

Synthesis of Metal-Containing Cured Resins from Divalent Metal Salts of Mono(hydroxyethyl) Phthalate, Anhydrides, and Bisepoxides

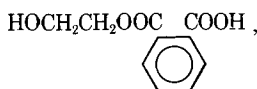
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Synopsis

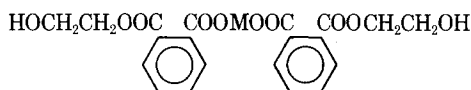
Synthesis of novel metal-containing cured resins based on divalent metal salts of mono(hydroxyethyl) phthalate were investigated by the metal salt-anhydride-bisepoxide reactions. As the anhydrides, maleic anhydride (MA) and hexahydrophthalic anhydride (HPA) were used, and hexahydrophthalic acid diglycidyl ester (HPDG), bisphenol A diglycidyl ether (BADG), and ethylene glycol bis(glycidyl phthalate) (EBGP) were the bisepoxides used. The reactions were further studied in model reactions using the Ca salt of monoethyl phthalate. The metal carboxylate groups of the metal salts catalyzed the reactions. The reactivity of the bisepoxides decreased in the order HPDG >> BADG > EBGP, and MA was more reactive than HPA. Some of the metal-containing cured resins obtained showed excellent physical properties. Resistance to chemical attack and boiling water, thermal behavior, and electrical resistance are also discussed.

INTRODUCTION

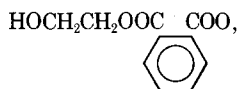
Recently the author has studied¹⁻⁹ with great interest the syntheses of polymers by using divalent metal salts of mono(hydroxyethyl) phthalate (HEP),



that is, (HEP—)₂M,

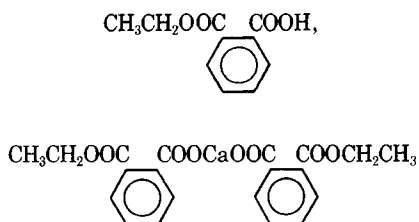


where HEP— denotes HEP residue and M is divalent metal (Mg or Ca). These

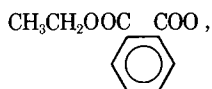


metal salts are considered useful ionic monomers from the scientific and industrial standpoint because they contain an ionic bond formed between —COO⁻ and M²⁺ and two hydroxyl groups. Previously it was shown⁵ that metal-containing polyesters were synthesized by the (HEP—)₂M-phthalic anhydride (PA)-epoxide reactions in dimethylformamide (DMF) solvent, as shown by eq.

The Ca salt of monoethyl phthalate (EP), namely, $(EP-)_2Ca$,



where EP— denotes EP residue was synthesized by the previously reported



method.²

HPDG was prepared by the reaction of the dipotassium salt of hexahydrophthalic acid with epichlorohydrin (Ep) (epoxide value = 6.702–6.756 eq/kg; calcd = 7.035 eq/kg). BADG was prepared by the reaction of bisphenol A, Ep, and NaOH (epoxide value = 5.589–5.779 eq/kg; calcd = 5.875 eq/kg). EBGp was prepared by the reaction of the dipotassium salt of ethylene glycol diphthalate and Ep (epoxide value = 3.934–4.052 eq/kg; calcd = 4.251 eq/kg).

Model Reactions

The general procedure was as follows: Into a 100-ml flask equipped with a stirrer, a thermometer, and a condenser were placed given amounts of reactants and $(EP-)_2Ca$, and the mixture was stirred at a fixed temperature for a given time. Samples were taken during the reactions for analyses of acid and/or epoxide. When the reaction was exothermic, care was taken not to exceed the fixed temperature by cooling the flask.

Curing Reactions

Curing reactions were carried out as follows: In a 18 × 180 mm test tube, $(HEP-)_2M$ and anhydride were placed at a mole ratio of 1:10, except in case of the $(HEP-)_2Ca$ -HPA system, where the ratio was 1:4. The mixture was heated at 130°C with stirring with a glass rod until it became homogeneous (transparent). Next, given amounts of bisepoxide and, if necessary, anhydride were added to the test tube to a desired mole ratio, and the test tube was placed in a constant-temperature bath while stirring the mixture with a glass rod. The amount of the mixture in the test tube was about 5 g. The stirring was continued until gelation occurred. After a desired time, the mixture was subjected to analyses of acid and epoxide. Moreover, the exothermic temperature for the curing systems of about 5 g was followed using a thermocouple.

Resin boards for determining physical and other properties were prepared as follows: Into a 1-liter flask equipped with a stirrer, a thermometer, and a condenser were placed $(HEP-)_2M$ and anhydride at a mole ratio of 1:10, except in case of the $(HEP-)_2Ca$ -HPA system, where the ratio was 1:6. The mixture

was heated at 140°C with stirring until it became homogeneous. Next, maintaining the temperature at 60°–80°C, given amounts of bisepoxide and, if necessary, anhydride were added to a desired mole ratio, and the mixture was stirred at the same temperature range until it became homogeneous. After degassing under reduced pressure, the mixture was poured into molds and cured at fixed temperatures for fixed periods.

Analytical Methods

Insoluble rubbery samples were cut into small pieces and subjected to analysis; similarly, when a sample was an insoluble hard solid, it was filed into powder and subjected to analysis.

