Mechanical relaxation properties of spiro-type epoxide resins cured with acid anhydrides

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Low-temperature relaxation behaviour has been investigated for a bisphenol-A type and three spiro-type epoxide resins cured with acid anhydrides. In the spiro-type resin systems, one new relaxation, denoted here as the β' relaxation, is clearly observed near room temperature. It is suggested that the β' relaxation is related to the motion of p-phenylene group adjacent to the spiro ring. The impact strength of epoxide resin systems that show the β' relaxation is considerably higher than that of other cured systems and is proportional to the intensity of the β' relaxation. Consequently, it is concluded that the existence of the room-temperature relaxation such as the β' relaxation is associated with increased toughness of cured epoxide resins.

(Keywords: epoxide resin; mechanical relaxation; dielectric relaxation; toughness; acid anhydride)

INTRODUCTION

Dynamic mechanical measurements show clearly that cured epoxide resins have low-temperature relaxations. The mechanism for these relaxations has been studied to analyse segmental motion in the epoxide resin networks[1-16].

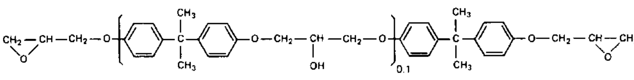
In a previous paper[17], it was demonstrated that diamine-cured epoxide resins with the spiro ring structure have a well-defined mechanical and dielectric relaxation (β' relaxation) near room temperature and that the β' relaxation is due to the motion of the p-phenylene group adjacent to the spiro ring.

In the present paper, the relation between the low-temperature relaxation and chemical structure of spiro-type epoxide resins cured with various acid anhydrides is investigated in detail to determine whether the mechanism of the β' relaxation suggested for the diamine-cured system[17] can be applied to the anhydride-cured system. Moreover, the effect of the intensity of the β' relaxation on the impact strength of these systems is investigated.

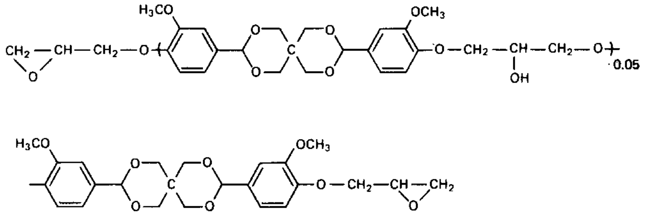
EXPERIMENTAL

Materials

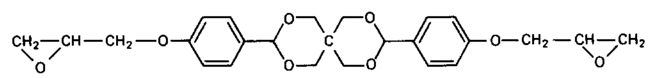
The epoxide resins used were liquid bisphenol-A type epoxide resin (DGEBA, Epikote 828, epoxide eq. 190 ± 5, $\bar{M}_n$ 380),



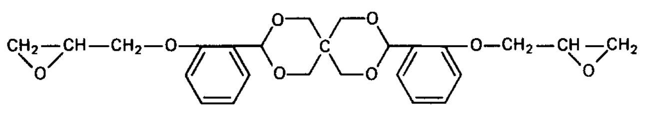
3,9-bis[(3-methoxy-4-glycidyl)phenyl]-2,4,8,10-tetroxaspiro[5,5]undecane (BMPTU, epoxide eq. 290, $\bar{M}_n$ 540),



3,9-bis[(4-glycidyl)phenyl]-2,4,8,10-tetroxaspiro[5,5]undecane (BGPTU, epoxide eq. 228, $\bar{M}_n$ 456),



and 3,9-bis[(2-glycidyl)phenyl]-2,4,8,10-tetroxaspiro[5,5]undecane (o-BGPTU, epoxide eq. 228, $\bar{M}_n$ 456).



Three acid anhydrides were used as curing agents, i.e. hexahydrophthalic anhydride (HHPA), phthalic anhydride (PA), and nadic anhydride (NA). The chemical structures of the anhydrides are shown in *Table 1*. N,N'-dimethylbenzylamine was used as an accelerator. The curing agents and accelerator were EP grade materials and were used without further purification.

