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Synthesis of Polymers by Using Divalent Metal Salts of Mono(hydroxyethyl)phthalate: Metal-Containing Unsaturated Polyesters

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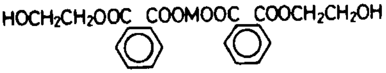
ABSTRACT

Syntheses of metal-containing unsaturated polyesters based on divalent metal salts (I) of mono(hydroxyethyl)phthalate were investigated by the polycondensation reactions of I—glycols with maleic anhydride (MA)-phthalic anhydride (PA). Among various combinations of components, the systems of MA-PA-diethylene glycol (DEG)-Mg salt, and MA-PA-ethylene glycol (EG)-propylene glycol (PG)-Mg salt gave polyesters soluble in styrene. Viscosities of styrene solutions of the polyesters obtained showed a tendency to increase with increase in metal content in the polyester. The styrene solutions could be cured. The cured polyester resins were evaluated for physical properties. Generally, the polyesters of MA-PA-EG-PG-Mg salt have good physical properties. Further, resistance to chemical attack and boiling water, and thermal behavior are also discussed.

INTRODUCTION

Since divalent metal salts (I) of mono(hydroxyethyl)phthalate (HEP) contain an ionic bond formed between $-COO^-$ and M^{2+}, and two hydroxyl groups, Structures I are considered to be of interest as ionic monomers from the scientific and industrial standpoints. The author has been active in the syntheses of ionic polymers by using I.



I

where M = divalent metal (Mg or Ca).

In previous studies the metal-containing polyurethanes [1], polyurethane-ureas [2] and isocyanurate-type cross-linked polyurethanes [3] based on I were synthesized, and interesting results were obtained.

In the present study, syntheses of metal-containing unsaturated polyesters based on I were investigated. These unsaturated polyesters contain ionic links in the main chain. The usual method of preparation of unsaturated polyesters containing ionic links in the main chain is such that an acid-terminated polyester is first prepared, and then the styrene solution of this polyester is neutralized with divalent metal ions [4-8]. This neutralization reaction, frequently referred to as "thickening," leads to a viscosity increase up to the semisolid state.

The metal-containing unsaturated polyesters in the present study were synthesized by the polycondensation reactions of I-glycols with maleic anhydride (MA)-phthalic anhydride (PA). The ionic unsaturated polyesters prepared by such a method are little known, so far as the author is aware. They were evaluated for physical and other properties.

EXPERIMENTAL

Materials

Divalent metal salts (I) of HEP were prepared according to the method reported in a previous paper [1].

MA and PA of extra pure grade were used without further purification.

Ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG) of extra pure grade, and polyethylene glycol (PEG) whose molecular weight was 200 (reagent chemical), were used as the glycols without further purification.

General Procedure of Polycondensation Reactions

One-Step Method. In a 200-ml flask equipped with a stirrer, a thermometer, a nitrogen inlet tube, and an apparatus to collect the water were placed fixed amounts of anhydrides, glycols, and I, and the mixture was heated to 190°C with stirring. The reaction was continued at this temperature for a fixed time. (Nitrogen gas was passed through the mixture during reaction.)

Two-Step Method. In a flask of the same type as above were placed fixed amounts of PA and glycols, and the mixture was heated to 200°C with stirring. The first-step reaction was continued for 6 hr at this temperature. Next, heating was discontinued and fixed amounts of MA and I were introduced to the reaction vessel and it was heated to 190°C with stirring. The second step reaction was continued at this temperature for a fixed time. (Nitrogen gas was passed through the mixture during reaction.) In the case of two-step method, the reaction times in Table 1 are those of the second-step reaction.

Syntheses of Metal-Containing Unsaturated Polyesters for Determination of Physical Properties and Others

The following two combinations of components were selected for the syntheses of polyesters for determination of physical and other properties: MA-PA-DEG-Mg salt and MA-PA-EG-PG-Mg salt.

A typical example of the syntheses of polyesters of MA-PA-DEG-Mg salt was as follows (two-step method): In a 1-liter flask equipped with a stirrer, a thermometer, a nitrogen inlet tube, and an apparatus to collect the water were placed 266.6 g (1.8 moles) of PA and 376.5 g (3.548 moles) of DEG, and the mixture was stirred at 190°C for 5 hr and then at 195°C for 5 hr (first-step reaction). Next, 176.5 g (1.8 moles) of MA, 23.11 g (0.0522 mole) of Mg salt and 0.1 g of hydroquinone as a polymerization inhibitor were added to the reaction vessel, and the mixture was stirred at 180°C for 3 hr and then at 200°C for 3 hr (second-step reaction). (Nitrogen gas was passed through the mixture during reaction.) The product (polyester) was slightly yellow, transparent, and had an acid value of 50.