Acidity. The acidities of systems of the model reactions EM or EHP–PGE, MA or HPA–PGE, and EM or EHP–OctOH were determined by titration in nonaqueous solvent. Meanwhile, the acidities of system of the model reaction MA or HPA–OctOH were determined by titration in a water-containing solvent. The acidities of curing reaction systems were determined 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.

Acidities by titration in nonaqueous solvent were determined as follows: About 0.1 g sample in the form of powder or small pieces was weighed to the nearest milligram into a flask and 10 ml acetone was added. After standing overnight, the mixture was titrated with 0.1*N* methanolic potassium hydroxide. For soluble samples, the same procedure as in the previous study⁵ was applied.

Acidities by titration in water-containing solvents were determined as follows: About 0.1 g sample in the form of powder or small pieces was weighed to the nearest milligram into a flask and 10 ml acetone was added. After standing overnight, 10 ml water was added. Again, standing for 1 hr, the mixture was titrated with 0.1*N* methanolic potassium hydroxide. The same procedure as in the previous study⁵ was applied for soluble samples.

Epoxide Value. For reaction system not containing acid anhydride groups, epoxide values were determined by the HCl–dioxane method.¹⁰ For reaction systems containing acid anhydride groups, epoxide values were determined, as in the previous paper,⁵ by the HBr method.^{11,12} When the sample was insoluble, the method was as follows: About 0.1 g sample in the form of powder or small pieces was weighed to the nearest milligram into a flask and 10 ml monochlorobenzene was added. After standing overnight, 7 ml 0.1*N* HBr–glacial acetic acid solution was added and the mixture was allowed to stand for 90–120 min. Next, 10 ml 0.1*N* solution of PGE in monochlorobenzene was added and the mixture was further allowed to stand for 10–20 min. It was back-titrated with 0.1*N* HBr–glacial acetic acid. (With the samples containing Mg, 5 ml acetone was further added to the mixture immediately before the back titration.) A blank experiment was also run. Since HBr reacts with metal carboxylate groups to produce MBr₂, correction was made for this factor.

Infrared Spectra. Infrared spectra were determined with a Shimazu IR-400 instrument.

Thermogravimetric Analysis. TGA was carried out in a Shimazu microthermobalance TGA-20 at a heating rate of 10°C/min in air.

Differential Thermal Analysis. DTA was carried out with a Shimadzu thermal analyzer DT-20 B at a heating rate of 10°C/min in air.

Determination of Physical and Other Properties

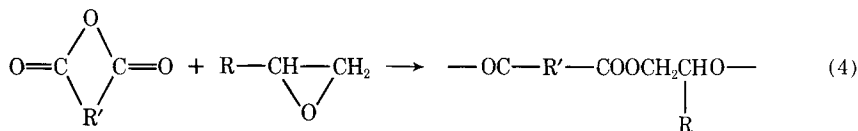
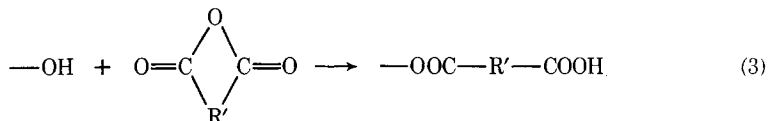
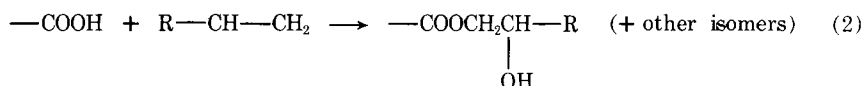
Heat distortion temperature (HDT) was determined according to ASTM-D 648-56; tensile strength, according to ASTM-D 638-68, flexural strength, according to ASTM-D 790-66; compressive strength, according to ASTM-D 695-69; impact strength, according to ASTM-D 256-56 (with Izod notch); and Rockwell hardness (M scale), according to ASTM-D 785-62.

Resistance to chemical attack was determined according to ASTM-D 543-67; and boiling water resistance, according to ASTM-D 570-63. Electrical resistances were determined using an instrument for JIS K 6911 at 5°C.

RESULTS AND DISCUSSION

Model Reactions

The (HEP—)₂M-phthalic anhydride (PA)-epoxide reactions in the previous study⁵ were carried out in DMF solvent at 90°C; it has been found that in this system the following main reactions occur:



In the present study, maleic anhydride (MA) and hexahydrophthalic anhydride (HPA) were selected as the anhydrides which are suitable for the curing systems without DMF. PA was excluded because the systems of (HEP—)₂M-PA-bisepoxide did not become homogeneous at high curing temperatures (100°–150°C).

To gain information on whether the above reactions occur also in the curing systems in the present study dealing with MA and HPA, model reactions were carried out using the Ca salt of monoethyl phthalate (EP), that is, (EP—)₂Ca, where EP— denotes EP residue, in the absence of DMF. Monoethyl maleate (EM), monoethyl hexahydrophthalate (EHP), 2-octyl alcohol (OctOH), and phenyl glycidyl ether (PGE) were chosen as model carboxylic acids, secondary alcohol, and epoxide, respectively.

