

Cross-linking of Bisepoxide with Divalent Metal Salts of *p*-Aminobenzoic Acid and Anhydride

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SYNOPSIS

Cross-linking of bisepoxide with divalent metal salts of *p*-aminobenzoic acid and dicarboxylic acid anhydride was investigated. As the bisepoxide, bisphenol A diglycidyl ether was used and hexahydrophthalic anhydride was the anhydride used. As the divalent metal, Mg and Ca were selected. In the cross-linking reactions, the metal salts showed catalytic activities. In this case, the salt containing Mg exhibited higher catalytic activities than that containing Ca. The cross-linking reaction was supposed to proceed via a complex mechanism. The cured resins obtained contained amide and ester groups and ionic linkages. As for the physical properties of the novel metal-containing cured resins, tensile and flexural strengths decreased with an increase in the metal content. However, Rockwell hardness was not affected by the metal content. There was a good correlation between heat distortion temperature and T_g determined by dynamic mechanical properties. Against boiling water, the resins exhibited low weight gain, low change in dimension, and no change in external appearance. In addition, thermal decomposition was accelerated by the incorporated metal.

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INTRODUCTION

The authors have been active in the syntheses of polymers by using divalent metal salts of *p*-aminobenzoic acid (ABA), that is, ABA(M) (where M is a divalent metal such as Mg or Ca).¹⁻³ Because the ABA(M)



ABA(M)

M = divalent metal (Mg or Ca)

salts contain an ionic bond formed between COO^- and M^{2+} and two amino groups, they are considered to be of interest as ionic monomers for the preparation of ionic polymers into which metal is firmly incorporated.

In the previous study,³ cross-linking of bisepoxide with ABA(M) and aromatic diamine was investigated. As the bisepoxide, bisphenol A diglycidyl ether (BADG) was used. 4,4'-Diaminodiphenylmethane (4,4'-methylenedianiline, MDA) was used as the aromatic diamine. It was found that the metal salts have catalytic activities for the cross-linking reaction. The metal-containing cured resins obtained showed higher compressive strengths than the resin not containing metal. However, heat distortion temperature (HDT) showed a tendency to decrease with an increase in the metal content.

On the other hand, in cross-linking of epoxy resins with dicarboxylic acid anhydrides, tertiary amines such as *N,N*-dimethylbenzylamine (DMBA), etc. are widely used as catalyst. Such tertiary amines are known to be toxic. ABA is much less toxic and the Mg and Ca carboxylate groups in ABA(M) were anticipated to have catalytic activities for the anhydride cure of epoxy resins. Therefore, in the present study, cross-linking of BADG with ABA(M) and anhydride was investigated to prepare novel metal-containing cured resins. As the anhydride, hexahydrophthalic anhydride (HPAn) was used. Further, the novel metal-containing cured

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resins obtained were evaluated for physical and other properties.

EXPERIMENTAL

Materials

ABA(M) salts were prepared by the same method as reported in the previous study.¹ HPAn, aniline, and MDA were of specialty grade and were used as received. As the BADG, EPOMIK R139 (Mitsui Petrochemical Epoxy Co.) was used. The epoxide value was 5.478 equiv/kg (calcd. = 5.875 equiv/kg).

Curing Reactions

Fixed amounts of aromatic amine [aniline, MDA, or ABA(M)], HPAn, and BADG (whose amount was equivalent to that of the aromatic amine) were mixed and stirred at 150°C until the mixture became homogeneous (transparent). After the mixture was cooled to 80°C, a remaining amount of BADG was further added, and dissolved to obtain homogeneous curable mixture. Next, in a 18 × 180 mm test tube was placed 5 g of the curable mixture and the test tube was placed in a 100°C bath. After a desired time, samples were taken for analyses of acid and epoxide values. Gel time was determined by measuring the time when the mixture would not flow in the test tube.

Cured resin moldings for determining physical and other properties were prepared as follows. A desired amount of the above curable mixture was degassed under a reduced pressure and was poured into molds. The mixture was cured at 130°C for 15 h, 150°C for 8 h, and then at 180°C for 5 h. Because the mixture containing aniline or MDA as aromatic amine was very slow to cure, DMBA (0.05 wt % based on the total weight of the mixture) was added as catalyst.

Analytical Methods

When a sample was an insoluble hard solid, it was filed into powder and subjected to analyses. The titrations were carried out by using a Hiranuma reporting titrater (COMMIT 101).