Curing of epoxide resin

The epoxide resins were degassed at 60°C (DGEBA) or 150°C (other resins) under reduced pressure with stirring. Then, 1 phr of accelerator and stoichiometric amounts

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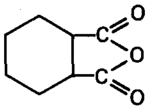
Table 1 Chemical composition of cured epoxide resins

Epoxide resin	Curing agent	Conversion of epoxide group (%)	Gel content of cured resin (%)	Gel content after saponification of cured resin (%)
BMPTU	HHPA[a]	99	100	0.2
	PA[b]	98	98	0.3
	NA[c]	97	101	0.3
BGPTU	HHPA	94	100	0.4
o-BGPTU	HHPA	92	96	0.2

[a]



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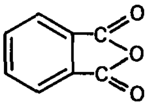

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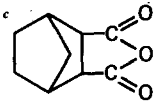

of curing agents were compounded with the resins: one mole of the epoxide group corresponds to one mole of the anhydride group. The mixtures were stirred at 80°C (DGEBA) or 150°C (other resins) until the curing agent dissolved in the epoxide resins, and were then poured into a silicone rubber container and allowed to cure in a forced-draught oven. The samples for the various tests were machined from cured epoxide resin plates.

Measurements

Dynamic mechanical properties were determined in the temperature range −160 to 250°C using an inverted, free-oscillation torsion pendulum (RD-1100AD, Rhesca Co. Ltd.) according to ASTM D2236-70 (ref. 17). The frequency of oscillation was adjusted to be within the range 0.1–2.0 Hz. Samples were heated *in vacuo* at 0.7 K min^{-1}.

Dielectric measurements were made with inductive-ratio-arm bridge type apparatus (TR-1100, Ando Electric Co. Ltd.). The measuring frequency was 50 Hz–1 MHz, in the temperature range −60 to 200°C. Samples were heated at 0.5 K min^{-1}.

The concentration, ν, of the network chains and the average molecular weight M_c between crosslinking points were calculated from the equation for ideal rubber elasticity[18,19],

$$G_r = \phi \nu R T$$

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

where G_r and ρ are the shear modulus and density in the rubbery region (40 K above the glass transition temperature), respectively; ϕ is the front factor, which is unity for ideal rubbers; R is the gas constant; and T is absolute temperature.

The conversion of epoxide and anhydride groups was determined according to the method of Shimazaki[20], and the saponification of the cured resins was carried out by the procedure of Luňák[21].

RESULTS AND DISCUSSION

Comparison of low-temperature relaxation behaviour of spiro ring type resin with that of bisphenol-A type resin

Dynamic mechanical properties of the spiro ring type and bisphenol-A type epoxide resins cured with an acid anhydride are shown in *Figure 1*. Similar glass transition temperature T_g and shear modulus G in glassy ($< T_g$) and rubbery ($> T_g$) regions were observed in these cured systems. The concentrations, ν, of network chains in these systems are also similar: 2.78×10^{-3} and 2.80×10^{-3} mol cm^{-3} for the spiro ring type and bisphenol-A type resin systems, respectively. These results show that both cured systems form tightly crosslinked network structures.

