

Crosslinking by Etherification of Bisepoxide with Adducts of Divalent Metal Salts of *p*-Aminobenzoic Acid and Anhydride

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SYNOPSIS

Crosslinking by etherification of a large excess of bisepoxide with adducts of divalent metal salts of *p*-aminobenzoic acid and dicarboxylic acid anhydride was investigated. As the divalent metals, Mg and Ca were selected and hexahydrophthalic anhydride was the anhydride used. As the bisepoxide, bisphenol A diglycidyl ether was used. In the crosslinking reactions, the metal carboxylate groups showed catalytic action and the Ca carboxylate group showed higher catalytic activity than did the Mg carboxylate group. Therefore, the crosslinking reactions were supposed to proceed via an ionic mechanism in which the carboxylate anion is concerned. As for the physical and other properties of the metal-containing cured resins, the T_g determined by dynamic mechanical properties increased with increase in the metal content. Also, the heat-distortion temperature increased with increase in the metal content. Interestingly, the cured resins showed very high impact strength and the strength increased markedly with decrease in the T_g . Scanning electron micrographs for fracture surfaces of the cured resins with high impact strength showed uneven patterns, which suggests microphase separation. From TGA and DTA, it was suggested that the metal carboxylate groups accelerated thermal decomposition. In addition, the cured resins exhibited high boiling water and water resistances. © 1996 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), are of interest as ionic monomers for the preparation of ionic polymers into which metal is firmly incorporated¹⁻⁵:



ABA(*M*)

M = divalent metal (Mg or Ca)

In a previous study,⁵ crosslinking by etherification of a large excess of bisepoxide with ABA(*M*) was

investigated. As the bisepoxide, bisphenol A diglycidyl ether (BADG) was used. This route was an extension of a study³ on the crosslinking of BADG with ABA(*M*) and aromatic diamine. It was found that the metal carboxylate groups in ABA(*M*) catalyzed the reaction of amine and epoxy groups. In this case, the salt-containing Ca with lower electronegativity showed higher catalytic activities than that containing Mg. Hence, the crosslinking reaction was supposed to proceed via an ionic mechanism. Further, the metal carboxylate groups in ABA(*M*) were also found to have catalytic activity for etherification of an epoxy group as a side reaction.

On the other hand, crosslinking of BADG with ABA(*M*) and dicarboxylic acid anhydride was also investigated.⁴ As the anhydride, hexahydrophthalic anhydride (HPAn) was used. In the initial stage of the curing reactions, adducts of ABA(*M*) and HPAn are formed first. The carboxyl groups in the adducts are starting points for chain extension, i.e., to the carboxyl group, the epoxy group adducts to form a

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new hydroxyl group. Next, the reaction of the hydroxyl group so-produced with the acid anhydride group again occurs. Thus, these addition reactions are considered to repeat alternately, so that ample opportunity for further growth of a three-dimensional network structure is provided. In this case, the Mg carboxylate group exhibited higher catalytic activities than did the Ca carboxylate group. Hence, the crosslinking reaction was supposed to proceed via a complex mechanism. It seemed of interest to prepare novel metal-containing cured resins by etherification of epoxy groups of BADG by the catalytic action of the metal carboxylate groups in the adducts of ABA(*M*) and HPAn.

Therefore, in the present study, crosslinking of curable mixtures prepared from ABA(*M*), HPAn, and a large excess of BADG was investigated by taking advantage of the catalytic activity of the ABA(*M*)-HPAn adducts for the etherification of epoxy groups. 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 previously.¹ HPAn, 4,4'-methylenedianiline (MDA), and *N,N*-dimethylformamide (DMF) were of speciality grade and were used as received. As the BADG, EPOMIK R139 (Mitsui Petrochemical Epoxy Co.) was used. The epoxy value was 5.478 equiv/kg (calcd = 5.875 equiv/kg).

