Metal-Containing Cured Polyesters from Divalent Metal Salts of Mono(hydroxyethyl) Phthalate, Bisester Anhydrides, and Monoepoxide

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Synopsis

Synthesis of novel metal-containing cured polyesters was investigated by the reaction of divalent metal salts of mono(hydroxyethyl) phthalate–bisester anhydride–monoepoxide. As the bisester anhydride, ethylene glycol bis(trimellitate) dianhydride (ETDA), diethylene glycol bis(trimellitate) dianhydride (DETDA), and polyethylene glycol bis(trimellitate) dianhydride (PETDA) were used. They were prepared from trimellitic anhydride and glycols. Phenyl glycidyl ether was the monoepoxide used. In the reactions, the Mg salt showed considerably higher catalytic activities than the Ca salt. As for the physical properties of the cured resins, heat distortion temperature, Rockwell hardness, and compressive strength decreased in the order ETDA > DETDA > PETDA. Generally, the resins containing Mg showed better physical properties than those containing Ca. Resistance to chemical attack and boiling water, thermal behavior, and electrical resistances are also discussed.

INTRODUCTION

Recently, extensive investigations have been carried out for the synthesis of polymers by using divalent metal salts of mono(hydroxyethyl) phthalate (HEP), that is, (HEP-)$_2$M (where HEP- denotes HEP residue and M is divalent metal).[1-10] Since these metal salts contain an ionic bond formed between —COO$^-$ and M^{2+} and two hydroxyl groups, they are considered to be of interest as ionic monomers from the scientific and industrial standpoints. Previously, syntheses of metal-containing polyesters containing ionic links in the main chain were investigated by the (HEP-)$_2$M–phthalic anhydride (PA)–epoxide reactions, as shown by eq. (1)[5]:

$$\tag{1}$$

where M = Mg or Ca.

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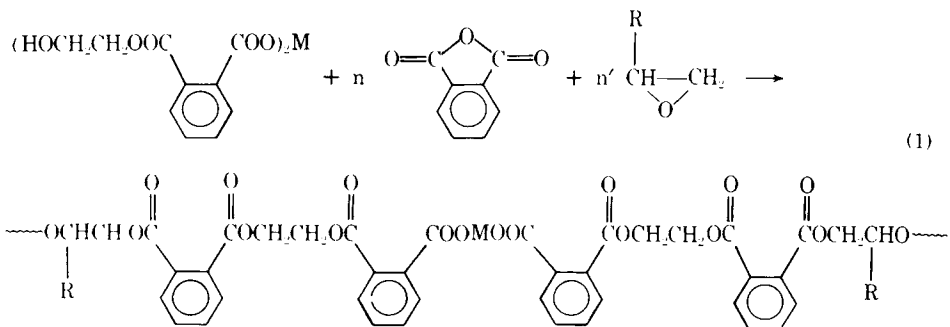
By applying the above synthetic route to the synthesis of three-dimensional polymers, metal-containing three-dimensional polyesters have been prepared by the (HEP-)$_2$M–pyromellitic dianhydride (PMDA)–epoxide reactions.[8] In the present study, extending the species of dianhydride to bisester anhydride, the author investigated the preparation of novel metal-containing cured polyesters by the (HEP-)$_2$M–bisester anhydride–monoepoxide reactions. As the bisester anhydride, ethylene glycol bis(trimellitate) dianhydride (ETDA), diethylene glycol bis(trimellitate) dianhydride (DETDA), and polyethylene glycol bis(trimellitate) dianhydride (PETDA) were used; the monoepoxide used was phenyl glycidyl ether (PGE):
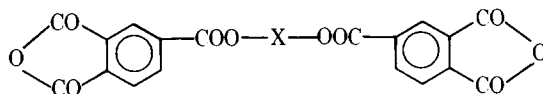
bisester anhydride

where X = —CH$_2$CH$_2$—, —CH$_2$CH$_2$OCH$_2$CH$_2$—, or —CH$_2$CH$_2$—(OCH$_2$CH$_2$)$_{\overline{n}}$—

To our knowledge, cured polyesters prepared by the above reaction using monoepoxide are little known. They are evaluated for physical and other properties. Idealized main structures of the metal-containing cured resins obtained in the present study may be represented as follows:

EXPERIMENTAL

Materials

(HEP-)$_2$M was prepared according to the method reported in a previous paper.[1] PGE was purified by distillation. Trimellitic anhydride (TMA) was a reagent-grade chemical and used as received. Ethylene glycol, diethylene glycol of extra pure grade, and polyethylene glycol of molecular weight 200 (reagent chemical) were used as received.

