diaminodiphenylmethane



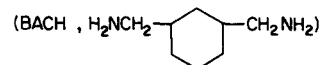
m-xylenediamine



4,4'-methylenebis(cyclohexylamine)



and 1,3-bis(aminomethyl)cyclohexane



The accelerator was salicylic acid. These curing agents and accelerator were E.P. grade materials and were also used without further purification.

Curing of epoxide resin

Epoxide resin containing 1 phr of accelerator was compounded stoichiometrically with curing agent: one epoxide group corresponds to one active hydrogen of the amino group. The mixture was stirred at 80°C until the curing agent dissolved in the epoxide resin, and was then poured into a silicon rubber container and allowed to cure

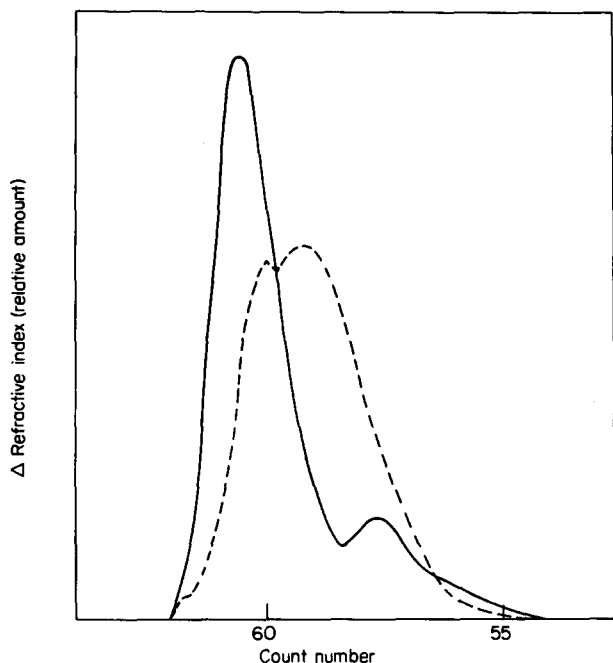


Figure 1 G.p.c. and chemical analysis of epoxide resins. (—) Bisphenol-A DGE, (----) hydrogenated bisphenol-A DGE

Epoxide resins	Molecular weight			Epoxide equiv.
	M_w	M_n	M_w/M_n	
Bisphenol A DGE	438	383	1.14	190
Hydrogenated bisphenol A DGE	518	480	1.10	245

at 80°C for 2 h and then at 180°C for 6 h in a forced-draft oven. It was confirmed that the conversion of epoxide group is not increased by further curing, as the conversion of this group was not changed even if the sample was cured at 180°C for 10 h.

Measurements

Dynamic mechanical properties were determined using

an inverted, free-oscillation torsion pendulum (RD-1100AD, Rhesca Co. Ltd.) according to ASTM 2236-70¹⁷⁻²⁰. The frequency of oscillation was adjusted to be within the range 0.3 to 3.0 Hz. The temperature range -160° to 250°C was studied. Samples were heated at 0.7°C min⁻¹ *in vacuo*.

The concentration ν of the network chains and the molecular weight \bar{M}_c between crosslinking points were calculated from the equations for rubber elasticity²³.

$$G = \Phi \nu RT$$

$$\bar{M}_c = \rho / \nu$$

where G and ρ are the absolute value of complex shear modulus and the density in the rubbery region (40°C above T_g), respectively; Φ is the front factor which is unity for ideal rubbers; R is the gas constant; and T is the absolute temperature. Since it is not possible to estimate exactly the value of Φ , ν and \bar{M}_c of cured epoxide resins are approximately determined regarding Φ as unity.

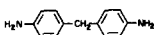
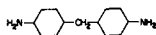
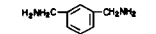
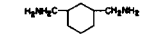
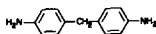
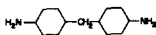
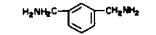
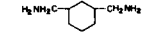
The contents of epoxide and primary amino groups were measured by the method of Bell²⁴: the former was determined by applying the pyridine-HCl method for sample powder swollen in the refluxing solvent, and the latter was measured by titration of the thiocarbamic acid with 0.2 N NaOH, which results from the reaction of the primary amino groups and CS₂. The tertiary amino groups were determined by direct titration with perchloric acid, after a preliminary acetylation of the primary and secondary amino groups with acetic anhydride²⁵. The gel content was determined by soaking for 21 days in THF at 25°C²⁶.

