

Cross-Linking of Bisepoxide with Divalent Metal Salts of *p*-Aminobenzoic Acid and Diamine

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SYNOPSIS

Cross-linking of bisepoxide with divalent metal salts of *p*-aminobenzoic acid and 4,4'-diaminodiphenylmethane (4,4'-methylenedianiline) was investigated. As the bisepoxide, bisphenol A diglycidyl ether was used. Mg and Ca were used as the divalent metal. The metal salts showed catalytic activities for the cross-linking reaction and also for etherification of epoxy groups. In this case, the salt containing Ca with the lower electronegativity exhibited higher catalytic activities than that containing Mg. Hence, the cross-linking reaction was supposed to proceed via an ionic mechanism. As for the physical properties of the cured resins, compressive strength was higher in the metal-containing cured resins than in the resin without metal. Heat-distortion temperature showed a tendency to decrease with increase in the metal content. However, glass transition temperature determined by dynamic mechanical properties were not influenced by the metal content. The metal-containing cured resins exhibited low weight gain and changes in dimension and external appearance against boiling water. In addition, thermal decomposition was accelerated by the incorporated metal. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Divalent metal salts of *p*-aminobenzoic acid (ABA), i.e., ABA(M) (where M is a divalent metal such as Mg or Ca), contain an ionic bond formed between —COO^- and M^{2+} and two amino groups. Therefore, the ABA(M) salts are considered to be of interest as ionic monomers from the scientific and industrial standpoints. Hitherto, the salts have been proposed to be useful as additives^{1,2} for rubbers and sunscreen materials.³ The authors have been active in the syntheses of ionic polymers by using ABA(M). In previous studies, a series of halato-telechelic polyureas⁴ and polyurethane-ureas⁵ were synthesized from ABA(M), diamine, and diisocyanate, or ABA(M), diamine, dialkylene glycol, and diisocyanate.

On the other hand, it is well known that epoxy resins are cured with amine compounds. Among various amine curing agents, aromatic primary amines are known to impart high glass transition temperature (T_g) to cured resins. This is a charac-

teristic effect of the aromatic ring. However, there is the disadvantage of a slow curing rate in using the aromatic amines. The metal carboxylate groups of ABA(M) were anticipated to have catalytic activities for the amine cure. Therefore, it seemed of interest to investigate the effects of using ABA(M) as one component of aromatic diamines on cure properties of the amine curing systems and on properties of cured resins.

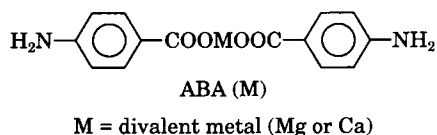
In the present study, cross-linking of bisepoxide with ABA(M) and aromatic diamine was investigated. As the bisepoxide, bisphenol A diglycidyl ether (BADG) was used. 4,4'-Diaminodiphenylmethane (4,4'-methylenedianiline, MDA) was used as the aromatic amine. MDA is commercially widely used as an aromatic curing agent. The novel metal-containing cured resins obtained were evaluated for physical and other properties.

EXPERIMENTAL

Materials

The ABA(M) salts were prepared by the same method as reported in the previous study.⁴ MDA

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and *N,N*-dimethylformamide (DMF) were of speciality grade from Wako Pure Chemical Industries Co. As the BADG, Epomik R 139 (Mitsui Petrochemical Epoxy Co.) was used. The epoxy value was 5.478 equiv/kg (calcd = 5.875 equiv/kg).

Curing Reaction

A fixed amount of ABA (M) was dissolved in a given amount of DMF and then a given amount of BADG was added to it. The solution thus obtained was heated at 100°C for 1 h and then the DMF was completely removed under a reduced pressure at 100°C. After cooling to 70°C, a given amount of MDA was added and dissolved to obtain a homogeneous curable mixture. Next, 5 g of the curable mixture was placed in an 18 × 180 mm test tube and the tube was placed in an 80°C bath. After a desired time, samples were taken for analyses of epoxy, primary amine, and tertiary amine contents. 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 80°C for 16 h and then at 150°C for 5 h in the presence of air.

Analytical Methods

When the conversion was beyond gelation, it was filed into powder and subjected to analyses. The titrations were conducted by using a Hiranuma reporting titrater (COMMIT 101).

Epoxy and primary amine contents were determined according to the method by Bell⁶ as follows: 10 mL of 0.1*N* solution of HCl in pyridine–isopropanol–H₂O (2 : 2 : 1 [v/v]) was added to a weighed sample in a flask and the flask was heated at 90°C for 25 min. After cooling, excess HCl was titrated with 0.1*N* NaOH to determine the epoxy content. Next, 2 mL of CS₂ was added to the mixture. After standing for 2 min, the titration was continued by adding 0.1 mL of 0.1*N* NaOH every 1 min to determine the primary amine content.