Synthesis of Bisester Anhydrides

Direct Synthesis from TMA and Glycols. Into a 100–200 ml four-necked flask equipped with stirrer, thermometer, nitrogen inlet and outlet adapter, and dropping funnel was placed a fixed amount of TMA, and the flask was heated to 190°C. Then, a quantity of glycol such as to give a [TMA]/[glycol] ratio of 2:1 was added with stirring over 15–30 min. After the addition, the temperature was gradually raised to 220°–260°C, and the mixture was stirred at this temperature range to remove water produced. (Nitrogen gas was passed through the mixture during the reaction.) When the evolution of water almost stopped, a small amount of acetic anhydride was added to the flask, and the mixture was stirred at 160°–180°C for 0.5–1 hr. Then, the temperature was gradually raised to 200°–250°C, and the flask was further kept under vacuum at this temperature range for about 2 hr to remove acetic acid effluent, etc. The product thus obtained was slightly brownish or brownish glassy material or semisolid, depending on the species of glycol.

Synthesis Via Isolated Intermediate Bisester Tetracarboxylic Acid. Into

a 300–1000 ml four-necked flask equipped with stirrer, thermometer, dropping funnel, and condenser were placed fixed amounts of TMA, N,N-dimethylben-zylamine as catalyst (0.1 mole/kg), and methyl ethyl ketone as solvent (weight ratio of solvent:reactants = 1:0.85–2.5), and the flask was heated to 95°C. Then, a quantity of glycol such as to give a [TMA]/[glycol] ratio of 2:1–1.2 was gradually added dropwise with stirring over 1–2 hr. After the addition, the mixture was stirred at the same temperature for 2–3 hr. As the reaction proceeded, the product separated as white powders or viscous precipitate. After the reaction, a suitable amount of benzene was added, and the mixture was stirred at 80°C for 15 min; after cooling, the product was filtered, washed with benzene, and dried. The product was obtained as white powder. Table I shows the results of the synthesis of the intermediates.

TABLE I
Intermediate Bisester Tetracarboxylic Acids Obtained by the Reaction of TMA and Glycol

		Bisester tetracarboxylic acids				
		Acid value	Ester value	Melting		
	Yield,	(calcd),	(calcd),	point,	Analyses (calcd)	
Glycol	%	mg KOH/g	mg KOH/g	°C	C, %	H, %
Ethylene glycol	92	504.7	251.6	225–227	54.05	3.40
		(502.9)	(251.4)		(53.82)	(3.16)
Diethylene glycol	88	450.3	226.3	202–203	53.95	3.80
		(457.7)	(228.9)		(53.88)	(3.70)
Polyethylene glycol	93	357.0	178.6	162–164	54.90	4.50
		(384.1)	(192.1)		(54.00)	(4.57)

A given amount of bisester tetracarboxylic acid obtained above was heated at 220°–230°C for 2–6 hr under vacuum. Next, a small amount of acetic anhydride was added to the flask, and the content was kept at 160°–180°C for 0.5–1 hr. Then, the temperature was gradually raised to 200°–260°C, and the content was further kept at this temperature range for more than 3 hr under vacuum to remove acetic acid effluent, etc. The product thus obtained could be recrystallized, depending on the species of glycol, as follows: ETDA could be recrystallized by acetic anhydride. In the case of DETDA, acetone was added to the crude product in the glassy state, and the acetone was refluxed; the glassy state changed into the crystalline state during the reflux. Further, a suitable amount of benzene was added to the mixture to wash the crystals. The crystals were filtered, washed with benzene, and dried.

Curing Reactions

To a given amount of bisester anhydride in the molten state was added a given amount of (HEP-)$_2$M with stirring over 5–30 min, and the mixture was further stirred for additional 5–30 min. After cooling, the mixturf was crushed into a powder in the case of ETDA and DETDA.

In a test tube, 18 × 180 mm, were placed the mixture obtained above and PGE at a desired mole ratio, and the test tube was placed in a constant-temperature bath with stirring the mixture with a glass rod. The stirring was continued until gelation occurred. After a desired time, the mixture was subjected to analysis of acid and epoxide. Moreover, the exothermic temperature was followed for the curing system of 5 g using a thermocouple.

Resin boards for determining physical and other properties were prepared as follows: In case of the systems containing ETDA or DETDA, a given amount of PGE was placed into a 500–1000 ml flask equipped with stirrer and thermometer. Maintaining the temperature of the flask at 100°–160°C, the mixture (powder) obtained was added to a desired mole ratio over 5 min. After the addition, the content was further stirred for an additional 2–5 min and poured into molds and cured at a fixed temperature for fixed periods.