A typical example of the syntheses of polyesters of MA-PA-EG-PG-Mg salt was as follows (one-step method): In a flask of the same type as above were placed 264.8 g (2.7 moles) of MA, 266.7 g (1.8 moles) of PA, 137.98 g (2.223 moles) of EG, 169.17 g (2.223 moles) of PG, and 23.9 g (0.054 mole) of Mg salt, and the mixture was stirred at 190°C for 1 hr and then at 180°C for 8 hr. (Nitrogen gas was passed through the mixture during reaction.) The product (polyester) was slightly yellow, transparent, and had an acid value of 88.

TABLE 1. Reaction of Dibasic Acid Anhydrides with Glycols-(HEP-)$_2$M at 190° C

Components[a] (molar ratio)	Metal content in feed (%)	Reaction time (hr)	Reaction system[b]	Method of reaction[d]
MA-PA-EG-(HEP-)$_2$Mg(5.5/5.5/10/1)	1.01	2	-	
MA-PG-(HEP-)$_2$Mg(10.5/10/0.5)	0.60	2	-	
MA-PA-PG-(HEP-)$_2$Mg(5.25/5.25/10/0.5)	0.53	2	-	
MA-DEG-(HEP-)$_2$Mg(10.25/10/0.25)	0.28	2	-	
MA-PA-DEG-(HEP-)$_2$Mg(5.25/5.25/10/0.5)	0.47	6	+	B
MA-PEG-(HEP-)$_2$Mg(10.5/10/0.5)	0.37	3	-	
MA-PA-PEG-(HEP-)$_2$Mg(5.05/5.05/10/1)	0.66	10	+[c]	B
MA-PA-EG-PG-(HEP-)$_2$Mg(6.12/4.08/5/5/0.2)	0.25	8	+	A
MA-PA-EG-DEG-(HEP-)$_2$Mg(6.3/4.2/5/5/0.5)	0.53	15	+[c]	A
MA-PA-PG-DEG-(HEP-)$_2$Mg(6.3/4.2/5/5/0.5)	0.51	3	-	
MA-PA-EG-(HEP-)$_2$Ca(5.125/5.125/10/0.25)	0.50	1	-	
MA-PG-(HEP-)$_2$Ca(10.25/10/0.25)	0.53	1	-	
MA-PA-PG-(HEP-)$_2$Ca(5.125/5.125/10/0.25)	0.47	1	-	
MA-PA-(HEP-)$_2$Ca(10.25/10/0.25)	0.46	1	-	
MA-PA-DEG-(HEP-)$_2$Ca(5.125/5.125/10/0.25)	0.41	1	-	

MA-PEG-$(\text{HEP-})_2$Ca(10.25/10/0.25)	0.32	1	-
MA-PA-PEG-$(\text{HEP-})_2$Ca(5.125/5.125/10/0.25)	0.30	1	-
MA-PA-EG-PG-$(\text{HEP-})_2$Ca(6.12/4.08/5/5/0.2)	0.40	1	-
MA-PA-EG-DEG-$(\text{HEP-})_2$Ca(6.12/4.08/5/5/0.2)	0.38	1	-
MA-PA-PG-DEG-$(\text{HEP-})_2$Ca(6.12/4.08/5/5/0.2)	0.36	1	-

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[a] MA = Maleic anhydride. PA = Phthalic anhydride. EG = Ethylene glycol. PG = Propylene glycol. DEG = Diethylene glycol. PEG = Polyethylene glycol.

[b] (+) Reaction system was homogeneous during reaction in case of the reaction method indicated. (-) In each of the one-step and two-step methods, reaction system became heterogeneous within the reaction time indicated.

[c] Reaction system became very viscous and was almost insoluble in styrene.

[d] A: One-step method. B: Two-step method.

Epoxide adducts of metal-containing unsaturated polyesters was prepared as follows: First, a metal-containing unsaturated polyester with an acid value of 77 to 86 was prepared in the same manner as above, and then, to this polyester, a fixed amount of propylene oxide (PO), or butylene oxide (BO), or glycidyl methacrylate (GM) was slowly added over 2 hr at 110 to 120° C. After the addition the reaction was continued for an additional 2 hr at the same temperature. The product (epoxide adduct) was slightly yellow, transparent, and had an acid value of 35 to 40.