Curing Reactions

A typical curable mixture [ABA(Mg) : HPAn : BADG = 0.5 : 1 : 40] was prepared as follows: To the solution of 0.30 g (1 mmol) of ABA(Mg) and 0.31 g (2 mmol) of HPAn in 20 g of DMF was added 28.68 g (80 mmol) of BADG and the mixture was heated at 130°C for 1 h. Then, the DMF was completely removed under a reduced pressure at 100°C to obtain a homogeneous curable mixture. Next, in an 18 × 180 mm test tube was placed 5 g of the curable mixture and the test tube was placed in a 150°C bath. After a desired time, samples were taken for analysis of epoxy values. Gel time was determined by measuring the time at which the mixture would not flow in the test tube.

Cured resin moldings for determining physical and other properties were prepared as follows: A de-

sired 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 fixed time and at 180°C for 8 h.

Analytical Methods

Analytical methods were the same as those reported in a previous article.⁴ Determinations of physical and other properties were conducted by the same methods as reported previously.³ The observations of fracture surfaces of cured resins were carried out in a Nihon Denshi scanning micrograph JSM-T100.

RESULTS AND DISCUSSION

Curing Reactions

The ABA(*M*) salts are insoluble in BADG even at high temperatures. However, homogeneous curable mixtures could be obtained when a large excess of BADG was added to the solution of ABA(*M*) and HPAn in DMF and then the DMF was removed after the mixture was heated at 130°C for 1 h. In this case, amino groups in ABA(*M*) are considered to have reacted with the anhydride group in HPAn, forming soluble adducts of ABA(*M*) and HPAn. It is well known that the amino group-anhydride group reaction proceeds much more rapidly than do the reactions of the epoxy group with the anhydride group and with the amino group. Hence, it is considered that the amino groups in ABA(*M*) react preferentially with the acid anhydride group in HPAn. The adducts formed contain amide and carboxyl groups in addition to the metal carboxylate group. Furthermore, the epoxy group-carboxyl group reaction is well known to proceed much more rapidly than the etherification reaction of epoxy groups. Hence, the epoxy groups in BADG are considered to react dominantly with the carboxyl groups in the adducts in the initial stage of the curing reaction.

Figure 1 shows the results of the curing reactions at 150°C of the systems obtained like this. The data for the system not containing ABA(*M*) are also shown for comparison. The epoxy value of the ABA(*M*)-containing systems decreased faster than that of the system not containing metal, indicating that the metal carboxylate groups catalyzed the etherification of the epoxy groups. Also, the salt-containing Ca with lower electronegativity showed higher catalytic activity than did the Mg salt. Therefore, the crosslinking reactions by etherification of BADG with the adduct of ABA(*M*) and

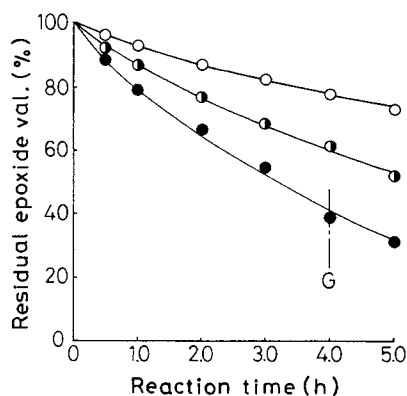


Figure 1 Curing reactions of systems of (O) MDA-HPAn-BADG (0.5 : 1 : 40), (●) ABA(Mg)-HPAn-BADG (0.5 : 1 : 40), and (●) ABA(Ca)-HPAn-BADG (0.5 : 1 : 40) at 150°C. *G* = gel point.

HPAn are supposed to proceed via an ionic mechanism in which the carboxylate anion is concerned. Meanwhile, about 25% of the epoxy groups in the MDA-HPAn-BADG (0.5 : 1 : 40) system disappeared after 5 h at 150°C. This result suggests that the amide linkage which is formed by the reaction of MDA with HPAn has a slight catalytic activity for the etherification of epoxy groups. In a previous article,⁵ it was reported that the tertiary amino group produced by the reaction of an amino group in ABA(*M*) with two epoxy groups showed a slight catalytic activity for the etherification of epoxy groups.