Acidities of the curing reaction system were determined⁴ by titration in nonaqueous solvent and also by titration in water-containing solvent. The anhydride content was calculated from the difference of the two titrations.

Epoxide value was determined by the HBr method^{5,6} as follows. For the samples that were sol-

uble in chloroform and glacial acetic acid, a given amount of sample was weighed to the nearest milligram into a 100-mL flask and the solvent was added to dissolve the sample. It was titrated with 0.1 N HBr-glacial acetic acid. When the sample was insoluble, a given amount of the sample in the form of powder was weighed to the nearest milligram into the flask and 10 mL of chloroform was added. After standing overnight, the mixture was titrated with 0.1 N HBr-glacial acetic acid. Because HBr reacts with the metal carboxylate groups to produce MBr₂, correction was made for this factor.

Hydrolysis of the cured resins was conducted as follows. To about 0.3 g of sample filed into powder was added 25 mL of 0.5 N KOH-ethanol-H₂O [ethanol : H₂O = 4 : 1 (v/v)] and refluxed for 1 h. The sample that did not contain ether linkages became a transparent solution by the hydrolysis.

Infrared (IR) spectra were determined with a Shimadzu IR-435 instrument.

Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were carried out in a Seiko thermal analyzer TG/DTA 220 (SSC/5200 Series) at a heating rate of 10°C/min in air.

Determinations of physical and other properties were conducted by the same method as in the previous study.³

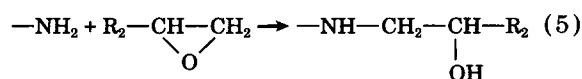
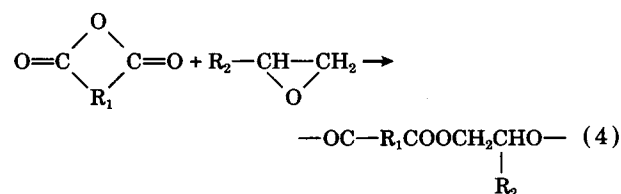
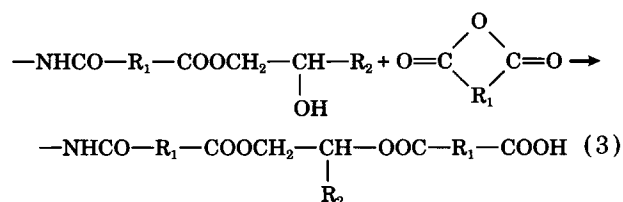
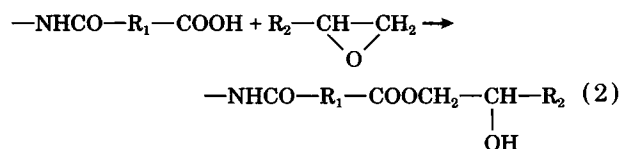
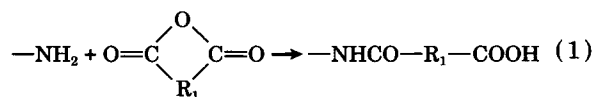
RESULTS AND DISCUSSION

Curing Reactions

As the result of preliminary experiments for the cross-linking reactions of the ABA(M)-anhydride-BADG systems, it was found that ABA(M) did not dissolve in the system when maleic anhydride was used as the anhydride. When phthalic anhydride was used as the anhydride, the system became homogeneous above ca. 130°C. However, phthalic anhydride solidified below ca. 130°C and curing of the mixture proceeded too rapidly above ca. 130°C to follow the curing reaction and cured resin moldings for determining physical and other properties could not be obtained. When HPAn was used as the anhydride, homogeneous curable mixtures of the ABA(M)-HPAn-BADG systems could be obtained. The homogeneous curable mixtures were prepared as follows. Given amounts of ABA(M), HPAn, and BADG [whose amount was equivalent to that of ABA(M)] were heated at 150°C with stirring until the mixture became homogeneous. Then, the mixture was cooled to 80°C and a remaining amount of BADG was further added and stirred at the same

temperature to obtain homogeneous curable mixtures.

In the curing of the ABA(M)-anhydride-BADG systems, the following main reactions of the functional groups are first considered.