In case of the systems containing PETDA, a given amount of (HEP-)$_2$M was added, over 30 min, into a given amount of PETDA in a 1000-ml flask at about 120°C, and the mixture was stirred for additional 30 min. Next, maintaining the temperature of the flask at about 100°C, PGE which had been kept at 80°–100°C was added, over 5 min, to the mixture to a desired mole ratio. After

the addition, the content was further stirred for an additional 5 min and poured into molds and cured at fixed temperature for fixed periods.

Analytical Methods

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

Acidity. Acidities of bisester anhydrides and of curing reaction systems were determined by titration in nonaqueous solvent and also by titration in water-containing solvent. The acid anhydride group content was calculated from the difference of the two titrations. The same procedures as in the previous study[10] were applied for the determination of acidities.

Epoxide Value. Epoxide values were determined, as described in the previous paper,[10] by the HBr method.[11,12]

Ester Value. Ester values of bisester tetracarboxylic acids and bisester anhydrides were determined as follows: 0.1–0.2 g of sample was weighed to the nearest milligram into a 100-ml flask, and 10 ml of 0.5N KOH was added by pipet. The mixture was heated at 90°C for 2.5 hr. When the mixture was cooled to room temperature, 10 ml 0.5N HCl was added by pipet. It was titrated with 0.5N KOH. A blank experiment was also run. Ester values were obtained by calculating by the usual method.

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

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

Diferential Thermal Analysis (DTA). DTA was carried out with a Shimazu 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 26°C (RH = 84%).

RESULTS AND DISCUSSION

Synthesis of Bisester Anhydrides

It has been known that bisester anhydrides can be synthesized by the reaction of trimellitic anhydride (TMA) with glycol diacetates[13] and glycols.[14,15] They are usually obtained in the crude state. Bisester anhydrides of as high a purity as possible are considered to be desirable for the curing reactions in the present study.

Therefore, synthetic experiments of bisester anhydrides from TMA and glycols were carried out in order to find the conditions for obtaining products in as high a purity as possible. The following two methods were investigated: (1) direct synthesis from TMA and glycols without isolating intermediate bisester tetracarboxylic acid and (2) synthesis via isolated intermediate bisester tetracarboxylic acid. By heating TMA and glycol (2:1) together in methyl ethyl ketone, intermediate bisester tetracarboxylic acids are easily formed. As shown in Table I, the intermediates could be isolated as white powders in good yield. Furthermore, the intermediates based on ethylene glycol and diethylene glycol were obtained in high purity.

Table II summarizes the results of syntheses of bisester anhydrides. By the direct synthesis, the products were not obtained in high purity; the purity of the product based on diethylene glycol was especially low. On the other hand, the products were obtained in higher purity by the synthesis via isolated intermediates; among them, the purity of the product based on diethylene glycol increased markedly. The purity of the product based on polyethylene glycol was not as high as in case of the other bisester anhydrides, probably due to the difficulty of isolating the corresponding intermediate in high purity.

Thus, the crude products from isolated intermediate bisester tetracarboxylic acids were found to be obtained in higher purity; they were further recrystallized as described in the experimental section.

Table III shows the recrystallized bisester anhydrides; they were considered to be suitable for the curing reactions. High purity could be attained for the bisester anhydrides based on ethylene glycol and diethylene glycol; it appears that bisester anhydrides of such high purity as shown in the table have not been reported before. However, the bisester anhydride based on polyethylene glycol could not be recrystallized because of the lack of solvents suitable for recrystallization.

The bisester anhydrides synthesized via isolated corresponding intermediates

TABLE II
Synthesis of Bisester Anhydrides

Bisester anhydride	Method of synthesis[a]	Acid value (calcd), mg KOH/g		Acid anhydride group, %	External appearance
		I[b]	II[c]		
ETDA	A	289.8 (273.5)	546.3 (547.0)	93.8	slightly brownish glassy material
	B	300.6 (273.5)	562.1 (547.0)	95.6	slightly brownish glassy material
DETDA	A	255.6 (247.0)	425.2 (494.0)	68.6	slightly brownish glassy material
	B	244.8 (247.0)	472.9 (494.0)	92.4	brownish glassy material
PETDA	A	219.1 (204.7)	386.8 (409.4)	81.9	slightly brownish semisolid
	B	212.6 (204.7)	390.3 (409.4)	86.8	slightly brownish semisolid

[a] A = By the reaction of TMA and glycol without isolating intermediate bisester tetracarboxylic acid; B = from isolated intermediate bisester tetracarboxylic acid.

[b] Determined by nonaqueous titration.

[c] Determined in water-containing solvent.