Table I shows the cure properties of various systems. The gelation time of these systems at 150°C decreased with increase in the metal content in the system. Further, at the same mol ratios of the components, the mixtures containing Ca exhibited a

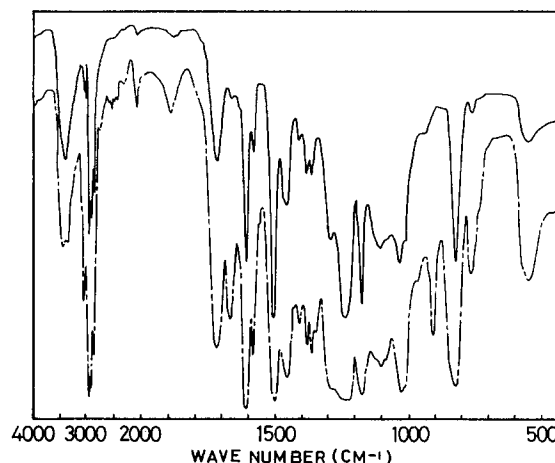


Figure 2 Infrared spectra of ABA(Mg)-HPAn-BADG (1 : 2 : 20) system: (---) initial curable mixture; (—) cured at 130°C for 24 h and at 180°C for 8 h.

shorter gelation time than those containing Mg, again indicating the higher catalytic activity of the Ca carboxylate groups. The final conversions of epoxy groups of all cured resins were above 97%.

Figure 2 shows, as a typical example, the IR spectra of the ABA(Mg)-HPAn-BADG (1 : 2 : 20) system. The absorption band at ca. 900 cm^{-1} (due to the epoxy group) observed in the spectrum before curing has almost disappeared in the spectrum after curing, and the band at ca. 1100 cm^{-1} due to the ether linkage has increased, showing that the cross-linking reaction by etherification of the epoxy groups has proceeded. Further, the bands at 1660 cm^{-1} (C=O of the amide of the amic acid) and 1710 and 3000–2700 cm^{-1} (—COOH of the amic acid) are noteworthy in the spectrum before the curing. These bands decreased in the spectrum after the curing,

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

Components	Mol Ratio of Components	Metal Content (%)	Gel Time at 150°C (min)	Final Conversion of Epoxide (%)
MDA-HPAn-BADG	0.5 : 1 : 40	—	> 500	98 ^a
	1 : 2 : 40	—	365	97 ^b
	2 : 4 : 40	—	95	97 ^c
ABA(Mg)-HPAn-BADG	0.5 : 1 : 40	0.08	> 500	97 ^b
	1 : 2 : 40	0.16	250	98 ^c
	2 : 4 : 40	0.31	40	97 ^c
ABA(Ca)-HPAn-BADG	0.5 : 1 : 40	0.14	240	99 ^b
	1 : 2 : 40	0.27	150	99 ^c

^a Cure condition = 130°C, 72 h, and 180°C, 8 h.

^b Cure condition = 130°C, 48 h, and 180°C, 8 h.

^c Cure condition = 130°C, 24 h, and 180°C, 8 h.

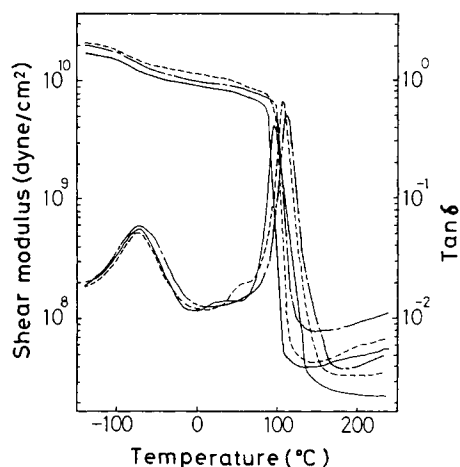


Figure 3 Dynamic mechanical properties of cured resins: (—) MDA-HPAn-BADG (1 : 2 : 40); (-----) ABA(Mg)-HPAn-BADG (1 : 2 : 40); (- - -) ABA(Ca)-HPAn-BADG (1 : 2 : 40).