That is, the reaction of the amino group in ABA(M) with the acid anhydride group in HPAn forms a carboxyl group [eq. (1)]; the reaction of the generated carboxyl group with the epoxy group in BADG forms a hydroxyl group [eq. (2)]; the reaction of the generated hydroxyl group with the acid anhydride group forms a half ester [eq. (3)]; the reaction of the acid anhydride group with the epoxy group forms an ester linkage [eq. (4)]; further, the reaction of the amino group with the epoxy group forms a hydroxyl group [eq. (5)].

It is well known that reaction (1) proceeds much more rapidly than reactions (3), (4), and (5). Hence, it is considered that the amino group reacts preferentially with the acid anhydride group in HPAn and reaction (5) is not significant. In the curing of systems of divalent metal salts of mono(hydroxyethyl)phthalate (HEP)-anhydride-bisepoxide, it was proved that reaction (3) proceeded more rapidly than reaction (2).⁴ In summary, the rate of these elementary reactions is considered to

decrease in the order, reaction (1) > reaction (3) > reaction (2). Therefore, although the complexity of the systems is inevitably high, in principle, the curing of the ABA(M)-HPAn-BADG systems is considered to proceed as follows. First, reaction (1) should occur to produce a carboxyl group. The carboxyl group is a starting point for chain extension. That is, the carboxyl group would enter into reaction (2) to produce a hydroxyl group. Next, the hydroxyl group would immediately enter into reaction (3). Thus, these addition reactions are considered to repeat alternately, so that ample opportunity for further growth of three-dimensional network structure will be provided.

Meanwhile, because the concentration of the acid anhydride group is high in the initial stages of the curing, reaction (4) is considered possible. However, reactions (2) and (3) are known to proceed more rapidly than reaction (4).⁴ Hence, reaction (4) would become less significant with the progress of the curing because of a decrease in the anhydride content.

Figure 1 shows, as a typical example, the result of the curing reaction of the ABA(Mg)-HPAn-BADG (1 : 20 : 10) system. The bath temperature was 100°C. The acidities shown were determined by nonaqueous titration and are caused by both anhydride and carboxyl groups. With an increase in the reaction time, the acidity and epoxide values decreased similarly, and the anhydride content decreased also, indicating that the curing proceeded

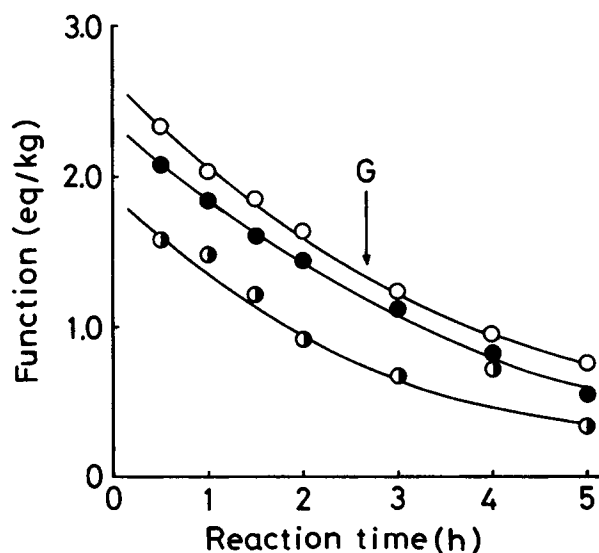


Figure 1 Curing reaction of system of ABA(Mg)-HPAn-BADG (1 : 20 : 10) at 100°C: (○) acidity; (●) epoxide value; (●) anhydride. G = gel point.

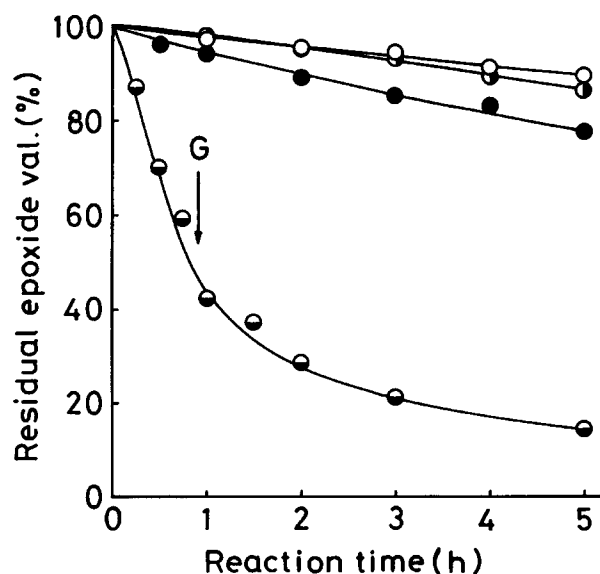


Figure 2 Curing reaction of systems of (○) aniline-HPAn-BADG (2 : 20 : 10); (○) MDA-HPAn-BADG (1 : 20 : 10); (●) ABA(Mg)-HPAn-BADG (1 : 20 : 10); (●) ABA(Ca)-HPAn-BADG (1 : 20 : 10) at 110°C. G = gel point.