RESULTS AND DISCUSSION

Chemical structure of epoxide resin cured with aromatic and alicyclic diamines

The chemical composition of the aromatic and alicyclic epoxide resins cured with the aromatic and alicyclic diamines are shown in Table 1. In all samples, the gel content and the total conversion of epoxide groups are more than 99 and 93%, respectively. Thus, we can

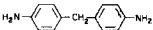
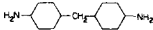
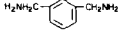
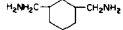
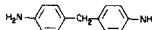
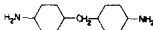
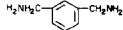
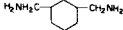
Table 1 Chemical composition of cured epoxide resins

Epoxide resins	Curing agents	Chemical structure	Gel content of cured resins (%)	Conversion of epoxide group (%) by titration			
				Total (A)	Reaction with primary amine (B)	Reaction with secondary amine ether (C)	Formation of (A)-(B)-(C)
BADGE*	DDM		100	99	49	17	33
	MBHA		99	97	48	25	24
	MXDA		102	93	47	21	25
	BACH		102	93	48	21	24
HBADGE†	DDM		99	99	49	34	16
	MBHA		99	98	45	43	10
	MXDA		99	99	46	41	12
	BACH		100	96	48	46	2

* BADGE : Bisphenol-A DGE

† HBADGE : Hydrogenated bisphenol-A DGE

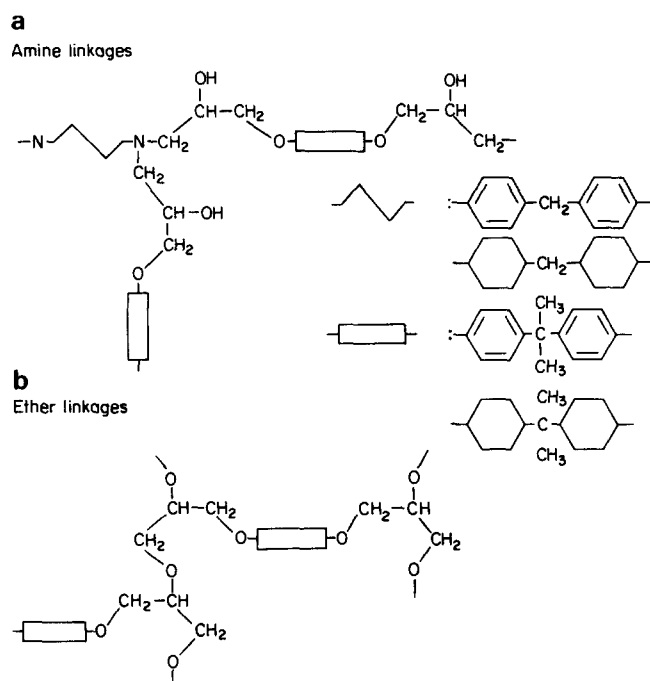
Table 2 Some properties of cured epoxide resins

Epoxide resins	Curing agents	Chemical structure	T_g ($^{\circ}\text{C}$)	G_r^1 (10^7 N/m^2)	ν^2 (10^{-3} mol/cm^3)	\bar{M}_c^3
BADGE	DDM		171	2.18	5.41	204
	MBHA		161	1.89	4.85	223
	MXDA		121	1.37	3.81	295
	BACH		140	1.27	3.37	326
HBADGE	DDM		106	0.729	2.12	512
	MBHA		101	0.632	1.87	571
	MXDA		110	0.667	1.89	556
	BACH		92	0.679	2.02	521

¹ Shear modulus of rubbery plateau (at 40°C above T_g)

² Concentration of network chains

³ \bar{M}_n between crosslinking points

**Figure 2** Structural schemes at crosslinking points

consider that the samples are all cured to the same degree and scarcely include the unreacted epoxide groups. In addition, the epoxide groups of these samples are mainly reacted with the primary and secondary amino groups, and 2 to 33% of epoxide groups form the ether bonds by self-polymerization²⁷ or the reaction with hydroxy groups²⁸.