Tertiary amine content was determined by the

method of Kakurai and Noguchi⁷ as follows: 2 mL of acetic anhydride–glacial acetic acid (9 : 1 [v/v]) was added to a weighed sample in a flask and the flask was heated at 50°C for 2 h, sometimes with shaking. It was titrated with 0.1*N* perchloric acid–glacial acetic acid to determine the tertiary amine content.

Secondary amine content was obtained by subtracting primary and tertiary amine contents from the total amine content in the feed.

Ether group content was obtained as follows: The relationship between the amount of reacted epoxy group (E_P), the amount of produced ether group (E_T), the amount of produced secondary amine group (A_2), and the amount of produced tertiary amine group (A_3) can be expressed as

$$E_P = E_T + A_2 + 2A_3 \quad (1)$$

On the other hand, the relationship between the amount of initial epoxy group (E_{P_0}) and the amount of initial primary amine group (A_0) is given by

$$E_{P_0} = 2A_0 \quad (2)$$

Further, the percentage of reacted epoxy group [E_P (%)] can be expressed as

$$E_P (\%) = 100E_P/E_{P_0} \quad (3)$$

Introducing eqs. (1) and (2) into eq. (3), we get

$$E_P (\%) = (E_T/2A_0 + A_2/2A_0 + A_3/A_0) \times 100 \quad (4)$$

By rearranging this equation, we get

$$100E_T/2A_0 = E_P (\%) - 100A_2/2A_0 - 100A_3/A_0 \quad (5)$$

Here, $100E_T/2A_0$ can be written as $100E_T/E_{P_0}$, which means the percentage of the produced ether group [E_T (%)]. Similarly, $100A_2/2A_0$ means the percentage of the produced secondary amine group [A_2 (%)] and $100A_3/A_0$ means the percentage of the produced tertiary amine group [A_3 (%)]. Therefore, E_T (%) can be expressed by following equation:

$$E_T (\%) = [2E_P (\%) - A_2 (\%) - 2A_3 (\%)] \times \frac{1}{2} \quad (6)$$

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.

Determination of Physical and Other Properties

Heat-distortion temperature (HDT) was determined according to ASTM-D 648-82; tensile strength, according to ASTM-D 638-82; flexural strength, according to ASTM-D 790-81; compressive strength, according to ASTM-D 695-80; impact strength, according to ASTM-D 256-81 (with Izod notch); and Rockwell hardness (M scale), according to ASTM-D 785-65.

Dynamic mechanical properties were determined using a freely damped torsion pendulum (Rhesca Co.), according to ASTM-D 2236-81, at frequencies of 0.15–3.0 Hz. In this case, the test pieces of 1.0 × 7.0 × 50 mm were used for the determination as follows: After the test pieces were cooled to −150°C and kept at −150°C for 30 min, the test was carried out at a heating rate of 2°C/min under reduced pressure.

Changes in dimension, weight, and external appearance in boiling water were determined by immersing test pieces in boiling water for 2 h, and water absorption was measured vs. time in deionized water at 23°C. In this case, the test pieces of 75 × 25 × 3 mm were used after conditioning at 110°C for 2 h and then at 50°C for 24 h.

RESULTS AND DISCUSSION

Curing Reactions

The ABA(M) salts are insoluble in BADG even at high temperatures and mixtures of ABA(M) and BADG do not cure even when heated at 150°C for a long time. However, the salts are soluble in DMF and homogeneous solutions were obtained by adding BADG to ABA(M) dissolved in DMF. ABA(M) precipitated again by removing the DMF from the solution. However, the precipitation of ABA(M) did not occur when the DMF was removed after heating the solution at 100°C for 1 h. In this case, part of the amino groups in ABA(M) are considered to have reacted with the epoxy groups in BADG, forming soluble adducts of ABA(M) and BADG. Further, by adding MDA, a homogeneous curable mixture could be obtained, as described in the Experimental section. For comparison, a curable mixture from MDA and BADG was prepared in the same manner.

In this case, first, one-tenth of the amount of MDA to be added was used for preparing the MDA-BADG-DMF solution by heating the system at 100°C for 1 h; then, the remaining MDA was added, after removing the DMF completely, to obtain the curable mixture.

Figures 1–3 show the state of the curing reaction of the systems obtained like this. At the beginning of the reaction, residual epoxy and primary amine groups were ca. 80–90%, i.e., ca. 10–20% of the epoxy and primary amine groups had been consumed during heating ABA(M) and BADG in DMF, indicating the formation of the above-described adducts. In the initial stage of the reaction, consumptions of the epoxy and primary amine groups were rapid, while formation of tertiary amine was slow. However, the produced tertiary amines began to increase when the reacted primary amines increased above ca. 50%, i.e., the epoxy groups in BADG react preferentially with the primary amines; however, when the remaining primary amines decrease below ca. 50%, the reaction of the epoxy groups with secondary amines produced by the reaction of the epoxy group with the primary amine becomes significant. It should be noted that the systems containing ABA(M) showed considerably higher reaction rate and shorter gel time than that without ABA(M), indicating a catalytic activity of the metal carboxylate groups of ABA(M).