via the above-mentioned elementary reactions. However, the decrease in epoxide value is consistently a little greater than the decrease in acidities. This suggests that etherification of epoxy groups as a side reaction occurred to only a slight degree.

Shimbo et al.^{7,8} hydrolyzed dicarboxylic acid-cured epoxy resins in alkaline solution, and deter-

mined the percentages of ester and ether linkages in the cured resins. Also in the present study, the obtained cured resins were subjected to the hydrolysis to confirm the existence of ether linkages. However, the hydrolyzed products dissolved in ethanol-H₂O [4 : 1 (v/v)] mixed solvent. Therefore, the etherification of epoxy groups appears least significant in the present study.

Figure 2 shows the results of the curing reactions of the systems containing ABA(M) and those not containing ABA(M) in terms of the conversion of epoxy groups. The systems containing aniline or MDA were also investigated for comparison. It should be noted that the systems containing ABA(M) exhibited higher reaction rate than those without metal, indicating catalytic activities of the metal carboxylate groups of ABA(M). This tendency was especially remarkable for the system containing Mg. In the curing reactions of BADG with ABA(M) and diamine in the previous study,³ the salt containing Ca with the lower electronegativity showed higher catalytic activities than that containing Mg. Hence, this curing was considered to proceed via an ionic mechanism.

In the curing reactions of the systems of divalent metal salts of HEP-anhydride-bisepoxide, the Mg salt exhibited higher catalytic activities than the Ca salt.⁴ This curing was supposed to proceed mainly by a complex mechanism where ion pairs are concerned.⁹ Also, the curing reactions in the present study are supposed to proceed via such a complex mechanism.

Table I Preparation of Cured Resins From Aniline, MDA or ABA(M), HPAn, and BADG

Components	Mole Ratio of Components	Metal Content (%)	Gel Time ^a (min)	Conversion of	
				Epoxide (%)	Acidity (%)
Aniline-HPAn-BADG ^b	1:20:10	—	420	97	99
	2:20:10	—	280	98	98
	4:20:10	—	200	96	94
MDA-HPAn-BADG ^b	0.5:20:10	—	400	96	99
	1:20:10	—	250	97	99
	2:20:10	—	150	97	97
ABA(Mg)-HPAn-BADG	0.5:20:10	0.17	110	100	96
	1:20:10	0.34	18	100	91
ABA(Ca)-HPAn-BADG	0.5:20:10	0.29	330	100	97
	1:20:10	0.56	170	98	94
	2:20:10	1.07	60	97	91

Cure condition: 130°C for 15 h, 150°C for 8 h, and 180°C for 5 h.

^a Curing temperature: 140°C.

^b DMBA (0.5 wt % based on the total weight of reactants) was added as catalyst.