TABLE III
Recrystallized Bisester Anhydrides[a] suitable for Curing Reactions

Bisester anhydride	Yield,[b] %	Acid value (calcd), mg KOH/g		Ester value (calcd), mg KOH/g	Acid anhydride group, %	Melting point, °C	Analyses (calcd)		External appearance
		I[c]	II[d]				C, %	H, %	
ETDA	80	277.1 (273.5)	546.6 (547.0)	272.2 (273.5)	98.5	166–168	58.70 (58.55)	2.55 (2.46)	slightly brownish powder
DETDA	62	249.9 (247.0)	492.9 (494.0)	245.1 (247.0)	98.4	209–212	58.25 (58.16)	3.15 (3.11)	slightly brownish powder
PETDA	100[e]	212.6 (204.7)	390.3 (409.4)	233.5 (204.7)	86.8	—	56.85 (57.53)	4.25 (4.14)	slightly brownish semisolid

[a] Obtained from isolated intermediate bisester tetracarboxylic acid.
[b] After recrystallization.
[c] Determined by nonaqueous titration.
[d] Determined in water-containing solvent.
[e] Not recrystallized.

and recrystallized (in the case of ETDA and DETDA) were used for the curing reactions in the present study.

Curing Reactions

Figures 1–3 show typical results of curing reaction of the systems (HEP-)$_2$-Ca–bisester anhydride–PGE at a mole ratio of 1:6:12. The bath temperature was 120°C, except in case of the (HEP-)$_2$Ca–DETDA–PGE system. Meanwhile, for the systems containing DETDA, the curing reaction did not proceed homogeneously below 160°C because of poor solubility of DETDA in the system; therefore, the bath temperature was 160°C in this case.

The curing reaction is exothermic in the initial stages. Gelation of the systems occurred when conversions reached 27%–56%. The acidities shown were determined by nonaqueous titration and are due to anhydride and carboxyl groups. In all cases, the decrease of epoxide value is consistently a little greater than that of acidity, indicating that etherification of epoxide groups as side reaction occurred to a slight degree. In the systems containing ETDA and PETDA, about 95%, and in that containing DETDA, about 90% of the epoxide groups reacted are considered to have reacted with carboxyl and anhydride groups rather than with each other. Also, anhydride groups decreased with the progress of reaction and were almost consumed when the conversions reached 80%–94%.

In the (HEP-)$_2$M–anhydride–bisepoxide systems of the previous study,[10] the following main reactions have been found to occur: (1) reaction of carboxyl group with epoxide group to form OH group; (2) reaction of the OH group with acid anhydride group to form terminal carboxyl group; (3) reaction of acid anhydride group with epoxide group to form ester linkage. In the curing reactions of the present study, the same main reactions as above are believed to occur. Moreover, it is advantageous for the metal carboxylate groups in (HEP-)$_2$M to catalyze this type of reactions.[5,10]

Table IV shows the results of curing reactions carried out on various combinations of components. Generally, at the same temperature, systems containing Mg showed shorter gel time and higher exotherm peak temperature than those containing Ca. Especially in the systems containing ETDA, this tendency was pronounced. This fact indicates that Mg has a considerably higher catalytic
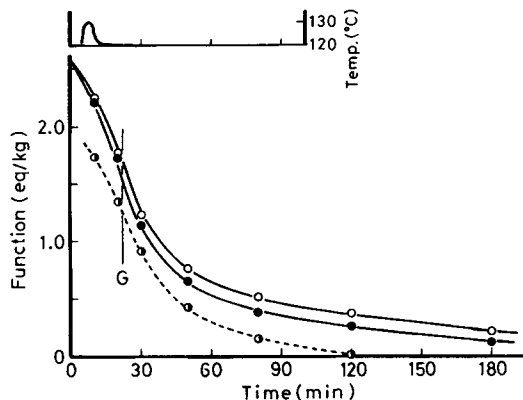

Fig. 1. Curing reaction of system of (HEP-)$_2$Ca–ETDA–PGE (1:6:12): (O) acidity; (●) epoxide value; (◐) anhydride; bath temp. = 120°C; G = gel point.
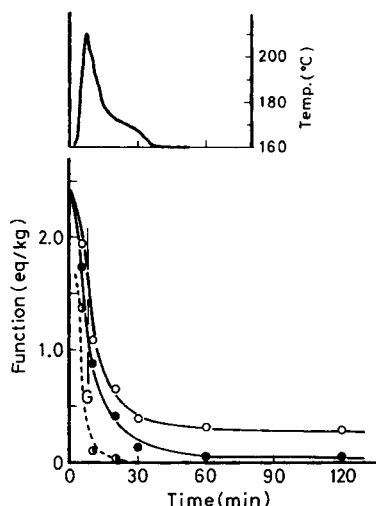
Fig. 2. Curing reaction of system of (HEP-)$_2$Ca–DETDA–PGE (1:6:12): (O) acidity; (●) epoxide value; (◐) anhydride; bath temp. = 160°C; G = gel point.

activity than Ca has toward the curing reaction. Furthermore, increase in temperature reduces the gel time and increases the exotherm peak temperature markedly; thus, the effect of temperature also appears clearly. On the other hand, it can be considered that the species of bisester anhydride has little effect on the cure properties.