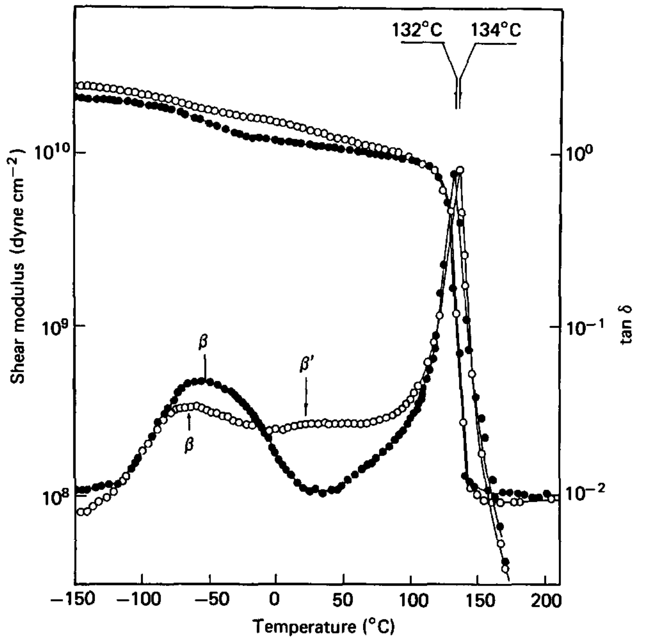

Figure 1 Dynamic mechanical properties of cured epoxide resins: (●) DGEBA, (○) BMPTU. Curing agent: HHPA. Accelerator: DMBA

Nevertheless, the low-temperature relaxation behaviour of the spiro ring resin systems is remarkably different from that of the bisphenol-A type resin systems. In the former, two relaxations are observed at about −70°C and +30°C, while in the latter, only one relaxation is seen, at about −70°C. It is clear that the mechanisms for the local motion of network chains in spiro ring type and bisphenol-A type resin systems differ. In ref. 17 the relaxations observed at about −70°C and +30°C are denoted β and β', respectively; it is suggested that the β relaxation of the anhydride-cured bisphenol-A type resin system is due to the motion of the diester segments introduced into the network by the anhydride curing agents[22–24]. It is reasonable to consider that the β relaxation of the spiro ring type resin system is due to a similar mechanism, because the mobility of diester segments is not influenced by the structure of the epoxide resin. Although the intensity of the β relaxation of the spiro type resin system is lower than that of the bisphenol-A type resin system, the concentration of the diester segments is 2.25×10^{-3} in the former and 2.91×10^{-3} eq g^{-1} in the latter.

It has not been reported that a well-defined relaxation, such as the β' relaxation, exists near room temperature. To confirm the existence of the β' relaxation, the dielectric relaxation of these cured systems is shown in *Figure 2*. The β' relaxation is clear in the temperature range from 50°C to 100°C for the spiro ring type system. This result shows that the β' relaxation definitely exists in the spiro ring type system.

Chemical composition of epoxide resin networks

The chemical composition of the acid anhydride-cured epoxide resins is summarized in *Table 1*. In all samples, the gel content and the conversion of epoxide groups exceed 96% and 92%, respectively. Therefore, the samples are all cured to the same degree and include a low proportion of unreacted epoxide groups. Furthermore, the gel content after saponification by alkali is about 0.2 ± 0.1% for all samples, which shows that the crosslinking points of these samples are mainly composed of ester linkages and include a small amount of ether linkages[25].

The parameters ν and $\bar{M}_c$ of these samples, which were estimated from the equation of ideal rubber elasticity[18,19], and the shear modulus in the rubbery plateau are shown in *Table 2*. In all samples, ν and $\bar{M}_c$ have values from 2.78×10^{-3} to 3.77×10^{-3} mol cm^{-3}, and from 320 to 430, respectively. These values of ν and $\bar{M}_c$ show that these samples are tightly crosslinked. In addition, it seems reasonable to consider that these samples contain about one crosslinking point per one epoxide resin molecule, taking into account that the molecular weights of epoxide resins are 540, 460 and 460 for BMPTU, BGPTU and *o*-BGPTU, respectively.

From these results, structural schemes for the crosslinking points in these systems are estimated and shown in *Figure 3*. Ester linkages are formed by reaction between anhydride and expoxide or hydroxy groups. Ether linkages are formed by self-polymerization of epoxide groups. It is expected that the two types of crosslinking points would be randomly distributed in the networks. However, these networks may be regarded as completely ester-linked because the amount of ether linkages is negligible (*Table 1*).