ations at ca. 100–120°C and –70°C. These will be denoted by α and β relaxations, respectively. Since 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 glass transition temperature (T_g). Further, plateaus observed for G above T_g show that these cured resins have rubbery regions.

Since the G suddenly decreased and the $\tan \delta$ showed a sharp peak at the α relaxation, the α relaxation is considered to correspond to T_g . Table II summarizes the temperatures of α - and β -transitions, and $\tan \delta_{max}$ of all the cured resins are examined. While the T_g of the MDA-based cured resins was not affected by the content of MDA, that of the ABA(M)-based cured resins increased with increase in the ABA(M) content. Thus, the effect of intro-

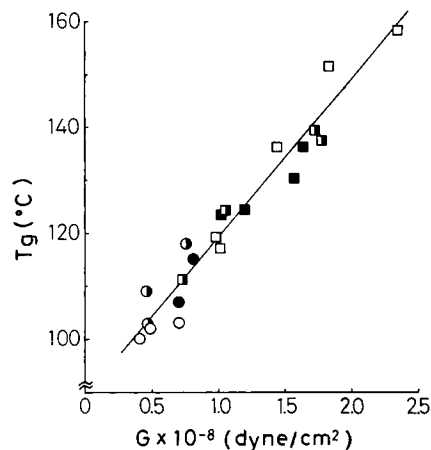


Figure 4 Relationship between shear modulus (G) at $T_g + 40^\circ\text{C}$ and T_g for cured resins: (○) MDA-HPAn-BADG systems; (●) ABA(Mg)-HPAn-BADG systems; (●) ABA(Ca)-HPAn-BADG systems; (□) MDA-BADG systems; (■) ABA(Mg)-BADG systems; (■) ABA(Ca)-BADG systems.

ducing metal appears clearly. This might be attributed to a possible aggregation of the metal carboxylate groups.

Murayama and Bell⁷ studied the dynamic mechanical properties of epoxy resins cured with an excess of MDA; they found that the G at a region above T_g decreased with increase in the molecular weight between crosslinking points (M_c), and the following relationship was presented:

$$G = dRT/M_c \tag{12}$$

Here, d is the density of cured resin and R and T are the gas constant and the measurement temperature, respectively, i.e., eq. (12) shows that the crosslinking density of the cured resin

Table II Dynamic Mechanical Properties of Cured Resins

Components	Mol Ratio of Components	α -Transition Temp (°C)	β -Transition	
			Temp (°C)	Tan δ_{max}
MDA-HPAn-BADG	0.5 : 1 : 40	103	-69	0.058
	1 : 2 : 40	100	-71	0.054
	2 : 4 : 40	102	-78	0.045
ABA(Mg)-HPAn-BADG	0.5 : 1 : 40	103	-72	0.057
	1 : 2 : 40	109	-73	0.052
	2 : 4 : 40	118	-76	0.054
ABA(Ca)-HPAn-BADG	0.5 : 1 : 40	107	-75	0.048
	1 : 2 : 40	115	-72	0.058

Table III Physical Properties of Cured Resins

Components	Mol 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)
MDA-HPAn-BADG	0.5 : 1 : 40	91	760	1240	94	6.5	1390
	1 : 2 : 40	88	780	1300	98	6.7	1420
	2 : 4 : 40	88	770	1240	105	6.1	1540
ABA(Mg)-HPAn-BADG	0.5 : 1 : 40	91	720	1270	98	6.3	1480
	1 : 2 : 40	94	830	1360	106	6.1	1390
	2 : 4 : 40	109	—	1360	109	4.9	1530
ABA(Ca)-HPAn-BADG	0.5 : 1 : 40	95	680	1320	103	5.8	1520
	1 : 2 : 40	104	690	1320	103	4.8	1430

is proportional to the G at a temperature (T) above T_g .