In systems containing PETDA, the reaction could proceed homogeneously even at such a low temperature as 100°C, due to good solubility of PETDA in the system. The exotherm was small; however, final conversions, especially in the systems with higher metal content, were fairly low. When the curing reactions were conducted at above 120°C, the conversions in most of the systems reached nearly the maximum attainable (90%–99%) within 2–4 hr, and the differences of conversions between acidity and epoxide value were generally below about 10%.

Figure 4 shows, as a typical example, the infrared spectra of the system of (HEP-)$_2$Ca–ETDA–PGE (1:6:12). In spectrum (a), of the initial curable mixture, absorption bands at 1850 and 1780 cm^{-1} (characteristic of the anhydride) and

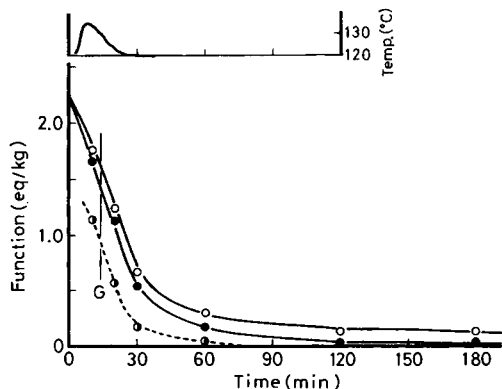Fig. 3. Curing reaction of system of (HEP-)$_2$Ca–PETDA–PGE (1:6:12): (O) acidity; (●) epoxide value; (◐) anhydride; bath temp. = 120°C; G = gel point.

890 cm^{-1} (epoxy ring) are noteworthy. On the other hand, in spectrum (b), of the cured resin, these bands have disappeared, indicating that the polyesterification has proceeded. Moreover, the cured resin showed bands at 3450–3550 cm^{-1} (OH stretching), 1730 cm^{-1} (C=O stretching), 1590–1600 cm^{-1} (carboxylate group and phenyl ring), and 1400 cm^{-1} (carboxylate group). From this it is considered that the metal-containing cured resin has ionic links and, in addition, is OH terminated.

Based on these results, curing reactions for obtaining samples for determining physical and other properties were further carried out under the following conditions: for systems containing ETDA or PETDA, 120°C for 2 hr and 140°C for 3 hr; for systems containing DETDA, 160°C for 5 hr.

Physical Properties

The physical properties of the metal-containing cured polyesters of various combinations of components are summarized in Table V. As for the influence of bisester anhydrides on the physical properties, HDT, Rockwell hardness, and compressive strength decrease in the order ETDA > DETDA > PETDA, probably due to the plasticizing effect imparted by the oxygen ether group in DETDA and PETDA. On the other hand, in the resins of (HEP-)$_2$Ca–bisester anhydride–PGE (1:10:20), tensile, flexural, and impact strengths have a tendency to increase in the order ETDA < DETDA < PETDA. Moreover, the resins of (HEP-)$_2$Ca–PETDA–PGE (1:6:12) and of (HEP-)$_2$Mg–PETDA–PGE (1:10:20) were too flexible to be broken during flexural strength measurement.

As for the mole ratio of components, the resins in which the mole ratio of (HEP-)$_2$M:bisester anhydride:PGE is 1:10:20 showed generally higher HDT, Rockwell hardness, tensile, flexural, and impact strengths than those in which the ratio is 1:6:12, due to higher crosslinking densities of the former resins.
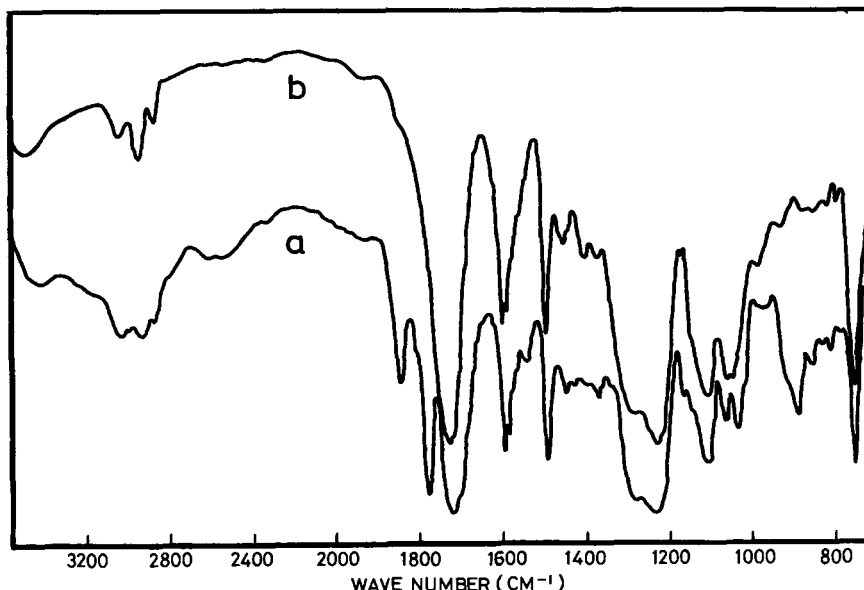