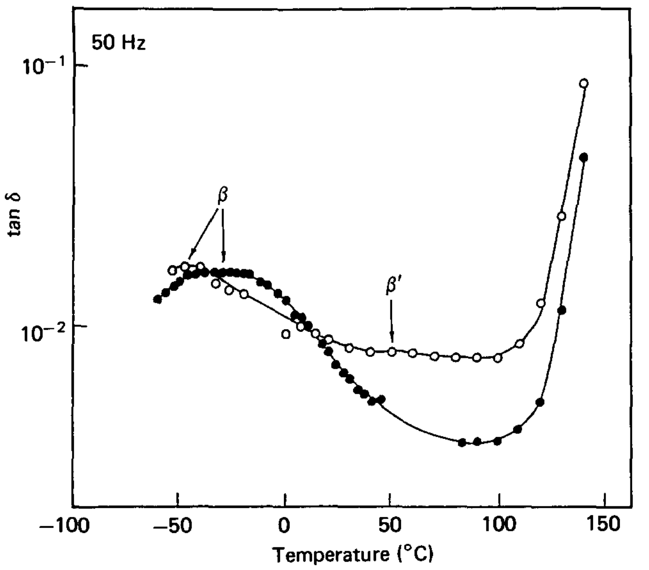

Figure 2 tan δ (dielectric) *versus* temperature of cured epoxide resins: (●) DGEBA, (○) BMPTU. Curing agent: HHPA. Accelerator: DMBA

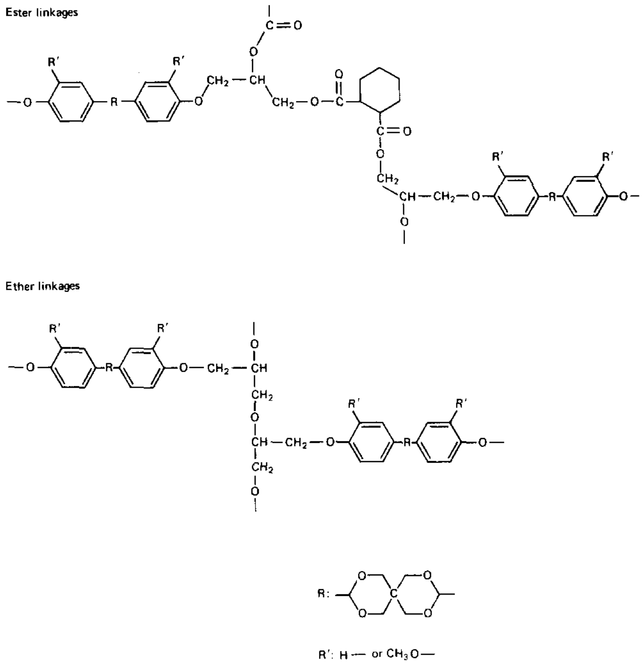

Figure 3 Structure near crosslinking points

Table 2 Some properties of cured epoxide resins

Epoxide resin	Curing agent	T_g (°C)	G_r[a] (10^8 dyne cm^{-2})	ν[b] (10^{-3} mol cm^{-3})	$\bar{M}_c$[c]
BMPTU	HHPA	134	0.94	2.78	432
	PA	138	1.16	3.40	353
	NA	147	1.00	2.86	420
BGPTU	HHPA	170	1.39	3.77	318
o-BGPTU	HHPA	149	1.15	3.28	366

[a] Shear modulus of rubbery plateau (at 40 K above T_g)
[b] Concentration of network chains
[c] $\bar{M}_n$ between crosslinking points

Effect of the structure of epoxide resins and curing agents on the β′ relaxation

The mechanical relaxation behaviour in the range −150 to +100°C of the bisphenol-A type and the spiro ring type epoxide resin cured with acid anhydrides (HHPA and NA) is shown in *Figure 4*. The β relaxation of these systems varies in peak height and peak position when the chemical structure of the curing agents is changed. This result supports the β relaxation mechanism described previously[17], that is, the β relaxation of the anhydride-cured systems is due to the motion of the diester segments.

The β′ relaxation of these systems is observed for both spiro ring type resins and not for the bisphenol-A type resins even if the chemical structure of the curing agent is varied. This shows that the appearance of the β′ relaxation depends on the structure of the epoxide resins, and is independent of the structure of the curing agents. Accordingly, it is reasonable to consider that the β′ relaxation is related to the motion of the epoxide resin portion in the networks.