Figure 4 shows the relationship between G at $T_g + 40^\circ\text{C}$ and T_g for the cured resins. Also, the data for the ABA(M)-BADG and the MDA-BADG resins⁵ which were cured by the etherification of epoxy groups are shown for comparison. The data for the ABA(M)-HPAn-BADG- and the MDA-HPAn-BADG-cured resins and those for the ABA(M)-BADG- and the MDA-BADG-cured resins fall on essentially a straight line, indicating that the T_g for these cured resins are nearly proportional to the G of the resins at the region above the T_g . It follows from this that the T_g of the cured resins which have formed a network structure by etherification of epoxy groups of BADG increases with decrease in the molecular weight between crosslinking points, i.e., with increase in the crosslinking density. Further, Figure 4 shows that, as a whole, the G and the T_g of the ABA(M)-BADG- and the MDA-BADG-cured resins are higher than those of the ABA(M)-HPAn-BADG- and the MDA-HPAn-BADG-cured resins. This suggests that, in general, the former cured resins have higher crosslinking densities than those of the latter. This is also supposed by comparing the idealized main structure part⁵ of the former cured resins with that of the latter cured resins.

Table IV Impact Strength of Cured Resins from MDA-HPAn-BADG(1 : 2 : 40) System

Catalyst (Wt %)	Impact Strength (kg cm/cm)	T_g Determined by DMA (°C)
None	6.7	100
DMBA (2.0)	2.9	121
2-EIz (0.8)	1.4	148

On the other hand, the β -relaxations of the cured resins showed a broad peak at ca. -70 to -78°C . The β -relaxations are inferred to be attributable to the local mode of the bisphenol A skeleton⁸ and their neighboring mobile structure parts such as the hydroxy ether structure.^{9,10}

Physical Properties

Table III shows the physical properties of the cured resins. When MDA was used as an aromatic amine, heat-distortion temperatures (HDT) were almost constant (ca. 90°C) regardless of the mol ratio of MDA in the feed. However, the HDT of the ABA(M)-based cured resins increased with increase in the mol ratio of ABA(M) in the feed. Thus, also for HDT, the effect of introducing metal appears,

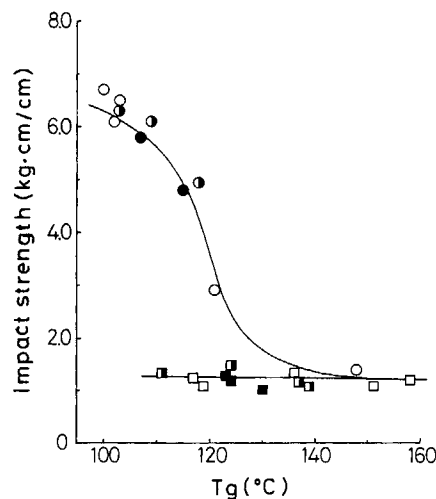


Figure 5 Relationship between T_g and impact strength of cured resins: (○) MDA-HPAn-BADG systems; (●) ABA(Mg)-HPAn-BADG systems; (●) ABA(Ca)-HPAn-BADG systems; (□) MDA-BADG systems; (■) ABA(Mg)-BADG systems; (■) ABA(Ca)-BADG systems.

probably due to a possible aggregation of the metal carboxylate groups. Further, there is a good correlation between the HDT and the T_g of these cured resins, and the HDT showed 9–15°C lower values than the T_g . This suggests that these cured resins have a uniform crosslinking structure, as described in previous articles.^{4,5}

The HDT is a temperature at which the sample is deformed as a whole by a fixed load. Hence, the HDT would depend on a 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, e.g., T_g is a temperature of relaxation of the main crosslinked structure part. 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 a uniform crosslinked structure and do not contain a measurable amount of the linear chain structure part.