The parameters ν and \bar{M}_c of these samples, which were estimated from the equation of ideal rubber elasticity²³, and the shear modulus in the rubbery plateau are shown in Table 2. In the aromatic resin system, ν and \bar{M}_c have values from 3.4×10^{-3} to $5.4 \times 10^{-3} \text{ mol cm}^{-3}$, and from 200 to 330, respectively. While, ν and \bar{M}_c of the alicyclic resin system is in 1.9×10^{-3} to $2.1 \times 10^{-3} \text{ mol cm}^{-3}$, and from 510 to 570, respectively. These results show that the latter system has a loosely crosslinked network more than the former system. This is expected, since the latter system

includes more dimer (about 51%, Figure 1). Moreover, we can conclude from the values of \bar{M}_c that both systems contain about one crosslinking point per one epoxide resin molecule, taking into account that the molecular weight of aromatic and alicyclic epoxide resins is about 380 and 480, respectively.

Structural schemes for the crosslinking points in these samples are shown in Figure 2. It is supposed, for all samples, that the two types of crosslinking points would be randomly distributed in the networks. One type is the amine-linkage as shown in Figure 2a, which is formed by the reaction between epoxide and amino groups. Another type is the ether-linkage as shown in Figure 2b, which results from self-polymerization of epoxide groups²⁷ or the reaction of epoxide with hydroxy groups²⁸.

α' Relaxation of aromatic and alicyclic epoxide resins

The mechanical relaxation behaviour of the aromatic and alicyclic epoxide resins cured with DDM and MBHA is shown in Figure 3. In the aromatic resin system, α' relaxation is clearly observed (Figure 3a). In the alicyclic resin system, the aromatic diamine-cured sample shows a small α' relaxation, but this relaxation is not observed at all in the alicyclic diamine-cured sample (Figure 3b). Namely, the α' relaxation appeared in the cured systems where either epoxide resins or curing agents include the aromatic rings. We can consider from this result that the motion of the aromatic rings is related to the α' relaxation of the cured epoxide resins.

In these cured systems, the peak temperature of α' relaxation, $T_{\alpha'}$, was not constant. This seemed to be due to the change of $T_{\alpha'}$ caused by the overlap of α relaxation to α' relaxation. Namely, we consider that the difference of $T_{\alpha'}$ in each system does not mean the difference of the α relaxation mechanism.

Similar mechanical relaxations were found in poly(1,4-phenyleneoxide)^{29,30}, polyimide³¹ and polyimide-amide³¹. It was reported for their relaxations to arise from oscillations of *p*-phenylene groups²⁹⁻³¹. Moreover, Yee³² reported a relaxation which is due to the motion of *p*-phenylene groups for some polymers containing the bisphenol-A units.

The mechanical relaxation of the epoxide resin cured

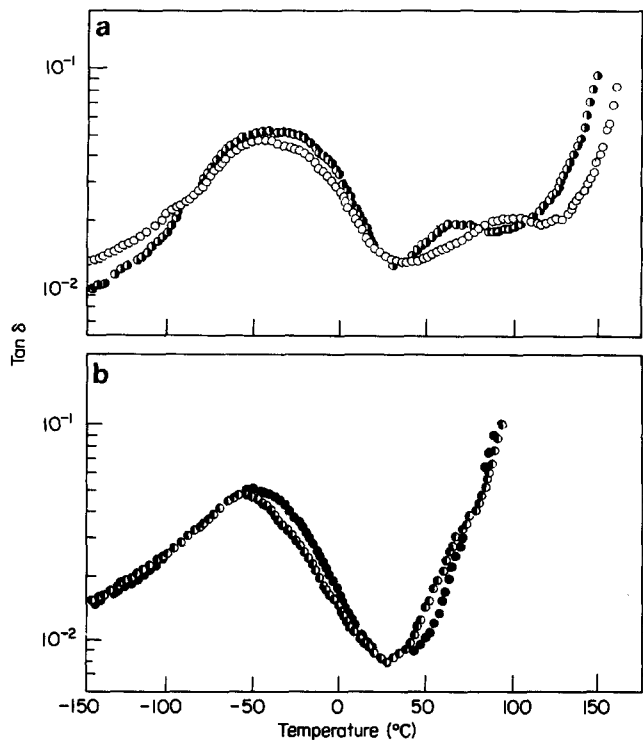


Figure 3 Dynamic mechanical properties of cured epoxide resins. (a) Epoxide resin: bisphenol-A DGE. Curing agents: (○) DDM, (●) MBHA. (b) Epoxide resin: hydrogenated bisphenol-A DGE. Curing agents: (◐) DDM, (◑) MBHA