At the initial stage of the curing reactions, carboxyl groups of adducts formed by the reaction of anhydride with (HEP—)₂M must be present. Hence, reaction of the carboxyl group with epoxy group of bisepoxide, that is, reaction (2),

probably occurs. As the model, EM or EHP-PGE reactions were carried out. As shown in Figures 1 and 2, the reaction in the presence of $(EP-)_2Ca$ proceeded much more rapidly than that without $(EP-)_2Ca$; thus, $(EP-)_2Ca$ catalyzes the reaction. Moreover, the conversion of epoxide in the systems without $(EP-)_2Ca$, especially in that containing EM, was consistently fairly greater than that of the acid. Thus, the carboxyl groups based on EM and EHP have considerable catalytic activity for the etherification of epoxide as side reaction. Meanwhile, the difference was very small in the systems containing $(EP-)_2Ca$. As is clear on comparing Figures 1 and 2, the systems containing EHP require higher temperatures than those containing EM to reach a same reaction rate; that is, EM is more reactive than EHP.

It is apparent from the above that reaction (2) readily occurs in the $(HEP-)_2M$ -anhydride-bisepoxide systems. In this reaction a new hydroxyl group is formed. Hence, the reaction of the hydroxyl group so produced with anhydrides, that is, reaction (3), may be assumed to occur. As the model for this, MA or HPA-OctOH reactions were conducted. As shown in Figure 3, the reaction was rapid even in the absence of $(EP-)_2Ca$; the reaction rate was further increased by $(EP-)_2Ca$ due to catalytic effect of $(EP-)_2Ca$. In addition, little difference in reactivity between MA and HPA was observed. Therefore, in the curing systems, reaction (3) will occur as soon as a new hydroxyl group is produced by reaction (2); the carboxyl group formed by reaction (3) will enter into reaction (2), so that ample opportunity for further growth of a three-dimensional network structure will be provided.

Since the concentration of anhydride is high in the initial stages of the curing

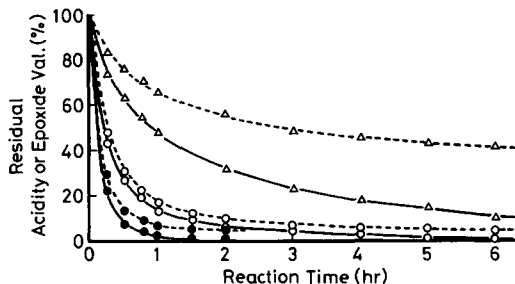


Fig. 1. Effect of $(EP-)_2Ca$ on EM-PGE (1:1) reaction: (Δ) without $(EP-)_2Ca$, at $110^\circ C$; (\circ) $(EP-)_2Ca$ -EM-PGE = 1:10:10, at $90^\circ C$; (\bullet) 1:10:10, at $110^\circ C$; (\circ) 1:10:10, at $150^\circ C$; (---) acidity; (—) epoxide value.

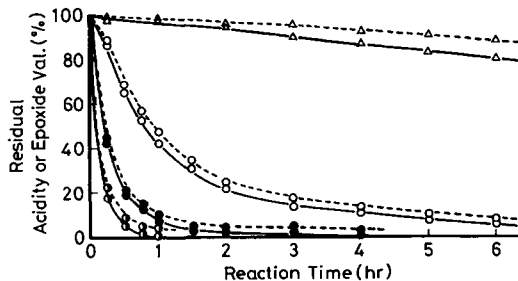


Fig. 2. Effect of $(EP-)_2Ca$ on EHP-PGE (1:1) reaction: (Δ) without $(EP-)_2Ca$, at $110^\circ C$; (\circ) $(EP-)_2Ca$ -EHP-PGE = 1:20:20, at $110^\circ C$; (\bullet) 1:10:10, at $130^\circ C$; (\circ) 1:10:10, at $150^\circ C$; (---) acidity; (—) epoxide value.

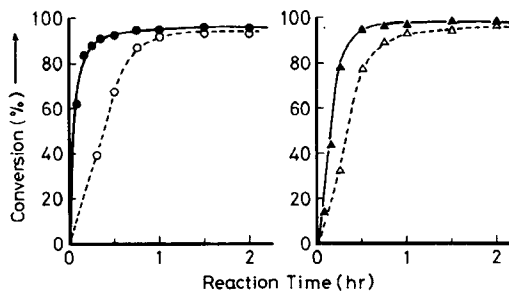


Fig. 3. Effect of $(EP-)_2Ca$ on MA or HPA-OctOH (1:1) reaction at $110^\circ C$: (○) MA-OctOH without $(EP-)_2Ca$; (●) $(EP-)_2Ca$ -MA-OctOH = 1:10:10; (△) HPA-OctOH without $(EP-)_2Ca$; (▲) $(EP-)_2Ca$ -HPA-OctOH = 1:10:10.

reaction, reaction (4) is considered possible. As the model for this, MA or HPA-PGE reactions were conducted. Figure 4 shows the epoxide data; the reaction is catalyzed markedly by $(EP-)_2Ca$. The difference between the decrease in epoxide value and the decrease in acidity determined by nonaqueous titration was generally very small (less than about 6%). Moreover, although not shown here, the reaction at $130^\circ C$ of the $(EP-)_2Ca$ -MA-PGE system at the mole ratio of 1:10:10 was uncontrollably very exothermic; the exothermic temperature increased above $200^\circ C$ during reaction, and the system became black in color and gelled. Thus, MA is more reactive than HPA also in this case. From the above results, reaction (4) is considered to occur to a considerable extent in the initial stages of the $(HEP-)_2M$ -anhydride-bisepoxide reaction.