Ochi et al. studied curing reactions of bisphenol A-type epoxy resins with MDA^{8,9} and divided the curing process into the following three stages⁸: The

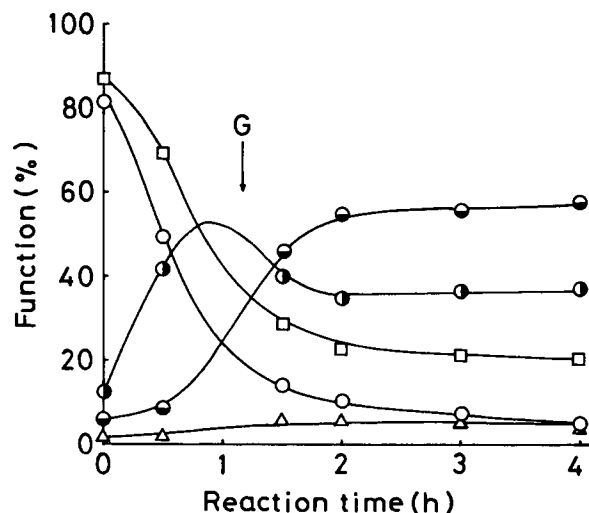


Figure 1 Curing reaction of MDA-BADG (1 : 2) system at 80°C: (□) residual epoxy group; (○) residual primary amine; (●) produced secondary amine; (●) produced tertiary amine; (△) produced ether group. G = gel point.

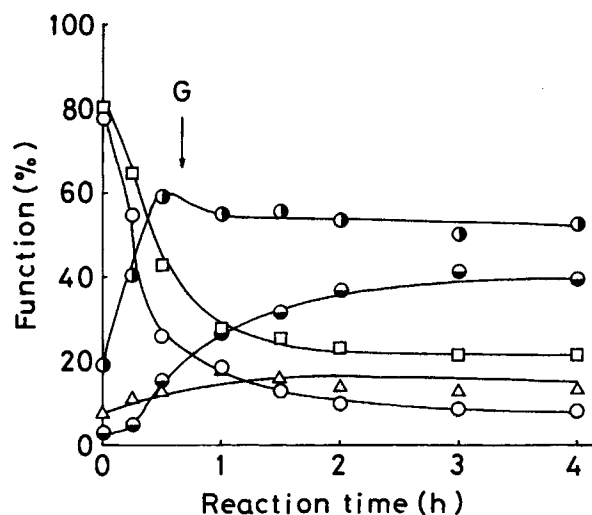


Figure 2 Curing reaction of ABA(Mg)-MDA-BADG (1 : 9 : 20) system at 80°C. Symbols are the same as in Figure 1.

first stage is a region of reacted epoxy groups below ca. 30%, where the epoxy groups react exclusively with the primary amines, resulting in chain extension. The second stage is a region of reacted epoxy groups up to ca. 50–60%, where the chain extension occurs rapidly, still leading to linear extended chains. The third stage is a region where further consumption of the epoxy groups occurs, leading to a cross-linked network structure.

Applying the above stages to the curing reaction of the metal-containing systems in the present study, the first stage is a region where formation of secondary amines is rapid, but little formation of tertiary amines is observed. The second stage is a region where the amount of the produced secondary amines increases rapidly up to a peak, though part of the secondary amines react with epoxy groups to produce tertiary amines. The third stage is a region where the amount of the secondary amines decreases and that of the tertiary amines increases above ca. 20%.

At 80°C, the curing reaction almost stopped when ca. 80% of the epoxy groups were consumed, whether the metal carboxylate group is present or not. This is attributed to the poor mobility of the reacting groups, i.e., due to vitrification as T_g rises above the cure temperature.

On the other hand, formation of ether groups was more rapid in the metal-containing systems than in the system without metal; in the former systems, the degree of the ether formation was ca. 10% at the beginning of the reaction. This indicates that the

metal carboxylate groups have a catalytic activity also for the etherification of the epoxy group.

Table I summarizes the cure properties of the systems of ABA(M)-MDA-BADG and MDA-BADG. The metal-containing systems showed considerably shorter gel times than that not containing metal, again indicating the catalytic activity of the metal carboxylate groups. In addition, the gel times of the systems containing Ca were shorter than those of the systems containing Mg. Thus, the salt containing Ca with the lower electronegativity has higher catalytic activity than that containing Mg. Hence, the curing reaction is considered to proceed via an ionic mechanism. Final conversions of epoxy groups after curing at 80°C for 16 h and then at 150°C for 5 h were above 93% for all the systems.