Fig. 4. Infrared spectra of system of (HEP-)$_2$Ca–ETDA–PGE (1:6:12): (a) initial curable mixture; (b) cured at 140°C for 4 hr.

TABLE IV
Curing Reactions of Systems of (HEP-)$_2$M–Bisester Anhydride–PGE

Components	Mole ratio of components	Cure conditions		Cure properties			Final conversions	
		Temp.,[a] °C	Time,[b] min	Gel time, min	Exotherm peak temp., °C	Exotherm time,[c] min	Epoxide value, %	Acidity, %
(HEP-)$_2$Ca–ETDA–PGE	1:6:12	120	240	22	130	8.2	98	94
	1:6:12	140	180	11	161	5.9	98	93
	1:10:20	120	240	25	124	8.6	97	93
	1:10:20	140	180	13	169	7.9	98	94
(HEP-)$_2$Mg–ETDA–PGE	1:6:12	120	240	9	144	4.6	97	93
	1:6:12	140	120	7	190	3.4	97	89
	1:10:20	120	180	12	163	4.0	97	90
	1:10:20	140	120	6	202	4.3	97	92
(HEP-)$_2$Ca–DETDA–PGE	1:6:12	160	120	8	211	7.8	99	89
	1:10:20	160	120	9	207	8	98	91
(HEP-)$_2$Mg–DETDA–PGE	1:6:12	160	60	4	229	4.7	96	85
	1:10:20	160	120	5	206	4.9	98	92
(HEP-)$_2$Ca–PETDA–PGE	1:6:12	100	240	32	108	18.2	87	81
	1:6:12	120	120	14	134	7.1	99	95
	1:6:12	140	120	10	168	8.3	99	96
	1:10:20	100	240	40	108	11.9	96	89
	1:10:20	120	240	17	136	8.3	97	90
	1:10:20	140	120	10	202	6.5	96	90
(HEP-)$_2$Mg–PETDA–PGE	1:6:12	100	240	27	111	8	83	76
	1:6:12	120	240	15	146	7	95	88
	1:6:12	140	180	7	185	5	96	92
	1:10:20	100	240	39	108	9.5	92	84
	1:10:20	120	180	14	129	6.5	96	90
	1:10:20	140	60	6	195	5	98	91

[a] Bath temperature.
[b] Time required to reach maximum conversion attainable.
[c] Time required to reach peak exotherm temperature.

Compressive strengths are a little higher in the latter resins than in the former resins, though the latter resins have lower crosslinking densities. Thus, the effect of introducing metal appears in the compressive strength. A similar tendency was also observed for the cured resins in the previous study.[10]

Comparing the resins which contain the same bisesteranhydride, at the same mole ratio, the resins containing Mg showed generally better physical properties than the resins containing Ca, probably due to higher interionic attraction of Mg^{2+}. This tendency is especially remarkable in the resins based on ETDA.

Of the resins obtained, the resin of (HEP-)$_2$Mg–ETDA–PGE (1:10:20) showed best combination of physical properties.

TABLE V
Physical Properties of Metal-Containing Cured Polyesters from (HEP-)$_2$M, Bisester Anhydrides, and PGE

Mole ratio of components	Metal in cured resin, %	HDT, °C	Tensile strength, kg/cm²	Flexural strength, kg/cm²	Rockwell hardness, M scale	Impact strength, kg·cm/cm	Compressive strength, kg/cm²
(HEP-)$_2$Ca–ETDA–PGE							
1:6:12	0.85	77	268	391	104	1.39	1300
1:10:20	0.53	78	259	476	106	1.46	1288
(HEP-)$_2$Ca–DETDA–PGE							
1:6:12	0.80	67	240	366	93	1.36	1182
1:10:20	0.50	70	410	622	94	1.67	1167
(HEP-)$_2$Ca–PETDA–PGE							
1:6:12	0.75	45	521	—	78	1.73	1023
1:10:20	0.47	48	557	796	79	2.16	991
(HEP-)$_2$Mg–ETDA–PGE							
1:6:12	0.52	81	459	892	106	1.96	1354
1:10:20	0.32	84	608	1459	107	2.08	1345
(HEP-)$_2$Mg–DETDA–PGE							
1:6:12	0.49	70	287	481	93	1.49	1201
1:10:20	0.30	74	390	890	95	1.71	1176
(HEP-)$_2$Mg–PETDA–PGE							
1:6:12	0.46	49	481	842	78	1.96	1009
1:10:20	0.29	50	500	—	79	2.11	986