As the model reaction for polymerization of epoxide group, polymerization of PGE was carried out in the presence of $(EP-)_2Ca$. The polymerization proved to be catalyzed by $(EP-)_2Ca$, in addition, temperature also had a considerable effect. For example, at the $(EP-)_2Ca$:PGE mole ratio of 1:10, the conversion of epoxide was 34% after 6 hr at $100^\circ C$ and 90% after 4 hr at $130^\circ C$. However, as will be shown later, in the practical curing systems, where carboxyl, anhydride and epoxide groups exist, the degree of etherification was very small. Thus, the metal carboxylate groups are considered to have much higher catalytic activities for polyesterification reactions than for etherification of epoxide groups. This is supported also by the above-mentioned model reactions, such as EM or EHP-PGE and MA or HPA-PGE. Therefore, the etherification of epoxide appears least significant in the present study.

Other elementary reactions such as hydroxyl group-carboxyl group reactions

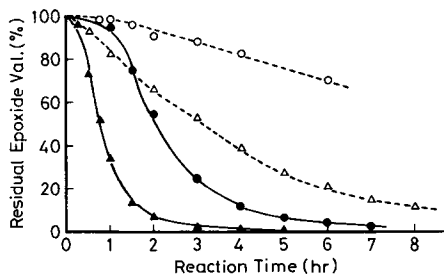


Fig. 4. Effect of $(EP-)_2Ca$ on MA or HPA-PGE (1:1) reaction: (○) $(EP-)_2Ca$ -MA-PGE = 1:40:40, at $100^\circ C$; (●) 1:10:10, at $100^\circ C$; (△) $(EP-)_2Ca$ -HPA-PGE = 1:40:40, at $130^\circ C$; (▲) 1:10:10, at $130^\circ C$.

can be omitted, judging from the EM or EHP-OctOH model reactions in the presence of $(EP-)_2Ca$ at $110^\circ C$, where there was no reaction.

In summary, the following may be concluded. In the $(HEP-)_2M$ -anhydride-bisepoxide curing systems, reactions (2), (3), and (4) are the main reactions. This conclusion is consistent with that obtained from the previous investigations⁵ devoted to the $(HEP-)_2M-PA$ -epoxide reactions in DMF.

Curing Reactions

Figures 5-7, as typical examples, show results of curing reaction of the systems of $(HEP-)_2Ca-MA$ -bisepoxide at a mole ratio of 1:10:5. The bath temperature was $100^\circ C$. The reaction is exothermic in the initial stages; the effect of the species of bisepoxides on peak exotherm temperature, gel time, and reaction rate appears clearly. Gelation of the systems occurred when conversions reached 50%-63%. The system containing HPDG with highest concentration of epoxide

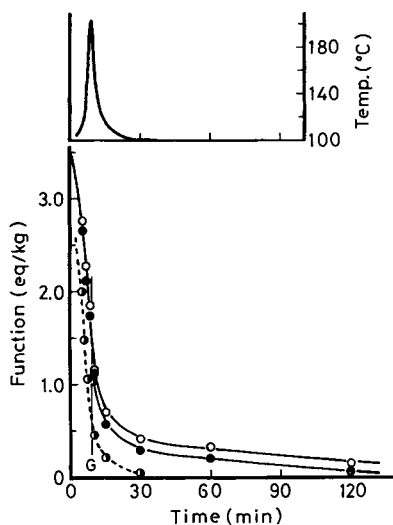


Fig. 5. Curing reaction of system of $(HEP-)_2Ca-MA-HPDG$ (1:10:5): (O) acidity; (●) epoxide value; (●) anhydride. Bath temp. = $100^\circ C$; G = gel point.

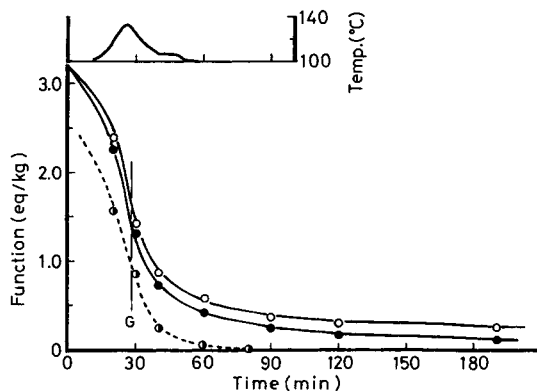


Fig. 6. Curing reaction of system of $(HEP-)_2Ca-MA-BADG$ (1:10:5): (O) acidity; (●) epoxide value; (●) anhydride. Bath temp. = $100^\circ C$; G = gel point.

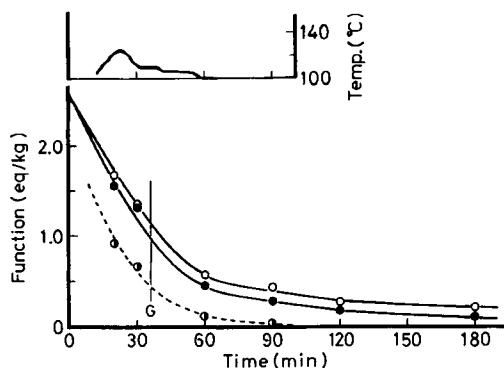


Fig. 7. Curing reaction of system of $(\text{HEP—})_2\text{Ca-MA-EBGP}$ (1:10:5): (○) acidity; (●) epoxide value; (●) anhydride. Bath temp. = 100°C; G = gel point.

groups showed the highest peak exotherm temperature and the shortest gel time. The reactivity of bisepoxide decreases in the order $\text{HPDG} \gg \text{BADG} > \text{EBGP}$.