Figures 4 and 5 show the IR spectra of the systems of MDA-BADG (1 : 2) and of ABA(Mg)-MDA-BADG (1 : 9 : 20), respectively. In the spectra before curing, absorption bands at 3200–3400 cm^{-1} due to the amino groups and at 905 cm^{-1} characteristic of the epoxy group are noteworthy. Meanwhile, in the spectra after the curing at 80°C for 16 h and at 150°C for 5 h, the former bands have changed to a broad band characteristic of the OH group and the latter band has almost disappeared, indicating that the curing has proceeded. However, the band at ca. 1400 cm^{-1} is a little stronger in the metal-containing cured resin than in that without metal, due to the carboxylate group. In addition, the band at ca. 1650 cm^{-1} due to the carbonyl group of DMF is not found, indicating that there is no residual DMF.

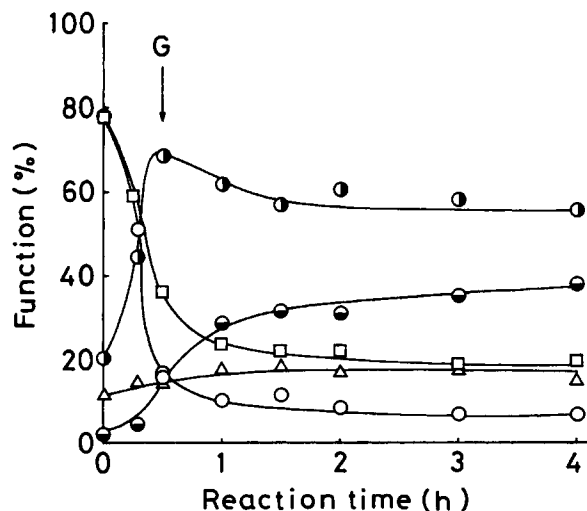


Figure 3 Curing reaction of ABA(Ca)-MDA-BADG (1 : 9 : 20) system at 80°C. Symbols are the same as in Figure 1.

Table I Cure Properties^a of ABA(M)-MDA-BADG and MDA-BADG Systems

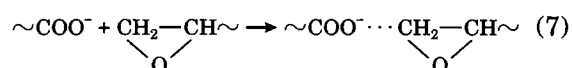
Components	Mol Ratio of Components	Metal Content (%)	Gel Time ^b (min)	Conversion ^a of Epoxy Group (%)
ABA(Mg)-MDA-BADG	1 : 19 : 40	0.13	40	97
	1 : 9 : 20	0.26	40	93
ABA(Ca)-MDA-BADG	1 : 19 : 40	0.21	33	98
	1 : 9 : 20	0.43	30	99
MDA-BADG	1 : 2	—	70	95

^a Cure condition = 80°C for 16 h and 150°C for 5 h.

^b Determined at 80°C.

It should be noted that the spectrum of the metal-containing system before the curing exhibits a small band at ca. 1690 cm⁻¹, which is not observed after the curing (Fig. 5). This band is not observed also in the spectra of the system not containing metal before and after the curing. This band is considered to be due to a carbonyl group. ABA(Mg) contains a carbonyl group, but the band due to this carbonyl group⁴ appears at ca. 1600 cm⁻¹ and not at ca. 1690 cm⁻¹. From this, the band at ca. 1690 cm⁻¹ is attributable to an intermediate formed by coordination

of the carboxylate anion dissociated from the metal carboxylate group in ABA(Mg) to the C atom of the epoxy group [eq. (7)]:



It is considered that the H atom and the N atom of the amino group add, respectively, to the O atom of the epoxy group in the intermediate and to the C atom of the epoxy group to which the carboxylate anion has coordinated, to eliminate the carboxylate