TABLE VI
Resistance of Metal-Containing Cured Polyesters to Chemical Attack

Components (mole ratio)	Change in weight, %, and external appearance[a]							
	30% H_2SO_4	10% NaOH	95% Ethanol	Acetone	$ClCH_2CH_2Cl$	10% NaCl	Benzene	Distilled water
(HEP-)$_2$Ca–ETDA–PGE (1:6:12)	+0.18 (UA)	−4.43 (SV)	+0.27 (UA)	— (DI)	— (DI)	+0.21 (UA)	+0.20 (UA)	+0.24 (UA)
(HEP-)$_2$Ca–ETDA–PGE (1:10:20)	+0.22 (UA)	−6.99 (SV)	+0.46 (UA)	— (DI)	— (DI)	+0.23 (UA)	+0.13 (UA)	+0.41 (UA)
(HEP-)$_2$Ca–DETDA–PGE (1:10:20)	+0.35 (UA)	−8.86 (SV)	+1.35 (UA)	— (DI)	— (DI)	+0.41 (UA)	+2.79 (UA)	+0.49 (UA)
(HEP-)$_2$Ca–PETDA–PGE (1:10:20)	+0.21 (UA)	— (DI)	+1.48 (UA)	— (DI)	— (DI)	+0.64 (UA)	+19.27 (CS)	+0.87 (UA)
(HEP-)$_2$Mg–ETDA–PGE (1:10:20)	+0.18 (UA)	−0.58 (SV)	+0.19 (UA)	— (DI)	— (DI)	+0.25 (UA)	+0.11 (UA)	+0.26 (UA)
(HEP-)$_2$Mg–DETDA–PGE (1:10:20)	+0.42 (UA)	−2.57 (SV)	+1.84 (UA)	— (DI)	— (DI)	+0.69 (UA)	+7.60 (SS)	+0.90 (UA)
(HEP-)$_2$Mg–PETDA–PGE (1:10:20)	+0.51 (UA)	−44.90 (SD)	+2.18 (UA)	— (DI)	— (DI)	+0.84 (UA)	+28.17 (CS)	+1.13 (UA)

[a] UA = Unaffected; SV = surfaces of sample became only slightly viscous; DI = disintegrated; SS = sample was slightly swollen; CS = corners of sample cracked and sample was considerably swollen; SD = surfaces of sample disintegrated.

TABLE VII
Boiling Water Resistance of Metal-Containing Cured Polyesters

Components (mole ratio)	Change in length, %	Change in thickness, %	Change in weight, %	External appearance
(HEP-)$_2$Ca–ETDA–PGE (1:6:12)	+0.26	+0.24	+0.77	unaffected
(HEP-)$_2$Ca–ETDA–PGE (1:10:20)	+0.19	+0.67	+1.03	unaffected
(HEP-)$_2$Ca–DETDA–PGE (1:10:20)	+0.57	+1.31	+1.36	unaffected
(HEP-)$_2$Ca–PETDA–PGE (1:10:20)	+0.51	+0.88	+1.49	unaffected
(HEP-)$_2$Mg–ETDA–PGE (1:10:20)	+0.32	+0.18	+1.29	unaffected
(HEP-)$_2$Mg–DETDA–PGE (1:10:20)	+0.38	+0.45	+1.82	unaffected
(HEP-)$_2$Mg–PETDA–PGE (1:10:20)	+0.51	+0.50	+2.20	unaffected

Resistance to Chemical Attack and Boiling Water

Table VI shows the resistance of representative metal-containing cured polyesters to chemical attack. They were unaffected in external appearance by 30% H_2SO_4, 95% ethanol, 10% NaCl, and distilled water, and changes in weight were generally small; Especially the resins based on ETDA showed low weight gain.

In 10% NaOH, the surfaces of the sample became only slightly viscous; and weight decrease was observed, except for the PETDA-based resins, which disintegrated on the surface or throughout. In acetone and ethylene dichloride, all of the resins disintegrated. In benzene, the resins based on ETDA were unaffected in external appearance, while the PETDA-based resins were considerably swollen, and the corners of the sample cracked.

Generally, resistance to chemical attack showed a tendency to decrease, depending on the bisester anhydride, in the order ETDA > DETDA > PETDA; in addition, the resins containing Ca showed generally higher resistance than those containing Mg. Among the above resins, the resin of (HEP-)$_2$Mg–ETDA–PGE (1:10:20) showed the best resistance to chemical attack.