The acidities shown were determined by nonaqueous titration and are due to anhydride and carboxyl groups. The decrease in epoxide value is consistently a little greater than the decrease in acidity, with a tendency similar to that observed in the model reactions. Thus, this also indicates that etherification of epoxide groups as side reaction occurred to only a slight degree. In the above curing systems, about 95% of the epoxide groups reacted are considered to have reacted with carboxyl and anhydride groups rather than with each other. Also, anhydride groups decreased as the reaction progressed and were almost consumed when the conversions reached 85%–92%. The conversions reached nearly maximum conversion attainable after 120–180 min.

In Table I the curing reactions of representative curing systems are further shown. With decrease in the metal content, the gel time becomes longer and the exotherm peak temperature decreases (sample 1 vs sample 2), again indicating the catalytic effect of the metal carboxylate group. Moreover, increase in temperature reduces the gel time and increases the exotherm peak temperature markedly (sample 3 vs sample 4); thus, the effect of temperature is also clearly demonstrated.

On comparing the cure properties of the systems containing the same species of anhydride and bisepoxide (sample 1 vs sample 5 and sample 3 vs sample 6), it becomes evident that Mg has considerably higher catalytic activities than Ca has toward the curing reaction. Furthermore, when comparing the systems containing the same species of metal and bisepoxide (sample 1 vs sample 3 and sample 5 vs sample 6), the systems containing MA showed shorter gel time and higher exotherm peak temperature than those containing HPA, though the cure temperature of the latter systems was 20°C higher than that of the former systems, suggesting that MA is more reactive than HPA in the curing reaction.

In most of the systems, the final conversions were 92%–98% and the conversions differences between acidity and epoxide value were generally very small.

In Figure 8, as typical examples, are shown the infrared spectra of the system of $(\text{HEP—})_2\text{Mg-MA-HPDG}$ (1:10:5). In spectrum (a) of the initial curable mixture, absorption bands at 1855 and 1780 cm^{-1} characteristic of the anhydride, and a band at 895 cm^{-1} characteristic of the epoxy ring are noteworthy.

TABLE I
Curing Reactions of $(\text{HEP}-)_{2}\text{M}-\text{Anhydride}-\text{Bisepoxide}$

Sample no.	Components	Mole ratio of components	Cure conditions		Cure properties			Final conversions	
			Temp., ^a °C	Time, min	Exotherm peak temp., °C	Gel time, min	Exotherm time, ^b min	Epoxide val., %	Acidity, %
1	$(\text{HEP}-)_{2}\text{Ca}-\text{MA}-\text{HPDG}$	1:10:5	100	120	206	9	8.5	98	96
2		1:20:10	100	180	175	12	14	95	95
3	$(\text{HEP}-)_{2}\text{Ca}-\text{HPA}-\text{HPDG}$	1:10:5	120	180	159	14.5	12	96	96
4		1:10:5	140	120	251	5.5	5	96	97
5	$(\text{HEP}-)_{2}\text{Mg}-\text{MA}-\text{HPDG}$	1:10:5	100	120	271	3.5	3	95	92
6	$(\text{HEP}-)_{2}\text{Mg}-\text{HPA}-\text{HPDG}$	1:10:5	120	120	250	5	5	96	92
7	$(\text{HEP}-)_{2}\text{Ca}-\text{MA}-\text{BADG}$	1:10:5	100	240	132	28	26	96	93
8	$(\text{HEP}-)_{2}\text{Mg}-\text{HPA}-\text{BADG}$	1:10:5	120	240	141	19.5	16	89	88
9	$(\text{HEP}-)_{2}\text{Ca}-\text{MA}-\text{EBGP}$	1:10:5	100	240	124	36	22.5	98	93

^a Bath temperature.

^b Time required to reach peak exotherm temperature.

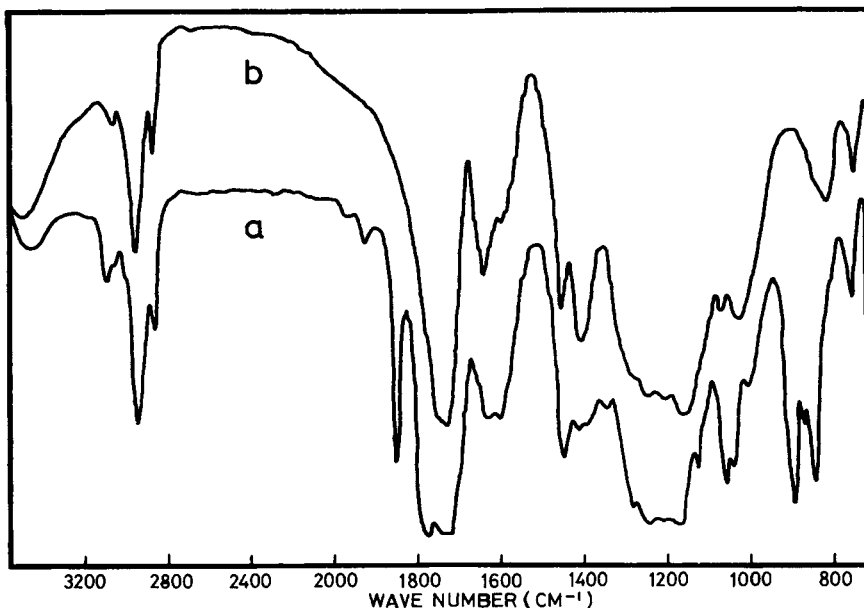


Fig. 8. Infrared spectra of system of $(\text{HEP}-)_{2}\text{Mg}-\text{MA}-\text{HPDG}$ (1:10:5): (a) initial curable mixture; (b) cured at 70°C for 1 hr, at 100°C for 0.5 hr, and at 140°C for 2 hr.