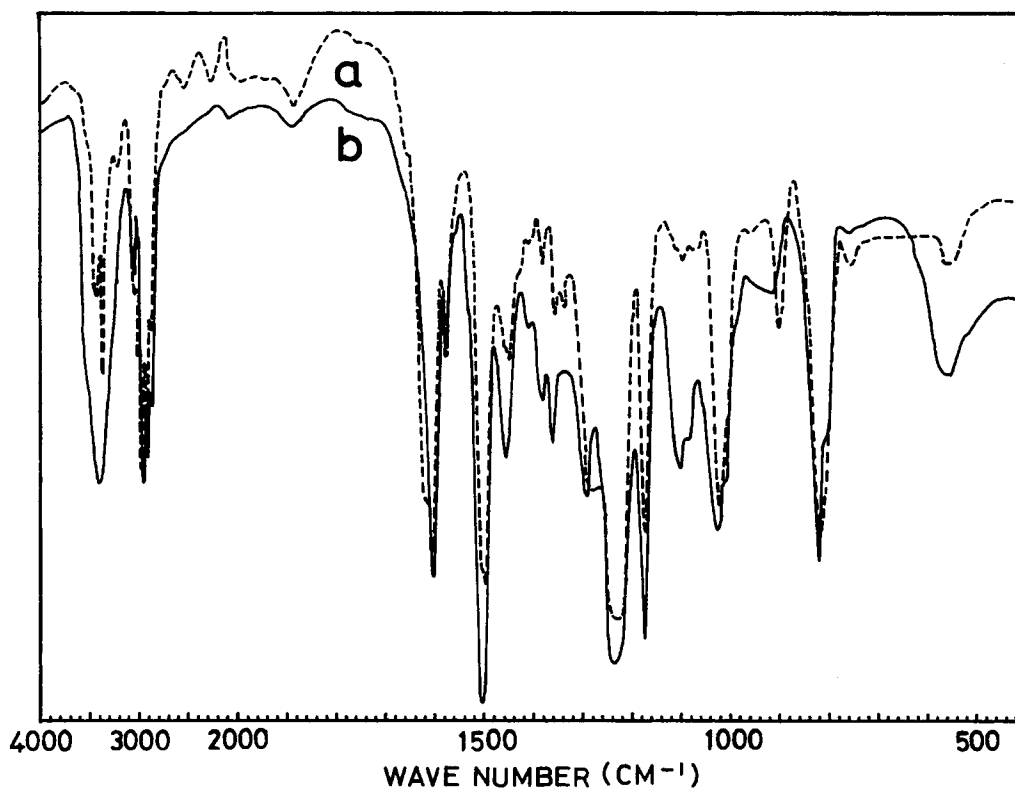


Figure 4 Infrared spectra of MDA-BADG (1 : 2) system: (a) initial curable mixture; (b) cured at 80°C for 16 h and at 150°C for 5 h.

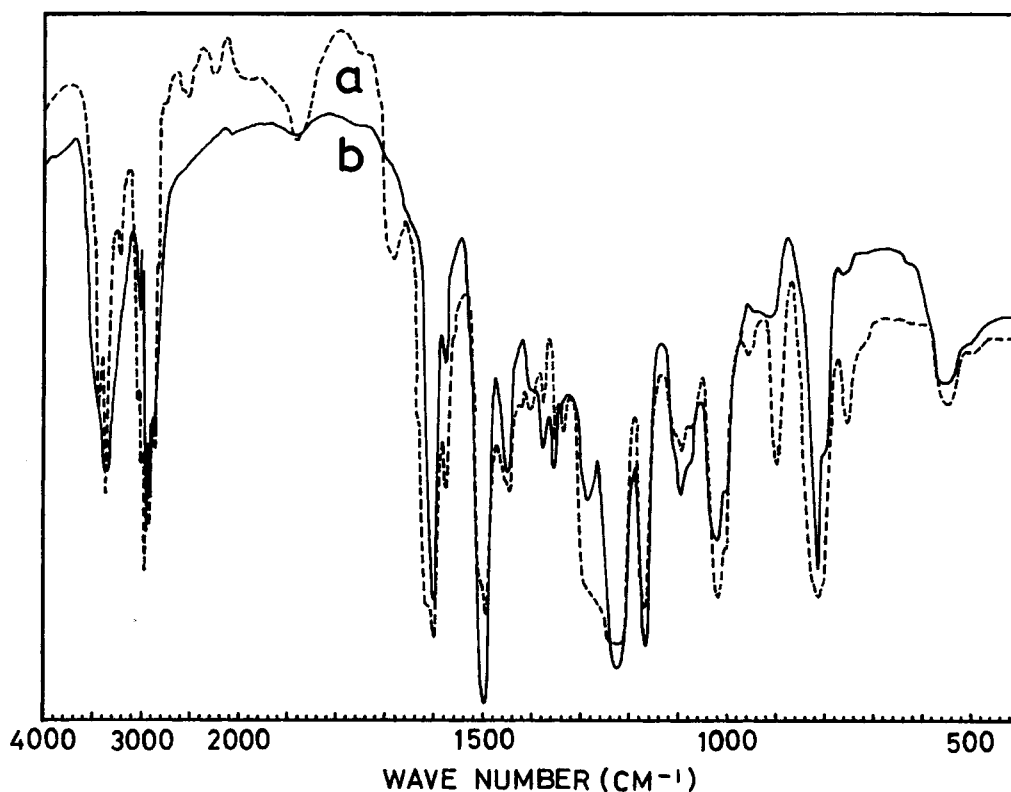
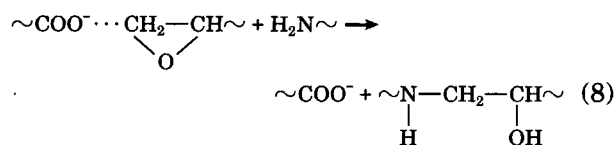


Figure 5 Infrared spectra of ABA(Mg)-MDA-BADG (1 : 9 : 20) system: (a) initial curable mixture; (b) cured at 80°C for 16 h and at 150°C for 5 h.

anion, producing the secondary amine, as shown by eq. (8):