Curing Reaction

The polyesters obtained were dissolved in fixed amounts of styrene, and, to the solutions, 0.5 wt% of a 60% dimethyl phthalate solution of methyl ethyl ketone peroxide and 0.5 wt% of a 10% styrene solution of cobalt naphthenate were added. The solutions were cured under the following condition, giving cured polyester resins: 40 C for 15 hr, 80 C for 4 hr, and 120° C for 2 hr.

Determination of Physical and Other Properties

Heat distortion temperature (HDT) was determined in accordance with ASTM-D 648-56. Tensile strength was determined according to ASTM-D 638-68. Flexural strength was determined according to ASTM-D 790-66. Compressive strength was determined according to ASTM-D 695-69. Impact strength was determined according to ASTM-D 256-56 (with Izod notch). Rockwell hardness was determined according to ASTM-D 785-62 (M scale).

Resistance to chemical attack was determined according to ASTM-D 543-67.

Boiling water resistance was determined according to ASTM-D 570-63.

Thermogravimetric analyses (TGA) were carried out in a Shimazu microthermobalance TGA-20 at a heating rate of 5 C/min. in air.

Differential thermal analyses (DTA) were carried out with a Shimazu thermal analyzer DT-20 B at a heating rate of 5 C/min in air.

RESULTS AND DISCUSSION

Syntheses of Metal-Containing Unsaturated Polyesters

Structure I will be hereafter denoted, in the same manner as in the previous papers [1-3], by $(\text{HEP-})_2\text{M}$, where HEP- denotes HEP residue.

Unsaturated polyesters are commercially prepared by reacting dicarboxylic acids or their anhydrides with glycols at comparatively high temperatures (generally at 160 to 200°C). MA is generally used as a component of unsaturated acid, and maleate groups are largely isomerized into fumarate homologs during esterification. With an increase in temperature, the degree of isomerization generally becomes higher [9], and the esterification reaction proceeds more rapidly.

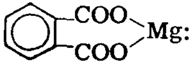
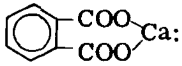
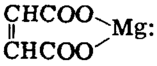
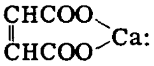
In the present study, synthetic experiments of metal-containing unsaturated polyesters were conducted at 190°C on various combinations of components. The following two methods were investigated in the experiments: A one-step method and a two-step method. In the one-step method all the components are placed in a reaction vessel at the beginning. In the two-step method the PA and glycols are reacted at 200°C for 6 hr in a flask (first step), and then MA and $(HEP-)_2M$ are added to the vessel to carry out the polycondensation at 190°C (second step). (In Table 1, reaction time in the case of two-step reaction is time of the second-step reaction.) The results are summarized in Table 1. At 190°C the reaction mixtures, except for some which were homogeneous (transparent) in the initial stage of reaction, became heterogeneous (opaque), producing white precipitates as the reaction proceeded. All the mixtures containing $(HEP-)_2Ca$ produced white precipitates within 1 hr. This tendency is not observed in the synthetic reactions of the usual unsaturated polyesters. The tendency to produce white precipitates was considered to be due to side reactions caused by $(HEP-)_2M$. With a view to obtaining information on side reactions, model reactions were carried out using MA or PA, EG, and $(HEP-)_2M$ at 190°C for 2 hr; all the reaction mixtures became heterogeneous and produced white precipitates during reaction. The white precipitates were separated from the mixture and purified by extracting the soluble part with dioxane. The analytical data of the white precipitates are shown in Table 2. The white precipitates contained considerably large amount of metal, and the yields were 3.2 to 6.3% (based on total components). From these results it follows that most of the $(HEP-)_2M$ which existed in the mixtures took part in side reactions to produce the white precipitates. The acid, OH, and ester values of the precipitates obtained from the PA-EG-$(HEP-)_2M$ systems were negligible, and the elemental analyses values found agreed well with the calculated values for the metal phthalates. Further, IR spectra showed a sharp absorption band at about 1400 cm^{-1}, which is characteristic of carboxylate groups. It is considered that the metal phthalates were formed through the interaction of PA with $(HEP-)_2M$.