Meanwhile, in spectrum (b) of the cured resin, these bands have disappeared, indicating that the polyesterification has proceeded. Moreover, the cured resin show clear bands at $3500\text{--}3550\text{ cm}^{-1}$ (OH stretching), 1730 cm^{-1} (C=O stretching), 1600 cm^{-1} (carboxylate group and phenyl ring), and 1410 cm^{-1} (carboxylate group). From this it is apparent that the metal-containing cured resin has ionic links in the molecule; in addition, the resin is considered to be OH terminated. The weak band at about 1400 cm^{-1} due to the maleate group is considered to be hidden by the strong band of the carboxylate group.

Based on these results, the curing reactions for obtaining samples for determining physical and other properties were further carried out generally under the following conditions: for the systems containing MA, $70^{\circ}\text{--}80^{\circ}\text{C}$ for 1–3 hr, 100°C for 0.5–4 hr, and $120^{\circ}\text{--}140^{\circ}\text{C}$ for 2–4 hr; for the systems containing HPA, $70^{\circ}\text{--}80^{\circ}\text{C}$ for 1–2 hr, $120^{\circ}\text{--}130^{\circ}\text{C}$ for 0.5–2 hr, and $140^{\circ}\text{--}160^{\circ}\text{C}$ for 4–6 hr.

Physical Properties

The physical properties of the metal-containing cured resins of various combinations of components are summarized in Table II. As for the influence of bisepoxides on the physical properties, HDT decreases in the order $\text{BADG} > \text{HPDG} > \text{EBGP}$; meanwhile, compressive strength increases in the order $\text{BADG} < \text{HPDG} < \text{EBGP}$. Generally, the cured resins based on EBGP showed comparatively low values of Rockwell hardness, probably due to the plasticizing effect imparted by the $-\text{COOCH}_2\text{CH}_2\text{OOC}-$ linkage in the EBGP.

As for the mole ratio of components, the resins in which the mole ratio of $(\text{HEP}-)_{2}\text{M}$:anhydride:bisepoxide is 1:20:10 showed generally higher HDT and flexural strength than those in which the ratio is 1:10:5, due to higher crosslinking densities of the former resins. On the other hand, compressive strengths are

TABLE II
Physical Properties of Metal-Containing Cured Resins from (HEP—)₂M, Anhydrides and Bisepoxides

Components	Mole ratio of components	Metal in cured resin, %	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
(HEP—) ₂ Ca-MA-HPDG	1:10:5	1.34	96	690	1075	111	2.38	1430
	1:20:10	0.73	100	540	1209	111	1.91	1371
(HEP—) ₂ Mg-MA-HPDG	1:10:5	0.84	92	302	463	111	1.57	1468
	1:20:10	0.45	95	688	1429	109	1.81	1388
(HEP—) ₂ Ca-HPA-HPDG	1:10:5	1.13	88	415	720	106	1.67	1251
	1:20:10	0.62	100	836	1246	108	1.44	1257
(HEP—) ₂ Mg-HPA-HPDG	1:10:5	0.69	92	510	1064	110	2.21	1357
	1:20:10	0.37	101	977	1459	110	2.04	1283
(HEP—) ₂ Ca-MA-BADG	1:10:5	1.24	103	422	573	110	2.26	1310
	1:20:10	0.67	113	614	810	111	1.55	1184
(HEP—) ₂ Mg-MA-BADG	1:10:5	0.76	104	345	675	110	1.24	1255
	1:20:10	0.41	117	579	820	107	1.41	1158
(HEP—) ₂ Ca-HPA-BADG	1:10:5	1.06	113	676	1249	106	1.69	1153
	1:20:10	0.56	105	842	1379	108	1.72	1177
(HEP—) ₂ Mg-HPA-BADG	1:10:5	0.64	110	901	1401	109	1.85	1168
	1:20:10	0.34	124	934	1243	110	1.82	1135
(HEP—) ₂ Ca-MA-EBGP	1:10:5	1.01	81	284	508	106	1.59	1578
	1:20:10	0.54	92	392	709	109	2.02	1572
(HEP—) ₂ Mg-MA-EBGP	1:10:5	0.61	82	358	474	108	1.36	1606
	1:20:10	0.34	88	333	507	106	1.55	1530
(HEP—) ₂ Ca-HPA-EBGP	1:10:5	0.89	83 ^a	383 ^a	467 ^a	94 ^a	1.56 ^a	1376 ^a
	1:20:10	0.47	89	614	746	103	1.53	1369
(HEP—) ₂ Mg-HPA-EBGP	1:10:5	0.54	80	869	878	104	2.33	1429
	1:20:10	0.28	89	775	1062	107	2.32	1405

^a Sample contained small bubbles.