The impact strengths of the cured resins in this article were above ca. 5 kg cm/cm. It is noteworthy that these values are very high for the cured epoxy

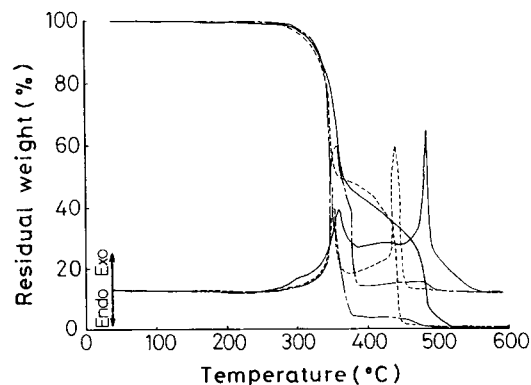


Figure 7 TGA and DTA curves of cured resins: (—) MDA-HPAn-BADG (1 : 2 : 40); (-----) ABA(Mg)-HPAn-BADG (1 : 2 : 40); (- - -) ABA(Ca)-HPAn-BADG (1 : 2 : 40).

resins. Table IV shows the impact strengths and the T_g of the MDA-HPAn-BADG (1 : 2 : 40) resins which were cured by various catalysts. It is apparent from Tables II–IV that the MDA-HPAn-BADG resins cured without a catalyst and the ABA(M)-HPAn-BADG-cured resins show lower T_g and much