Physical Properties of Metal-Containing Cured Resins

Table II summarizes the physical properties of the metal-containing cured resins from ABA(M), MDA,

and BADG. The final conversions of the epoxy groups of all the cured resins were above 93%. In this case, it was confirmed that the physical properties did not change with further curing. The HDT showed a tendency to decrease with increase in the metal content. This might be attributed to the fact that, with increase in the metal carboxylate groups, the degree of formation of ether groups becomes high; hence, the amount of unreacted secondary amines increases, leading to an increase in the part of linear chain structures. However, the compressive strength was higher in the metal-containing cured

Table II Physical Properties of Metal-Containing Cured Resins^a from ABA(M), MDA, and BADG

Components (Mol Ratio)	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)
ABA(Mg)-MDA-BADG (1 : 19 : 40)	153	871	1359	113	1.20	1560
ABA(Mg)-MDA-BADG (1 : 9 : 20)	145	850	1335	113	1.30	1597
ABA(Ca)-MDA-BADG (1 : 19 : 40)	151	905	1253	111	1.40	1556
ABA(Ca)-MDA-BADG (1 : 9 : 20)	132	927	1354	113	1.32	1574
MDA-BADG (1 : 2)	153	880	1304	113	1.29	1484

^a Cure condition = 80°C for 16 h and 150°C for 5 h.

resins than in the resin without metal. This is probably due to a formation of clusters of the metal carboxylate groups. However, the other physical properties were not affected by the metal content.

Dynamic Mechanical Properties of Metal-Containing Cured Resins

Figure 6 shows the dynamic mechanical properties of the metal-containing cured resins and the resin not containing metal. In addition, the data of the cured resin from aniline, MDA, and BADG are shown. All the resins exhibited relaxations at ca. 150 and -50°C . These will be denoted by α and β relaxations, respectively. Further, the metal-containing resins exhibited a relaxation at ca. 60°C . This will be denoted by α' relaxation. Since the measurements were conducted at small frequencies below 3.0 Hz, a temperature at which G suddenly decreases or $\tan \delta$ shows the major maximum is considered to be T_g .

The β relaxation shifted to slightly lower temperature and its area was smaller for the metal-containing resins than for that without metal. Ochi et al. studied dynamic mechanical properties of the amine-cured epoxy resins; they reported that the relaxation around -50°C is attributable to the mobile structure parts such as the hydroxy ether structure and the local mode of the bisphenol A skeleton and that the relaxation shifts to higher temperature with increase in the hydroxy ether structure.¹⁰ In this type of curing, the hydroxy ether structure is formed by the primary or secondary amine-epoxy reaction and the amount of the formation decreases as the degree of etherification increases. As shown in Figures 1-3, for the metal-containing cured resins, ca. 15% of the epoxy groups etherified, resulting in the lower degree of formation of the hydroxy ether structure. Therefore, the above-observed tendency for the β relaxation in Figure 6 is considered to support the results of Ochi et al.¹⁰

On the other hand, the α' relaxation is charac-

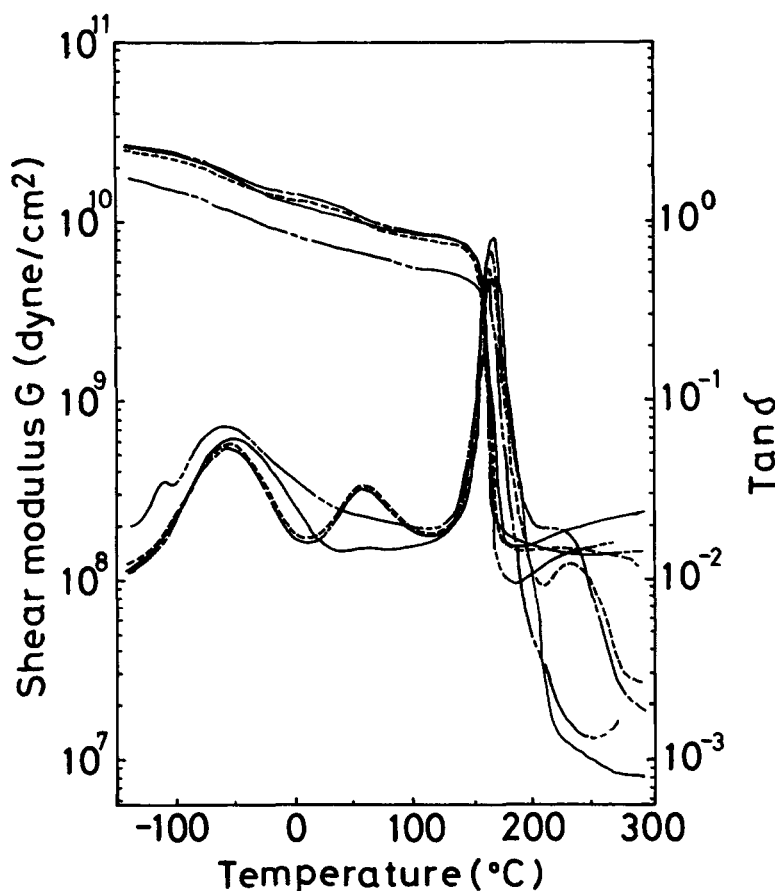


Figure 6 Dynamic mechanical properties of cured resins: (—) MDA-BADG (1 : 2); (-----) ABA(Mg)-MDA-BADG (1 : 9 : 20); (- - -) ABA(Ca)-MDA-BADG (1 : 9 : 20); (— — —) aniline-MDA-BADG (2 : 9 : 20).