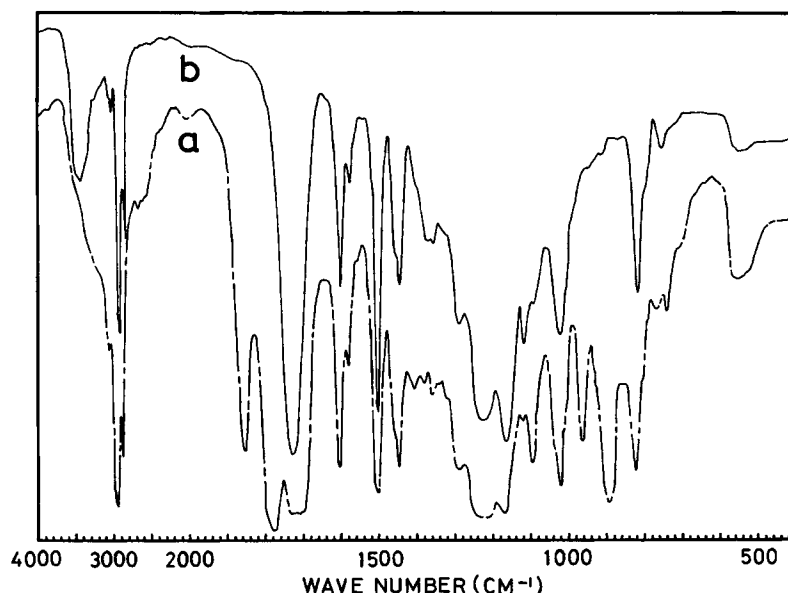
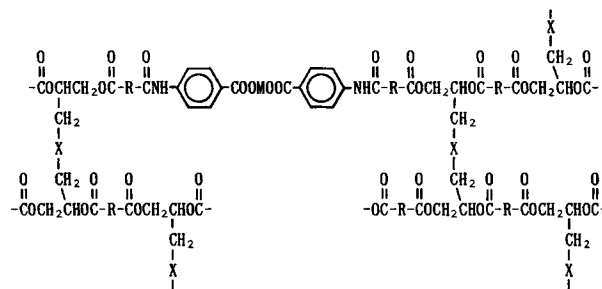


Figure 3 Infrared spectra of system of ABA (Mg)-HPAn-BADG (1 : 20 : 10): (a) initial curable mixture; (b) cured at 130°C for 15 h, at 150°C for 8 h, and 180°C for 5 h.

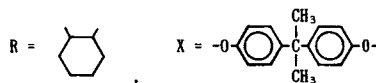
Table I summarizes the results of the preparation of the cured resins from aniline, MDA, or ABA (M), HPAn, and BADG. The curing reaction of the mixtures not containing metal were too sluggish to determine gel time even at 140°C. Meanwhile, in the case of the mixtures containing metal, gel time became shorter with an increase in the metal content. In addition, at the same mole ratios of the components, the mixtures containing Mg exhibited shorter gel time than those containing Ca. Thus, again the catalytic activities of the metal carboxylate groups are observed. The cured resin moldings for determining physical and other properties were prepared by curing at 130°C for 15 h, 150°C for 8 h, and 180°C for 5 h. In this case, for curing the mixtures not containing metal, DMBA was added as catalyst.

Figure 3 shows, as a typical example, the IR spectra of the ABA (Mg)-HPAn-BADG (1 : 20 : 10) system. In the IR spectrum of the initial curable mixture, absorption bands at 1855 and 1780 cm^{-1} , characteristic of the anhydride group, and at ca. 900 cm^{-1} , due to the epoxy group are noteworthy; further, the small band at ca. 1400 cm^{-1} is attributable to the metal carboxylate group. On the other hand, in the spectrum of the cured resin, the bands of the anhydride group and that of the epoxy group have disappeared, showing that the curing reaction has fully proceeded.

The idealized main structure part of the metal-containing cured resins obtained in the present study may be represented as follows:



where



Physical Properties

Table II shows the physical properties of the cured resins. HDT showed a tendency to decrease with an increase in the aromatic amine content, especially so for the aniline-based cured resins. This is attributed to the fact that cross-linking densities of the cured resins decrease with an increase in the amino groups in the feed. On the other hand, the HDT of the ABA (Mg)-based cured resins were equal to those of the MDA-based cured resins at the same mole ratios of components; however, the HDT of the ABA (Ca)-based cured resins were 5–8°C higher than those of the MDA-based resins, when the Ca content was high.

Table II Physical Properties of Cured Resins

Components	Mole Ratio of Components	HDT (°C)	Tensile Strength (kg/cm ²)	Flexural Strength (kg/cm ²)	Rockwell Hardness (M scale)	Impact Strength (kg · cm/cm)	Compressive Strength (kg/cm ²)
Aniline-HPAn-BADG ^a	1:20:10	120	710	1620	111	1.28	1460
	2:20:10	108	960	1550	111	1.30	1410
	4:20:10	90	870	1610	107	1.55	1360
MDA-HPAn-BADG ^a	0.5:20:10	133	810	1570	109	1.22	1610
	1:20:10	123	920	1500	106	1.22	1430
	2:20:10	110	950	1550	106	1.47	1560
ABA(Mg)-HPAn-BADG	0.5:20:10	132	800	1240	110	1.12	1210
	1:20:10	122	620	860	107	1.16	1340
ABA(Ca)-HPAn-BADG	0.5:20:10	133	730	1170	110	1.12	1330
	1:20:10	131	700	1030	110	1.12	1290
	2:20:10	115	550	860	108	1.14	1200

Cure condition: 130°C for 15 h, 150°C for 8 h, and 180°C for 5 h.