The mechanical relaxation behaviours in the range −150 to +100°C of three spiro ring type epoxide resins with different chemical structure are shown in *Figure 5*. The β′ relaxation is observed in two cured resin systems (BMPTU and BGPTU), which have *p*-phenylene group adjacent to spiro ring. However, this relaxation is not seen in the system with *o*-BGPTU, which has an *o*-phenylene group adjacent to the spiro ring. Therefore, we consider that the β′ relaxation is due to the motion of the *p*-phenylene group adjacent to the spiro ring.

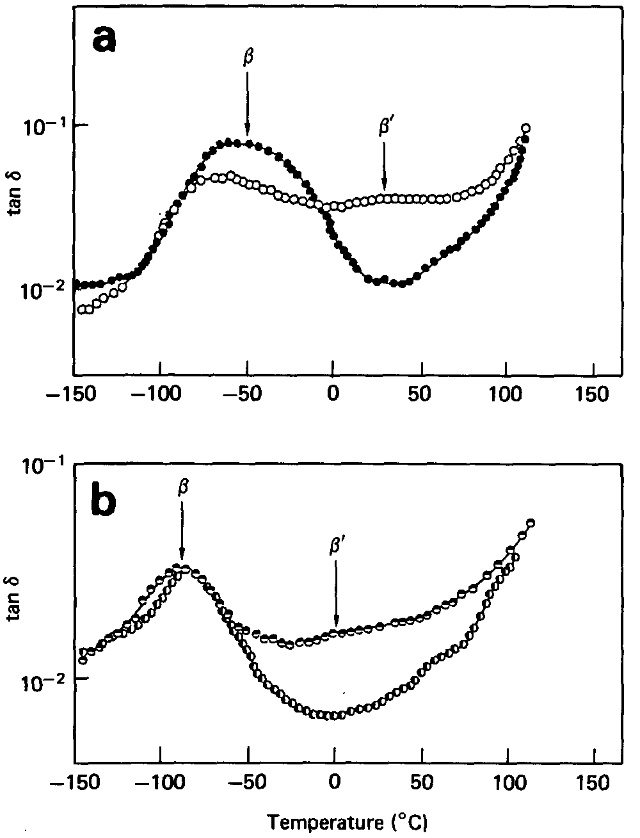

Figure 4 Dynamic mechanical properties of cured epoxide resins. (a) Curing agent: HHPA. Epoxide resins: (●) DGEBA, (○) BMPTU; (b) curing agent: NA. Epoxide resins: (◐) DGEBA, (◒) BMPTU

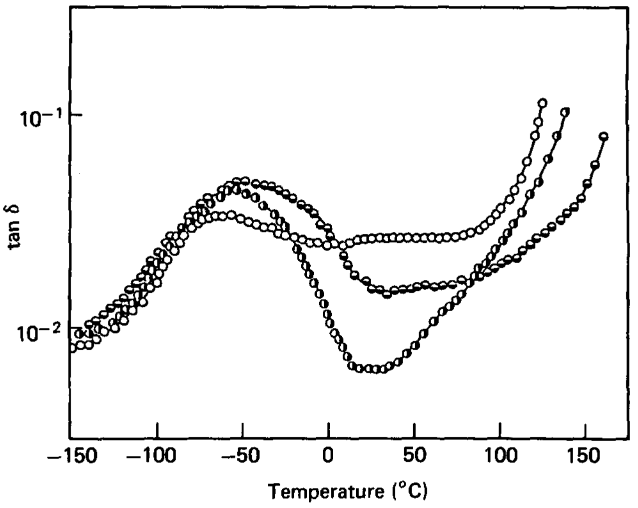

Figure 5 Dynamic mechanical properties of cured epoxide resins: (○) BMPTU, (◒) BGPTU, (◑) *o*-BGPTU. Curing agent: HHPA. Accelerator: DMBA

Table 3 Relation between the impact and the intensity of low-temperature relaxation of bisphenol-A and spiro ring type resin systems