On the other hand, the white precipitates obtained from the MA-EG-$(HEP-)_2M$ systems showed acid values of about 40 and the ester values of 171 to 196. Determination of OH values by the usual method was difficult because the solutions to be titrated became dark brown upon

TABLE 2. Analyses of White Precipitates Produced during Polycondensation Reaction

Components (molar ratio)	White Precipitate							Remarks
	Yield[a] (%)	Acid value	OH value	Ester value	Elemental analysis[b]			
					C (%)	H (%)	M (%)	
MA-EG-(HEP-)$_2$Mg (1.05/1/0.05)	4.4	41	-	196	35.90	4.50	9.57	Soluble in water
PA-EG-(HEP-)$_2$Mg (1.05/1/0.05)	3.2	0.4	0.7	11	49.70	2.05	13.06	Insoluble in water
MA-EG-(HEP-)$_2$Ca (1.05/1/0.05)	6.3	39	-	171	38.90	2.40	17.39	Soluble in water
PA-EG-(HEP-)$_2$Ca (1.05/1/0.05)	4.3	3.1	2.6	21	47.15	1.75	19.38	Insoluble in water

[a] Calculated on the basis of total components (wt-%).

[b] Analysis: Calculated for : C, 51.00%, H, 2.14%; Mg, 12.90%. Calculated for : C, 47.06%; H, 1.97%; Ca, 19.63%. Calculated for  $\overset{\text{CHCOO}}{\underset{\text{CHCOO}}{\|}}\!>\!\text{Mg}$: C, 34.72%; H, 1.46%; Mg, 17.57%. Calculated for  $\overset{\text{CHCOO}}{\underset{\text{CHCOO}}{\|}}\!>\!\text{Ca}$: C, 31.17%; H, 1.31%; Ca, 26.00%.

titration, a color known to be due to the interaction of the double bonds in maleate groups with pyridine. From this it is concluded that the white precipitates contain maleate groups. The elemental analyses values found for these precipitates did not agree with any of the calculated values for the metal phthalates or maleates. Therefore, the precipitates obtained from the systems containing MA are considered to be mixtures of various types of salts containing maleate groups. From these results it follows that at temperatures as high as 190° C the systems containing PA are apt to produce metal phthalates and those containing MA are apt to produce complicated salts other than metal maleates. Hence in Table 1 the precipitates produced are generally considered to consist of metal phthalates and complicated salts containing maleate groups.

As is clear from Table 1, the systems MA-PA-DEG-$(HEP-)_2$Mg and MA-PA-PEG-$(HEP-)_2$Mg were homogeneous when the two-step method was applied. Similarly, the systems MA-PA-EG-PG-$(HEP-)_2$Mg and MA-PA-EG-DEG-$(HEP-)_2$Mg were homogeneous when the one-step method was applied. The systems MA-PA-PEG-$(HEP-)_2$Mg and MA-PA-EG-DEG-$(HEP-)_2$Mg gave products (polyesters) which were almost insoluble in styrene, while the systems MA-PA-DEG-$(HEP-)_2$Mg and MA-PA-EG-PG-$(HEP-)_2$Mg gave products soluble in styrene. Therefore, MA-PA-DEG-$(HEP-)_2$Mg and MA-PA-EG-PG-$(HEP-)_2$Mg were selected for a study of the synthesis of metal-containing unsaturated polyesters containing various amounts of metal. In Table 3 are shown the results of syntheses of the polyesters of these two series. Series M-1 contains six polyesters in which the molar ratio of MA/PA was maintained constant at 1:1 but in which the glycols consisted of mixtures of DEG and $(HEP-)_2$Mg in various molar proportions. Series M-2 consisted of seven polyesters in which the molar ratios of MA/PA and EG/PG were maintained constant at 3:2 and 1:1, respectively, but in which the amount of $(HEP-)_2$Mg in the glycols varied.

It is generally recognized that fumarates are much more reactive than maleates toward styrene. The progress of the conversion of maleate to fumarate can be followed by IR measurement. In maleate polyesters a sharp, moderately strong absorption band at 7.17 μ, not present in fumarates, appears [10]. This band is known to give an excellent measure of the relative amounts of the maleate/fumarate forms. Further, the band at 8.42 μ is known to give a measure of the maleate form.