Table III Dynamic Mechanical Properties of Metal-Containing Cured Resins

Components (Mol Ratio)	α -Transition Temperature (°C)	β -Transition	
		Temperature (°C)	Tan δ_{\max}
ABA(Mg)-MDA-BADG (1 : 19 : 40)	162	-60	0.055
ABA(Mg)-MDA-BADG (1 : 9 : 20)	162	-55	0.057
ABA(Ca)-MDA-BADG (1 : 19 : 40)	162	-59	0.056
ABA(Ca)-MDA-BADG (1 : 9 : 20)	163	-63	0.056
MDA-BADG (1 : 2)	165	-52	0.062

teristic of the metal-containing cured resins. If the metal carboxylate groups dissociate around 60°C, the dissociated carboxylate groups would become mobile as the side chain, possibly leading to an appearance of the relaxation. The cured resin based on aniline has pendant phenyl groups almost similar to those bearing the dissociated carboxylate groups. However, this resin did not exhibit the relaxation around 60°C (Fig. 6). Therefore, the α' relaxation is not considered to be attributable to the dissociated carboxylate groups.

Ochi et al. reported that the MDA-BADG system that was in the initial curing stage, having linear chain structure, exhibited a T_g around 80°C.⁸ The metal-containing cured resins contained the larger amount of unreacted secondary amines, due to the higher degree of the etherification. The secondary amine part is a component of linear chain structure composed mainly of diphenylmethane. Therefore, it would be appropriate to consider that the linear structure causes the α' relaxation.

As shown in Table III, T_g did not decrease with increase in the metal content, contrary to HDT. This is attributed to the difference of the determination methods. There are many kinds of chemical structure in the cured resin. The HDT is a temperature at which the sample is deformed as a whole by a

fixed load. Therefore, the HDT is affected by the proportion of each chemical structure in the cured resin. Meanwhile, the dynamic mechanical properties reflect a temperature of relaxation of each structure part in the sample, e.g., T_g is a temperature of relaxation of the main cross-linked structure part. Since all samples in this study have the same main cross-linked structure part, T_g did not change with increase in the metal content and was not affected by the other chemical structures.

For $T > T_g$, G increases when there are no ions, whereas G decreases for the specimens with ions. The reason for this is not clear.

The cured resin of aniline-MDA-BADG (2 : 9 : 20) exhibited a relaxation at ca. -110°C, which is not observed for the other cured resins. The relaxation is considered to be attributable to the linear $-\text{CH}_2-\text{N}(\text{C}_6\text{H}_5)-\text{CH}_2-$ linkage derived from the reaction of aniline with two epoxy groups.

Boiling Water and Water Resistances of Metal-Containing Cured Resins

Table IV shows the boiling water resistance of the metal-containing cured resins and the resin without metal. In this study, the boiling water resistance was

Table IV Boiling Water Resistance of Metal-Containing Cured Resins

Components (Mol Ratio)	Change in Length (%)	Change in Thickness (%)	Change in Weight (%)	External Appearance
ABA(Mg)-MDA-BADG (1 : 19 : 40)	0.03	0.50	0.65	Unaffected
ABA(Mg)-MDA-BADG (1 : 9 : 20)	0.05	0.47	0.47	Unaffected
ABA(Ca)-MDA-BADG (1 : 19 : 40)	0.16	0.43	0.66	Unaffected
ABA(Ca)-MDA-BADG (1 : 9 : 20)	0.13	0.37	0.59	Unaffected
MDA-BADG (1 : 2)	0.11	0.18	0.40	Unaffected