TABLE IV
Boiling Water Resistance of Metal-Containing Cured Resins

Components	Mole ratio of components	Change in length, %	Change in thickness, %	Change in weight, %	External appearance ^a
(HEP—) ₂ Ca-HPA-HPDG	1:10:5	-0.10	+1.14	+0.89	UA
(HEP—) ₂ Ca-HPA-HPDG	1:20:10	-0.69	+1.72	+0.57	UA
(HEP—) ₂ Mg-HPA-HPDG	1:20:10	-0.15	+1.02	+0.98	UA
(HEP—) ₂ Ca-MA-BADG	1:20:10	0.00	+0.68	+0.73	SW
(HEP—) ₂ Mg-MA-BADG	1:20:10	0.00	+1.13	+0.92	SW
(HEP—) ₂ Ca-HPA-BADG	1:20:10	0.00	+0.26	+0.40	UA
(HEP—) ₂ Mg-HPA-BADG	1:20:10	0.00	+0.14	+0.32	UA
(HEP—) ₂ Mg-HPA-EBGP	1:20:10	-0.24	+1.61	+1.16	UA

^a UA = Unaffected; SW = surfaces of sample became slightly white.

generally rather higher in the latter resins than in the former, though the latter resins have lower crosslinking densities; thus, the effect of introducing metal appears in the compressive strength.

Interestingly, in the resins based on BADG, HPA imparts considerably higher tensile and flexural strengths than MA.

In summary, the cured resins in the present study have good physical properties; especially those of (HEP—)₂Mg-HPA-HPDG (1:20:10) and of (HEP—)₂Mg-HPA-BADG (1:10:5 or 1:20:10) showed the best balance of physical properties.

Resistance to Chemical Attack and Boiling Water

Table III shows resistance of representative metal-containing cured resins to chemical attack. They were unaffected in external appearance by 30% H₂SO₄, 95% ethanol, and benzene, and changes in weight were generally small. In 10% NaOH, the resins based on MA disintegrated, while other resins showed small weight change, though some of them became slightly white or white on the surface.

In acetone and ethylene dichloride, most of the BADG-based resins were unaffected in external appearance and, in addition, MA was more effective than HPA in decreasing the weight gain of the resin; other resins showed no resistance and, especially in ethylene dichloride, disintegrated or cracked. It is of interest to note that the HPDG-based resins with highest crosslinking densities have low resistance toward nonaqueous reagents such as acetone and ethylene dichloride, probably due to high concentration of ester linkages in the resins.

In 10% NaCl and distilled water, they were unaffected in external appearance, and weight gains were generally small, except for the MA-based resins, the surfaces of which became slightly white.

Among the above resins, the resin of (HEP—)₂Mg-HPA-BADG (1:20:10) showed the best resistance to chemical attack. Table IV shows the boiling water resistance of the resins. They were unaffected in external appearance, except for the MA-based resins, the surfaces of which became slightly white.

No resins showed deformation. The resin based on EBGp showed the highest weight gain, probably due to both low crosslinking density and high concentration

TABLE III
Resistance of Metal-Containing Cured Resins to Chemical Attack

Components	Mole ratio of components	Change in weight, %, and external appearance ^a									
		30% H ₂ SO ₄	10% NaOH	95% Ethanol	Acetone	ClCH ₂ -CH ₂ Cl	10% NaCl	Benzene	Distilled water		
(HEP→) ₂ Ca-HPA-HPDG	1:10:5	+0.15 (UA)	-0.09 (SW)	+0.35 (UA)	+29.42 (CR)	—	+0.20 (UA)	+1.30 (UA)	+0.21 (UA)		
(HEP→) ₂ Ca-HPA-HPDG	1:20:10	+0.16 (UA)	-0.06 (W)	+0.09 (UA)	+6.56 (SS)	—	+0.20 (UA)	+0.18 (UA)	+0.21 (UA)		
(HEP→) ₂ Mg-HPA-HPDG	1:20:10	+0.22 (UA)	+0.26 (SW)	+0.21 (UA)	+6.48 (SS)	+37.13 (CR)	+0.31 (UA)	+0.17 (UA)	+0.30 (UA)		
(HEP→) ₂ Ca-MA-BADG	1:20:10	+0.25 (UA)	—	+0.11 (UA)	+0.74 (UA)	+0.46 (UA)	+0.30 (SW)	+0.15 (UA)	+0.35 (SW)		
(HEP→) ₂ Mg-MA-BADG	1:20:10	+0.29 (UA)	—	+0.15 (UA)	+0.53 (UA)	+0.45 (UA)	+0.48 (SW)	+0.19 (UA)	+0.56 (SW)		
(HEP→) ₂ Ca-HPA-BADG	1:20:10	+0.19 (UA)	+0.25 (UA)	+0.11 (UA)	+1.71 (UA)	+17.21 (SW)	+0.24 (UA)	0.16 (UA)	0.28 (UA)		
(HEP→) ₂ Mg-HPA-BADG	1:20:10	+0.19 (UA)	+0.24 (UA)	+0.10 (UA)	+1.18 (UA)	+4.07 (UA)	+0.25 (UA)	+0.15 (UA)	+0.28 (UA)		
(HEP→) ₂ Mg-HPA-EBGP	1:20:10	+0.19 (UA)	-0.13 (W)	+0.10 (UA)	—	—	+0.24 (UA)	+0.22 (UA)	+0.27 (UA)		

^a UA = Unaffected; SW = surfaces of sample became slightly white; W = surfaces of sample became white; SS = sample was slightly swollen; CR = sample cracked; DI = disintegrated.

of ester linkages, while the weight gains of other resins were below 1%. In this case also, the resin of $(\text{HEP}-)_{2}\text{Mg}-\text{HPA}-\text{BADG}$ (1:20:10) showed the best boiling-water resistance.