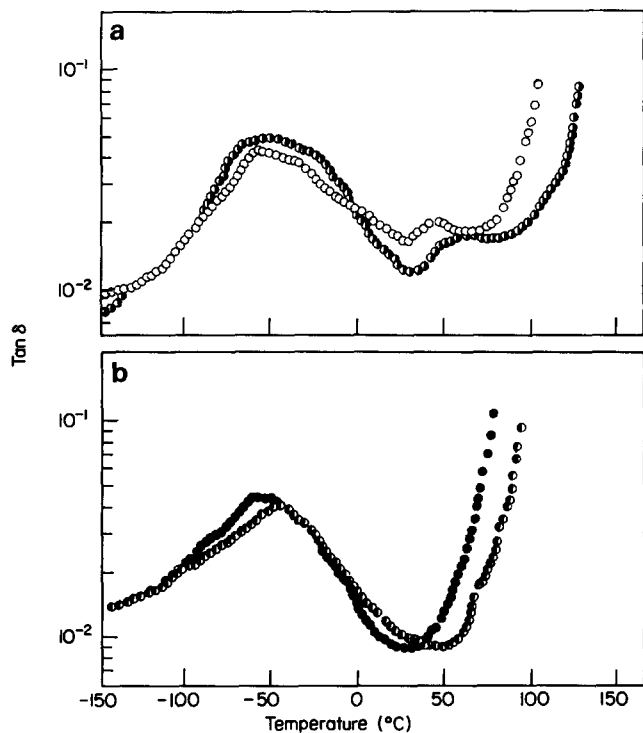


Figure 4 Dynamic mechanical properties of cured epoxide resins. (a) Epoxide resin: bisphenol-A DGE. Curing agents: (○) MXDA, (◐) BACH. (b) Epoxide resin: hydrogenated bisphenol-A DGE. Curing agents: (◑) MXDA, (●) BACH

with diamines, i.e. MXBA and BACH, which have amino groups at *meta* position are shown in Figure 4. In the aromatic resin systems, the obvious α' relaxations are observed (Figure 4a). But the relaxation is not seen at all in the alicyclic resin system, even if the curing agent includes

m-phenylene groups (Figure 4b). This result shows that the motion of *p*-phenylene groups in the networks is related to the α' relaxation of the cured epoxide resin systems.

Effect of the degree of cure on the α' relaxation of cured epoxide resins

The effects of the degree of cure on the mechanical relaxation of the aromatic and alicyclic epoxide resins cured with DDM and MBHA are shown in Figure 5. The α' relaxation is clearly observed in the aromatic resin system. When the conversion of epoxide groups is lower than 50%, the apparent peak height of the relaxation is high because of the overlap with α relaxation, i.e. glass-rubber transition.

In the alicyclic resin system which includes no *p*-phenylene groups, the α' relaxation is not observed in all samples having the different conversion of epoxide groups. Pogany²² and Arridge¹³ interpreted the α' relaxation as arising from the motion of the loosely crosslinked network embedded in the cured epoxide resins. However, we consider that the α' relaxation is due to the motion of *p*-phenylene groups, because this relaxation occurred only if the systems included the *p*-phenylene groups.

*Relation between the intensity of α' relaxation and the concentration of *p*-phenylene groups*

The α' relaxation was observed in the cured epoxide resin systems where either epoxide resin or curing agent have *p*-phenylene groups (Figures 3 and 4). Therefore, the relation between the area under the α' relaxation and the concentration of *p*-phenylene groups in the epoxide resin