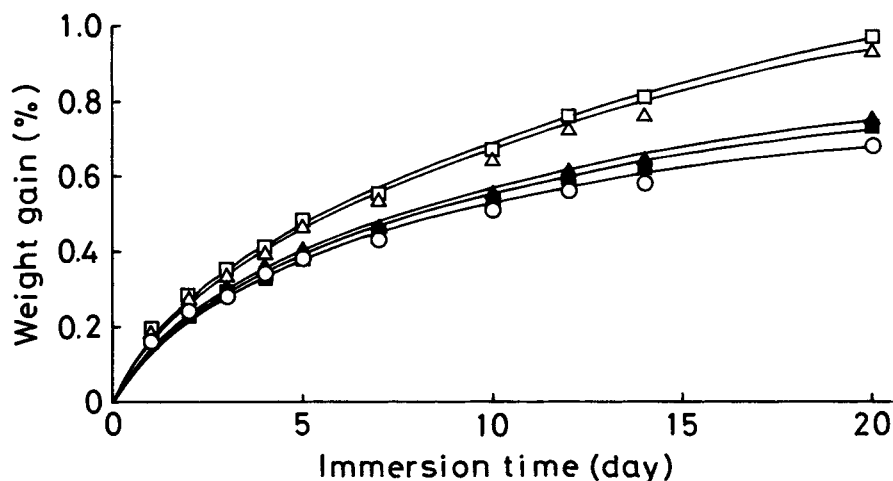


Figure 7 Water absorption of cured resins at 23°C: (○) MDA-BADG (1 : 2); (△) ABA(Mg)-MDA-BADG (1 : 19 : 40); (▲) ABA(Mg)-MDA-BADG (1 : 9 : 20); (□) ABA(Ca)-MDA-BADG (1 : 19 : 40); (■) ABA(Ca)-MDA-BADG (1 : 9 : 20).

evaluated by weight gain, changes in dimension, and external appearance. They exhibited high boiling water resistance. Similarly, as shown in Figure 7, they showed small weight gains of below 1% after the water immersion at 23°C for 20 days and their external appearance was unaffected. The weight gains by the boiling water and the water absorption were slightly higher for the metal-containing resins

than for the resin without metal. However, as is apparent on comparing the data of the metal-containing resins, the weight gains of those with the higher metal content were slightly lower. This is attributable to the fact that, with increase in the metal content, the amount of produced hydrophilic hydroxyl groups decreases because of the higher degree of the etherification.

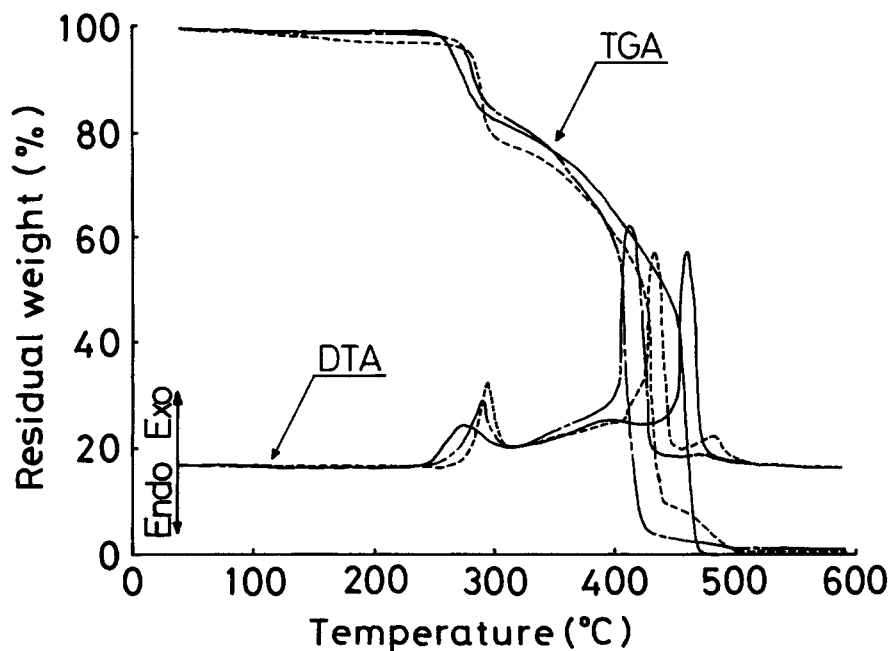


Figure 8 TGA and DTA curves of cured resins: (—) MDA-BADG (1 : 2); (-----) ABA(Mg)-MDA-BADG (1 : 9 : 20); (- - -) ABA(Ca)-MDA-BADG (1 : 9 : 20).

Thermal Properties of Metal-Containing Cured Resins

Figure 8 shows the TGA and DTA curves of the metal-containing cured resins and the resin not containing metal in air. All the resins exhibited thermal decomposition that can be divided into the following three stages: The first stage is a region of ca. 260–290°C, where abrupt weight loss of ca. 20% occurs with an exotherm. The second is a region of decomposition with a small exotherm from ca. 300 to ca. 400°C. The third is a region of ca. 400–460°C, where, again, rapid decomposition occurs with a large exotherm. The metal-containing resins began to decompose at slightly higher temperature than did the resin without metal. However, the rate of decomposition was higher for the former than for the latter. Thus, the incorporated metal accelerated the decomposition.

Keenan and Smith¹¹ studied the thermal decomposition of the MDA–BADG cured resin; they inferred that initially dehydration occurs by the H atom adjacent to the OH group produced by the amine–epoxy reaction, to form a double bond, and then cleavages of C—N, C—C, and C—O bonds occur. The same may be said of the thermal decomposition of the metal-containing cured resins in the present study.

Furthermore, the plateau observed above ca. 500°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.

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