^a DMBA (0.05 wt % based on the total weight of reactants) was added as catalyst.

Rockwell hardness (M scale) was not affected by the metal content, and the hardness values of the metal-containing cured resins were almost equal to those of the resins not containing metal.

In general, the tensile, flexural, impact, and compressive strengths of the metal-containing cured resins were lower than those of the resins without metal, and the former two strengths decreased with an increase in the metal content.

Dynamic Mechanical Properties

Figure 4 shows the dynamic mechanical properties of the cured resins. They exhibited relaxations at ca. 120–150°C and ca. –50°C. These will be denoted by α and β relaxations, respectively. Further, in Table III are summarized temperatures of α - and β -transitions, and $\tan \delta_{\max}$ of all the resins examined. Because the measurements were conducted at small frequencies below 3.0 Hz, a temperature at which shear modulus (G) suddenly decreases or $\tan \delta$ shows the major maximum is considered to be T_g .

T_g showed a tendency to decrease with an increase in the aromatic amine content in the feed. This tendency is similar to that of HDT, and is also attributed to the decrease of cross-linking densities of the cured resins with an increase in the amino groups in the feed. However, at the same mole ratios of components, the T_g determined by dynamic mechanical properties were 9–14°C higher than the HDT.

Meanwhile, in the previous study,³ such a good correlation was not observed between HDT and T_g

for the metal-containing cured resins obtained by cross-linking of BADG with ABA (M) and aromatic diamine. That is, HDT decreased with an increase in the metal content, and T_g determined by dynamic mechanical properties was not influenced by the metal content. It was guessed that this difference

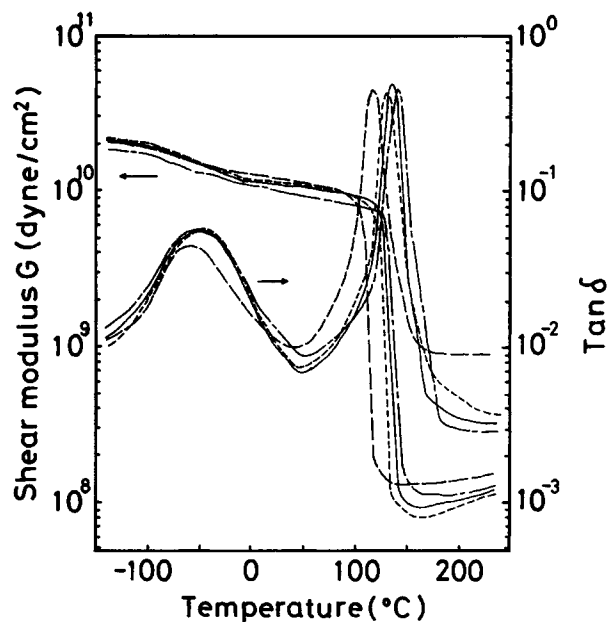


Figure 4 Dynamic mechanical properties of cured resins from (---) aniline-HPAn-BADG (2 : 20 : 10); (—) MDA-HPAn-BADG (1 : 20 : 10); (-·-) ABA(Mg)-HPAn-BADG (1 : 20 : 10); (- - -) ABA(Ca)-HPAn-BADG (1 : 20 : 10).

Table III Dynamic Mechanical Properties of Cured Resins

Components	Mole Ratio of Components	α -Transition Temp. ($^{\circ}\text{C}$)	β -Transition	
			Temp. ($^{\circ}\text{C}$)	$\tan \delta_{\max}$
Aniline-HPAn-BADG	1:20:10	131	-55	0.047
	2:20:10	120	-63	0.043
	4:20:10	101	-65	0.037
MDA-HPAn-BADG	0.5:20:10	144	-49	0.055
	1:20:10	137	-48	0.054
	2:20:10	122	-54	0.053
ABA(Mg)-HPAn-BADG	0.5:20:10	143	-48	0.054
	1:20:10	131	-48	0.054
ABA(Ca)-HPAn-BADG	0.5:20:10	143	-48	0.053
	1:20:10	140	-51	0.054
	2:20:10	126	-52	0.050