Table VII shows the boiling water resistance of the resins. They were unaffected in external appearance. Also in this case, weight gain increased in the order ETDA < DETDA < PETDA, probably due to the increased flexibility of the cured resin caused by the ether linkage in DETDA and PETDA and the increased hydrophylicity due to the polarity of the ether oxygen. Furthermore, as is obvious on comparing the resins based on the same bisester anhydride, the resins containing Ca showed lower weight gain than those containing Mg. A similar tendency was also observed for the cured resins in the previous studies.[7,9]
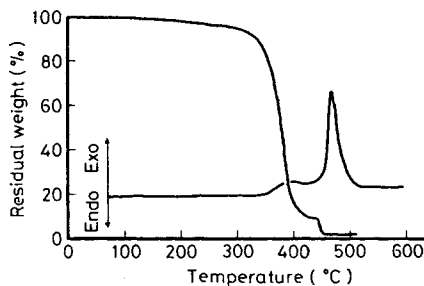

Fig. 5. TGA and DTA curves of metal-containing cured polyesters from (HEP-)$_2$Ca–ETDA–PGE (1:10:20).

TABLE VIII
Thermal Stability of Metal-Containing Cured Polyesters

Components	Mole ratio of components	Temperature of 10% weight loss, °C	Temperature of 50% weight loss, °C
(HEP-)$_2$Ca–ETDA–PGE	1:6:12	326	377
	1:10:20	334	377
(HEP-)$_2$Ca–DETDA–PGE	1:6:12	318	377
	1:10:20	322	376
(HEP-)$_2$Ca–PETDA–PGE	1:6:12	267	364
	1:10:20	276	364
(HEP-)$_2$Mg–ETDA–PGE	1:6:12	306	376
	1:10:20	324	378
(HEP-)$_2$Mg–DETDA–PGE	1:6:12	310	375
	1:10:20	317	374
(HEP-)$_2$Mg–PETDA–PGE	1:6:12	277	364
	1:10:20	274	363

Thermal Behavior and Electrical Resistance

Figure 5 shows, as a typical example, TGA and DTA curves in air of the metal-containing cured polyester from (HEP-)$_2$Ca–ETDA–PGE (1:10:20). In the TGA curve, the cured resin is thermally stable up to about 300°C, above which destruction proceeds rapidly. At 334°C the residual weight was 90%, and at 377°C it was 50%. The plateau observed above 450°C corresponds to the formation of CaCO$_3$.

The DTA curve, on the other hand, shows two exothermic peaks, probably due to degradations occurring via oxidative modes.

Table VIII shows the thermal stability data in air of the cured resins of various combinations of components. As is obvious on comparing the 10% weight loss temperatures of the resins containing the same components, the resins in which the mole ratio of (HEP-)$_2$M:bisester anhydride:PGE is 1:10:20 showed generally higher thermal stability than those in which the ratio is 1:6:12, due to higher crosslinking densities of the former resins. As for the influence of the species of bisester anhydride, the thermal stability decreases generally in the order ETDA > DETDA ≫ PETDA.

Furthermore, at the same mole ratio, as is obvious on comparing the resins based on the same bisester anhydride, Ca imparts generally better thermal stability than Mg; this tendency is especially remarkable in the resins based on ETDA. A similar tendency was observed also in the metal-containing cured resins of the previous studies.[8,10]

TABLE IX
Electrical Resistances of Metal Containing Cured Polyesters

Components (mole ratio)'	Volume resistivity, Ω·cm	Surface resistivity, Ω
(HEP-)$_2$Ca–ETDA–PGE (1:6:12)	2.99×10^{15}	5.90×10^{10}
(HEP-)$_2$Ca–ETDA–PGE (1:10:20)	2.44×10^{15}	2.77×10^{10}
(HEP-)$_2$Ca–DETDA–PGE (1:10:20)	1.45×10^{15}	2.94×10^{9}
(HEP-)$_2$Ca–PETDA–PGE (1:10:20)	2.80×10^{15}	2.19×10^{11}
(HEP-)$_2$Mg–ETDA–PGE (1:10:20)	2.33×10^{15}	3.92×10^{11}
(HEP-)$_2$Mg–DETDA–PGE (1:10:20)	1.81×10^{15}	8.57×10^{11}
(HEP-)$_2$Mg–PETDA–PGE (1:10:20)	1.16×10^{15}	9.42×10^{12}

Table IX shows electrical resistances of the representative cured resins.   They showed lower electrical resistances than the cured resins from $(HEP-)_2M$–anhydride–bisepoxide in the previous study.[10]   It is especially noteworthy that the surface resistivities of the former resins are considerably lower than those of the latter resins.

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