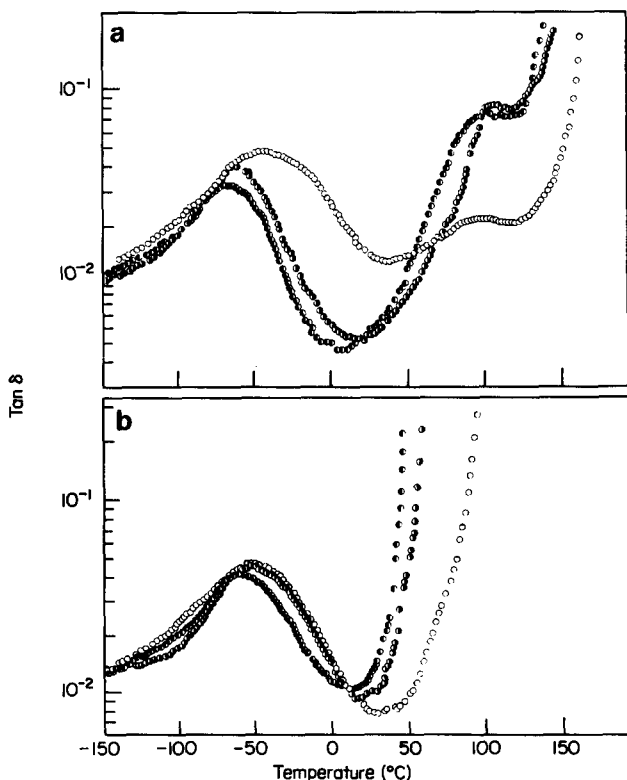


Figure 5 Dynamic mechanical properties of cured epoxide resins. (a) Epoxide resin: bisphenol-A DGE. Curing agent: DDM. Conversion of epoxide groups (%): (◐) 76, (◑) 84, (○) 99. (b) Epoxide resin: hydrogenated bisphenol-A DGE. Curing agent: MBHA. Conversion of epoxide groups (%): (◑) 72, (◐) 79, (○) 98

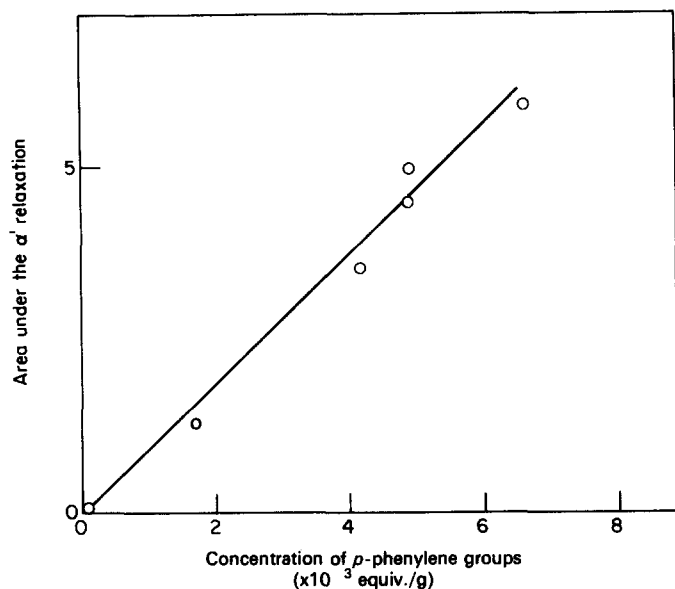


Figure 6 Area under the α' -relaxation curves versus concentration of *p*-phenylene groups in the cured epoxide resins

networks is plotted in Figure 6, which shows a good straight line through the origin. This means that the intensity of α' relaxation is dependent on the concentration of *p*-phenylene groups. Accordingly, we conclude that the α' relaxation of the cured epoxide resins is due to oscillation of the *p*-phenylene groups.

CONCLUSION

The bisphenol-A and hydrogenated bisphenol-A type epoxide resins were cured with two aromatic and two alicyclic diamines. The mechanism of the mechanical relaxation observed in the range of 50° to 90°C was investigated by comparing the dynamic mechanical properties and chemical structure of the networks. The following conclusions are obtained:

(1) The α' relaxation is observed in the epoxide resin networks having *p*-phenylene groups. Moreover, the linear relationship through the origin exists between the intensity of α' relaxation and the concentration of *p*-phenylene groups in the networks.

(2) The occurrence of the α' relaxation is independent of

the degree of cure, and depends on the existence of *p*-phenylene groups.

(3) The α' relaxation of the cured epoxide resins is attributed to oscillation of the *p*-phenylene groups in the networks.

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