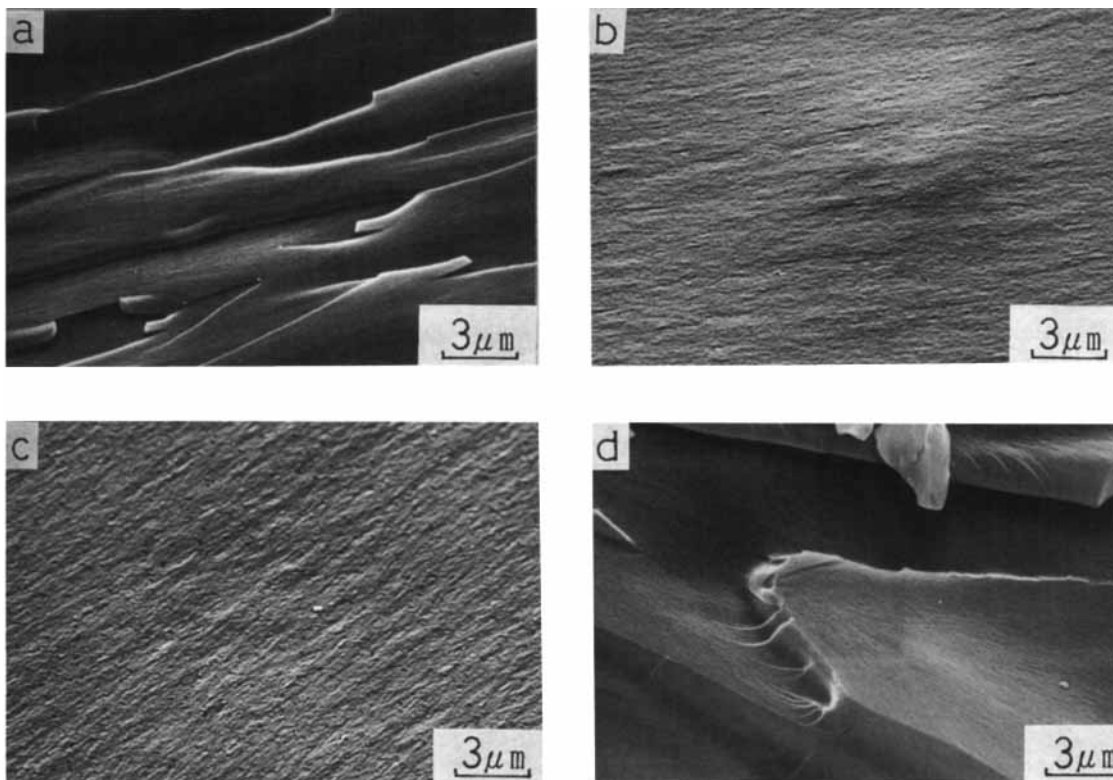


Figure 6 Scanning electron micrographs (SEM) for fracture surfaces of cured resins: (a) MDA-HPAn-BADG (1 : 2 : 40) with 2-EIz as catalyst; (b) MDA-HPAn-BADG (1 : 2 : 40) without catalyst; (c) ABA(Mg)-HPAn-BADG (1 : 2 : 40); (d) ABA(Ca)-HPAn-BADG (1 : 2 : 40).

higher impact strength than do the MDA-HPAn-BADG resins cured by using DMBA and 2-ethylimidazole (2-EIz). Also, the ABA(*M*)-BADG resins⁵ cured by the etherification of epoxy groups exhibited higher T_g and much lower impact strength than did the cured resins in the present study. Further, the impact strengths of the ABA(*M*)-HPAn-BADG-cured resins⁴ obtained by crosslinking of BADG with ABA(*M*) and HPAn were much lower than those of the cured resins in the present study, although the former contains much larger amounts of amide linkages than does the latter.

Figure 5 shows the relationship between the T_g and the impact strength for the ABA(*M*)-HPAn-BADG- and the MDA-HPAn-BADG-cured resins, together with that for the ABA(*M*)-BADG- and the MDA-BADG-cured resins in the previous study.⁵ The data in Table IV are also included. It is generally said that the impact strength of cured resin increases with decrease in the crosslinking density of the cured resin. For the ABA(*M*)-BADG- and the MDA-BADG-cured resins, the impact strength did not change with increase in T_g , being low, around ca. 1.3 kg cm/cm. Meanwhile, for the ABA(*M*)-HPAn-BADG- and the MDA-HPAn-BADG-cured resins, the impact strength increased markedly as the T_g decreased. Such a remarkable increase in the impact strength might be due not only to the decrease in the crosslinking density, but also to some interaction between molecular chains, i.e., the hydroxyl groups generated by reactions (8) and (10) and the amide linkages are supposed to form hydrogen bonding, resulting in an interaction between molecular chains, but in a decrease in the crosslinking density of cured resin. This would lead to some degree of contribution to the increase in the impact strength.

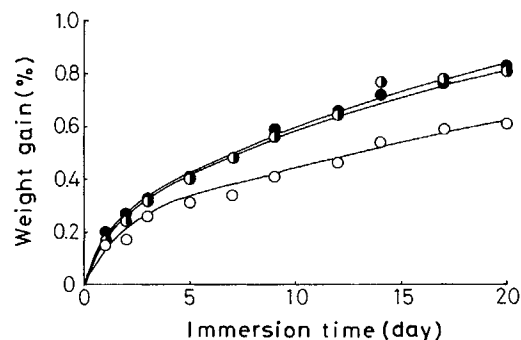


Figure 8 Effect of water on weight gain of cured resins at 23°C: (○) MDA-HPAn-BADG (1 : 2 : 40); (◐) ABA(Mg)-HPAn-BADG (1 : 2 : 40); (●) ABA(Ca)-HPAn-BADG (1 : 2 : 40).