between HDT and T_g is due to the difference of the determination methods. That is, the HDT is a temperature at which the sample is deformed as a whole by a fixed load. Hence, the HDT would depend on proportion of each chemical structure existing in the cured resin sample. Meanwhile, the dynamic mechanical properties are considered to reflect a temperature of relaxation of each structure part in the sample, for example, T_g is a temperature of relaxation of the main cross-linked structure part. The metal-containing amine-cured epoxy resins³ contained a large amount of unreacted secondary amines, in addition to the network structure part. The formation of the secondary amines was due to a high degree of etherification. The secondary amine part is a component of linear chain structure composed mainly of diphenylmethane. T_g of the main cross-linked structure part would not be affected even when there are many kinds of chemical structures in the cured resin sample. Therefore, the above observed good correlation between HDT and T_g of the cured resins obtained in this study suggests that the cured resins have uniform cross-linked structure and do not contain measurable amounts of linear chain structure parts.

Further, the metal-containing amine-cured epoxy resins exhibited a relaxation at ca. 60°C .³ This relaxation was supposed to be attributable to the linear chain structure. The metal-containing cured resins in the present study did not show such a relaxation around this temperature, suggesting that there is no linear chain structure in the cured resin. This will be supported also by the above-mentioned hydrolysis experiment that showed that there was no measurable amount of ether linkages in the cured resins.

In this study, the β relaxation around -50°C of the ABA(M) or MDA containing cured resins appeared at higher temperature and the $\tan \delta_{\max}$ increased a little as compared with the aniline containing cured resins.

Fukazawa and Wada¹⁰ studied dynamic mechanical properties of amine-cured epoxy resins and suggested that the relaxation around -50°C is due to a local mode of the bisphenol A skeleton. Similarly, Ochi et al.¹¹ reported that the relaxation around -50°C of the amine-cured epoxy resins is attributable to the mobile structure parts such as hydroxy ether structure and local mode of bisphenol A skeleton. Further, Cuddihy and Moacanin¹² also investigated dynamic mechanical properties of epoxy

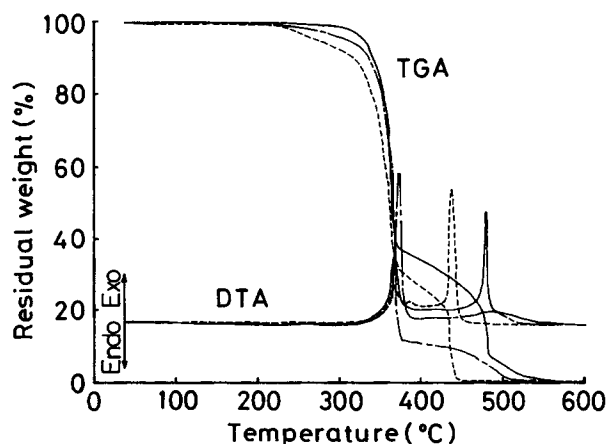


Figure 5 TGA and DTA curves of cured resins from (—) MDA-HPAn-BADG (1 : 20 : 10); (---) ABA(Mg)-HPAn-BADG (1 : 20 : 10); (- - -) ABA(Ca)-HPAn-BADG (1 : 20 : 10).

Table IV Boiling Water Resistance of Cured Resins

Components	Mole Ratio of Components (%)	Change in Length (%)	Change in Thickness (%)	Change in Weight (%)	External Appearance
Aniline-HPAn-BADG	1:20:10	0.03	0.25	0.32	UA
	2:20:10	0.09	0.18	0.41	UA
	4:20:10	0.17	0.44	0.61	UA
MDA-HPAn-BADG	0.5:20:10	0.12	0.15	0.31	UA
	1:20:10	0.03	0.21	0.35	UA
	2:20:10	0.09	0.21	0.51	UA
ABA(Mg)-HPAn-BADG	0.5:20:10	0.04	0.19	0.39	UA
	1:20:10	0.04	0.33	0.62	UA
ABA(Ca)-HPAn-BADG	0.5:20:10	0.06	0.09	0.35	UA
	1:20:10	0.03	0.20	0.44	UA
	2:20:10	0.05	0.45	0.67	UA

UA, unaffected.

resins cured with various curing agents; they estimated that the β relaxation is attributable to the local mode of bisphenol A skeleton and their neighboring mobile structure parts.