It is noteworthy that the above resins showed lower weight gains than the metal-containing crosslinked polyester resins of previous studies.^{4,6,7,9}

Thermal Behavior and Electrical Resistance

Figure 9 shows representative TGA and DTA curves in air of the metal-containing cured resins. In the TGA curves, the resins of $(\text{HEP}-)_{2}\text{Ca}-\text{HPA}-\text{BADG}$ (1:10:5) and of $(\text{HEP}-)_{2}\text{Mg}-\text{HPA}-\text{BADG}$ (1:10:5) showed 50% weight loss temperatures of 366° and 355°C, respectively. The plateaus observed above 520°C correspond to the formation of CaCO_3 in the case of Ca and to the formation of MgO in the case of Mg. The DTA curve of the Ca-containing resin shows two exothermic peaks, while that of the Mg-containing resin shows three exothermic peaks, probably due to degradations occurring via oxidative modes.

Table V shows the thermal stability data in air of representative metal-containing cured resins. In the $(\text{HEP}-)_{2}\text{Ca}-\text{MA}-\text{bisepoxide}$ series, it is noted that the thermal stability decreases, depending on the bisepoxide, in the order $\text{BADG} > \text{HPDG} > \text{EBGP}$. Furthermore, in the BADG-based resins, as is obvious when comparing the resins based on the same anhydride, Ca imparts better thermal stability than Mg. A similar tendency was also observed in the metal-containing three-dimensional polyesters of the previous study.⁸ In addition, on comparing

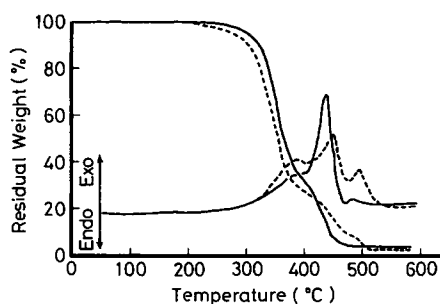


Fig. 9. TGA and DTA curves of metal-containing cured resins: (—) $(\text{HEP}-)_{2}\text{Ca}-\text{HPA}-\text{BADG}$ (1:10:5); (---) $(\text{HEP}-)_{2}\text{Mg}-\text{HPA}-\text{BADG}$ (1:10:5).

TABLE V
Thermal Stability of Metal-Containing Cured Resins

Components	Mole ratio of components	Temperature of 10% weight loss, °C	Temperature of 50% weight loss, °C
$(\text{HEP}-)_{2}\text{Ca}-\text{MA}-\text{HPDG}$	1:10:5	293	344
$(\text{HEP}-)_{2}\text{Ca}-\text{MA}-\text{HPDG}$	1:20:10	301	352
$(\text{HEP}-)_{2}\text{Mg}-\text{HPA}-\text{HPDG}$	1:10:5	283	331
$(\text{HEP}-)_{2}\text{Ca}-\text{MA}-\text{BADG}$	1:10:5	302	351
$(\text{HEP}-)_{2}\text{Mg}-\text{MA}-\text{BADG}$	1:10:5	285	343
$(\text{HEP}-)_{2}\text{Ca}-\text{HPA}-\text{BADG}$	1:10:5	323	366
$(\text{HEP}-)_{2}\text{Mg}-\text{HPA}-\text{BADG}$	1:10:5	302	355
$(\text{HEP}-)_{2}\text{Ca}-\text{MA}-\text{EBGP}$	1:10:5	292	337

TABLE VI
Electrical Resistances of Metal-Containing Cured Resins

Components	Mole ratio of components	Volume resistivity, $\Omega\text{-cm}$	Surface resistivity, Ω
(HEP—) ₂ Ca-HPA-HPDG	1:10:5	4.84×10^{16}	9.42×10^{15}
(HEP—) ₂ Ca-HPA-HPDG	1:20:10	2.20×10^{17}	8.65×10^{15}
(HEP—) ₂ Mg-HPA-HPDG	1:20:10	1.71×10^{17}	9.42×10^{16}
(HEP—) ₂ Ca-MA-BADG	1:20:10	1.65×10^{16}	4.96×10^{16}
(HEP—) ₂ Mg-MA-BADG	1:20:10	1.65×10^{17}	3.92×10^{16}
(HEP—) ₂ Ca-HPA-BADG	1:20:10	2.49×10^{17}	7.86×10^{16}
(HEP—) ₂ Mg-HPA-BADG	1:20:10	5.18×10^{16}	9.42×10^{15}
(HEP—) ₂ Mg-HPA-EBGP	1:20:10	4.25×10^{17}	5.79×10^{15}

the resins based on the same metal, it becomes evident that HPA imparts better thermal stability than MA.

Table VI shows the electrical resistances of the resins; they have both high volume and surface resistivities.

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