SEM for Fracture Surfaces

Figure 6 shows scanning electron micrographs (SEM) of the fracture surfaces of the cured resins of ABA(*M*)-HPAn-BADG (1 : 2 : 40) and MDA-HPAn-BADG (1 : 2 : 40). Small uneven patterns with a separation distance below 200 nm were observed for the cured resins which have very high or slightly lower impact strength (Table III), except for the MDA-based one with 2-EIz, which has the lowest impact strength (Table IV). It is suggested that in these cured resins which show the small uneven patterns, microphase separations have occurred, although these cured resins were transparent.

Thermal Properties

Figure 7 shows the TGA and DTA curves of typical cured resins. The cured resin of MDA-HPAn-BADG (1 : 2 : 40) exhibited thermal decomposition

Table V Boiling Water Resistance of Cured Resins

Components	Mol Ratio of Components	Change in Length (%)	Change in Thickness (%)	Change in Weight (%)	External Appearance ^a
MDA-HPAn-BADG	0.5 : 1 : 40	0.28	0.14	0.86	UA
	1 : 2 : 40	0.33	0.12	0.75	UA
	2 : 4 : 40	0.34	0.45	1.05	UA
ABA(Mg)-HPAn-BADG	0.5 : 1 : 40	0.31	0.21	0.91	UA
	1 : 2 : 40	0.29	0.19	0.97	UA
	2 : 4 : 40	0.17	0.84	1.14	UA
ABA(Ca)-HPAn-BADG	0.5 : 1 : 40	0.32	0.09	0.85	UA
	1 : 2 : 40	0.14	0.45	0.84	UA

^a UA = unaffected.

which can be divided into the following four stages: The first stage is a region of ca. 300–350°C, where an abrupt weight loss of ca. 50% occurs with a large exotherm. The second is a region from ca. 350 to 470°C where gradual weight loss occurs with a moderate exotherm. The third is a region of ca. 480°C, where, again, an abrupt weight loss of ca. 20% occurs with a large exotherm. The fourth is a region above ca. 490°C, where a slow weight loss of ca. 10% occurs with a small exotherm.

On the other hand, the Ca-containing cured resin showed thermal decomposition which can be divided into the following two stages: The first stage is a region of ca. 300–380°C, where an abrupt weight loss of ca. 95% occurs with a large exotherm. The second is a region above ca. 380°C, where slow weight loss occurs with a small exotherm.

The Mg-containing cured resin exhibited thermal decomposition which can be divided into the following four stages: The first stage is a region of ca. 300–350°C, where an abrupt weight loss of ca. 50% occurs with a large exotherm. The second is a region of ca. 350–440°C, where a gradual weight loss occurs with a small exotherm. The third is a region of ca. 450°C, where, again, an abrupt weight loss of ca. 30% occurs with a large exotherm. The fourth is a region above ca. 460°C, where a slow weight loss occurs.

The first and the later decompositions of the metal-containing cured resins occur at a lower temperature than those of the MDA-based cured resin without metal. Further, above ca. 350°C, the decomposition of the Ca-containing cured resin proceeded more rapidly than that of the Mg-containing cured resin. It is suggested that the metal carboxylate groups act as a catalyst for the thermal decomposition, and the decomposition proceeds via an ionic mechanism. Furthermore, the plateau observed above ca. 500°C in the TGA curves of the metal-containing cured resins corresponds to the formation of MgO for the Mg salt and CaCO₃ for the Ca salt.

Boiling Water and Water Resistances

Table V shows the boiling water resistance of the cured resins. The boiling water resistance of the

cured resins was evaluated by a change in dimension, weight gain, and external appearance after immersion in boiling water for 2 h. The weight gains of these cured resins were around 1%, and the metal-containing cured resins exhibited only slightly higher weight gains than did the resins without metal. Further, they showed a small change in dimension and did not show any change in external appearance.

Figure 8 shows the water absorption of the cured resins at 23°C. The weight gain was slightly higher for the metal-containing cured resins than for the resins without metal. However, all the resins showed small weight gains of below 1% after water immersion at 23°C for 20 days. In summary, the metal-containing cured resins in the present study have high boiling water and water resistances.

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