Epoxide resin	Curing agent	Impact strength (kg cm^{-1})	Peak height of β relaxation	Peak height of β′ relaxation
DGEBA	HHPA	6.50	0.047	nd[a]
	THPA	5.98	0.036	nd[a]
	NA	4.99	0.032	nd[a]
BMPTU	HHPA	10.0	0.034	0.0267
BGPTU	HHPA	7.4	0.049	0.0162
o-BGPTU	HHPA	6.1	0.044	nd[a]

[a] Not detected

Relation between impact strength and intensity of the β′ relaxation of cured epoxide resin systems

Many investigators have reported that impact strength of polymeric materials depends on the magnitude of low-temperature relaxation[26,27]. Ochi *et al.*[23] suggested that the impact strength of epoxide resin cured with various acid anhydrides varies in proportion to the intensity of the β relaxation, if the glass transition temperature and the cross-linking density for the cured resins are nearly constant.

Spiro ring type epoxide resins cured with anhydrides have a β′ relaxation near room temperature. It is expected that such room temperature relaxation affects considerably the toughness of cured epoxide resins. To confirm this prediction, the impact strength and the intensity of β and β′ relaxations of bisphenol-A and spiro ring type resins cured with various anhydrides are listed in *Table 3*.

The impact strength of epoxide resin systems that lack the β′ relaxation increases with the intensity of the β relaxation. However, the impact strength of epoxide resin systems (BMPTU and BGPTU) that have the β′ relaxation is considerably higher than that of other cured systems. This means that the β′ relaxation affects the impact strength of cured resin systems.

The relationship between the impact strength and the loss tangent (tan δ) at room temperature for cured

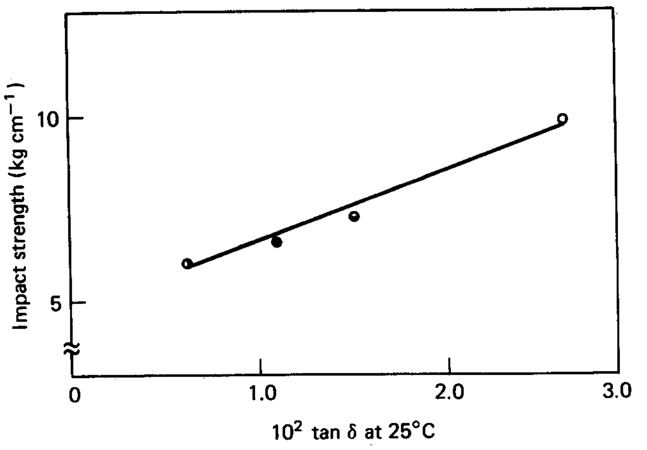

Figure 6 Impact strength *versus* tan δ at room temperature of cured epoxide resins: (○) BMPTU, (◒) BGPTU, (●) DGEBA, (◑) *o*-BGPTU. Curing agent: HHPA. Accelerator: DMBA

epoxide resins with or without the β′ relaxation is shown in *Figure 6*. The impact strength increases in proportion to the loss tangent at room temperature. Consequently, the mechanical relaxation such as the β′ relaxation, which is observed near room temperature, is effective in increasing toughness of cured epoxide resins.

CONCLUSION

Bisphenol-A and spiro ring type epoxide resins were cured with acid anhydrides with a variety of chemical structures. The mechanism of the low-temperature mechanical relaxation in these cured resins was investigated in detail. The effect of the intensity of this relaxation on the mechanical properties of these systems was studied. From these results, the following conclusions were obtained.

(1) Epoxide resin systems that include the spiro ring structure and an adjoining *p*-phenylene group have a large mechanical relaxation (β′ relaxation) near room temperature.

(2) The β′ relaxation is attributed to the motion of the *p*-phenylene groups adjacent to the spiro ring.

(3) The impact strength of the cured epoxide resins with the β′ relaxation is considerably higher than that of other cured resins. Moreover, the impact strength of these systems increases in proportion to the intensity of the β′ relaxation.

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