From the above it is inferred that the β relaxation in this study is attributable to the local mode of associated ionic linkages or diphenyl methane skeleton in addition to the local mode of bisphenol A skeleton and their neighboring mobile structure parts.

Thermal Properties

Figure 5 shows the TGA and DTA curves of the metal-containing cured resins and those not con-

taining metal in air. The metal-containing resins began to decompose at a lower temperature than the resin without metal. The MDA-based cured resin exhibited thermal decomposition that can be divided into the following four stages. The first stage is a region of ca. 340–370°C, where abrupt weight loss of ca. 60% occurs with a large exotherm. The second is a region of decomposition with a small exotherm from ca. 370 to 480°C, where slow weight loss of ca. 20% occurs. The third is a region of ca. 480°C, where again rapid decomposition occurs with a large exotherm. The fourth is a region of ca. 490–550°C, where final decomposition occurs. On the other hand, the Ca-containing resin showed thermal de-

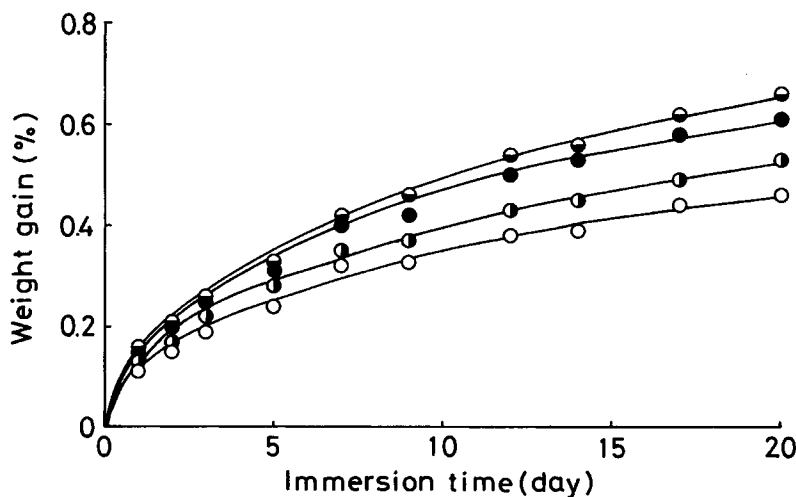


Figure 6 Water absorption of cured resins at 23°C: (O) aniline-HPAn-BADG (2 : 20 : 10); (●) MDA-HPAn-BADG (1 : 20 : 10); (◐) ABA(Mg)-HPAn-BADG (1 : 20 : 10); (●) ABA(Ca)-HPAn-BADG (1 : 20 : 10).

composition that can be divided into the following three stages. That is, the first stage is a region of ca. 350–370°C, where abrupt weight loss of ca. 85% occurs with a large exotherm. The second is a region of decomposition with a small exotherm from ca. 380 to 470°C. The third is a region of ca. 470–510°C, where final decomposition occurs. The first stage of the Ca-containing resin seems to combine the first, the second, and the third stages of the MDA-based resin. The Mg-containing resin exhibited the middle thermal decomposition behavior between those of the MDA-based resin and the Ca-containing resin. This suggests that the metal carboxylate groups act as a catalyst for the thermal decomposition; and the salt containing Ca with the lower electronegativity exhibited higher catalytic activities than that containing Mg. Therefore, the thermal decomposition of the cured resins are supposed to proceed via an ionic mechanism.

Furthermore, the plateau observed above ca. 450°C or ca. 550°C in the TGA curves of the metal-containing resins corresponds to the formation of MgO for the Mg salt and CaCO₃ for the Ca salt.

Boiling Water and Water Resistances

Table IV shows the boiling water resistance of the metal-containing cured resins and the resins without metal. The boiling water resistance was evaluated by weight gain, changes in dimension, and external appearance. All the resins did not show any change in external appearance and showed low weight gain and small change in dimension by boiling water for 2 h. However, the weight gain of the metal-containing resins were only slightly higher than those of the resins without metal at the same mole ratios of components.

Similarly, as shown in Figure 6, they showed small weight gains of below 1% after water immersion at 23°C for 20 days and their external appearance did not change. The weight gains by the water absorption were slightly higher for the metal-containing resins than for the resins without metal; and the Mg-containing resin showed only slightly higher weight gains than the Ca-containing resin.

In summary, the metal-containing cured resins in the present study have high boiling water and water resistances.

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Received February 25, 1993

Accepted June 23, 1993