The polyesters of the M-1 series were prepared by the two-step method. In the second-step reaction at 180° C the degree of isomerization of maleate was not high as measured by IR spectra. However, it was found that by raising the temperature to 200° C the conversion of maleate to fumarate occurred to a comparatively high degree. Moreover, the reactions were carried out to acid values of 50 to 70 because the mixtures showed a tendency to become slightly translucent when

TABLE 3. Synthesized Polyesters of MA-PA-DEG-(HEP-)$_2$Mg and MA-PA-EG-PG-(HEP-)$_2$Mg

Polyester code	Molar ratio of components				Synthesis condition	Acid value of polyester	Metal content in polyester (%)	Viscosity of solution at 23°C in 30% styrene (cP)
	MA	PA	DEG	(HEP-)$_2$Mg				
M-1-B	1	1	2	-	First step:	69	-	400
M-1-1	18	18	35.48	0.522	190° C/5 hr	50	0.16	820
M-1-2	18	18	34.94	1.062	195° C/5 hr	60	0.32	1070
M-1-3	17	17	32.48	1.717	Second step:	61	0.53	1060
M-1-4	17	17	31.13	2.873	180° C/3 hr	63	0.85	1392
M-1-5	17	17	30.29	3.706	200° C/3 hr	68	1.04	1532
	MA	PA	EG	PG	(HEP-)$_2$Mg			
M-2-B	3	2	2.5	2.5	-	180° C/8 hr	84	-	1820
M-2-1	27	18	22.23	22.23	0.54	190° C/1 hr 180° C/8 hr	88	0.17	2020
M-2-2	22.5	15	18.3	18.3	0.9	180° C/8 hr	78	0.32	2348
M-2-2'	22.5	15	18.3	18.3	0.9	170° C/10 hr 200° C/2 hr	53	0.32	3800
M-2-3	24	16	18.6	18.6	2.8	180° C/9 hr	83	0.85	2217
M-2-3'	24	16	18.6	18.6	2.8	170° C/7 hr 200° C/5 hr	45	0.85	9160
M-2-4	24	16	18.18	18.18	3.648	190° C/1 hr 170° C/5 hr	84	1.07	2970

the acid value was reduced below about 50. The viscosities of styrene solutions of the polyesters increased with an increase in the metal content.

On the other hand, the polyesters of the M-2 series were prepared by the one-step method. When the reactions were conducted at above 200° C, the mixtures showed a tendency to produce white precipitates as the reaction proceeded. Thus, at too high temperature (above 200° C), side reactions producing white precipitates began to occur. The conditions for the M-2 series polyesters were as shown in Table 3. In the case of reactions at 180° C, when the acid value was reduced to below about 60, the mixtures showed a tendency to become slightly translucent. Hence the reactions were stopped when the acid value became 78 to 88. Infrared spectra showed that at 180° C, maleate fully isomerized to fumarate. It is known that in the polyesterification of MA the longer the chain of the glycol, the lower the isomerization rate, due mainly to the steric effects caused by the different types of glycols used in the polycondensation, and that in systems containing PG the isomerization rate is much higher than it is in systems containing DEG [9]. At 170° C the mixtures were transparent even after 7 to 10 hr, with acid values was 60 to 70. Raising the temperature to 200° C caused full isomerization, and the acid value could be reduced to 45 to 53 after an additional 2 to 5 hr. The mixtures were still transparent; however, carrying out the polycondensation further was difficult because the mixtures showed a tendency to become very viscous as the acid values were further reduced. The polyesters of M-2-2' and M-2-3' were prepared under these conditions. It is of interest that raising the temperature to 200° C after the degree of condensation had become comparatively high caused no side reactions. In the case of the M-2-4 polyester containing 1.07% Mg, as the reaction proceeded the mixtures became very viscous due to very high metal content; that is, there was a high concentration of ionic links in the mixture, thus, reducing the acid value to about 60 was difficult at 170° C. Also in the M-2 series polyesters the viscosity of the styrene solution showed a tendency to increase with an increase in the metal content. Moreover, in case of the M-2-2' and M-2-3' polyesters with lower acid values, the viscosities of the styrene solutions were higher. In the case of the latter polyester the viscosity was extremely high.

In order to obtain products with acid value below 40, epoxides such as PO, BO, and GM were used. That is, first the polyester corresponding to M-2-2 was prepared, and then the above epoxides were added to the terminal unreacted carboxyl groups of the polyester through the addition reaction of the epoxy group with the carboxyl group to produce an ester linkage. The addition reactions were carried out by slowly adding epoxides into the polyester at 110 to 120° C. The results are shown in Table 4. Epoxide adducts with acid values below 40 were obtained.

TABLE 4. Epoxide Adducts of Metal-Containing Unsaturated Polyesters

Epoxide adduct code	Epoxide[a]	Acid value before addition of epoxide	Acid value after addition of epoxide	Epoxy value	Metal content in adduct (%)	Viscosity of solution at 23°C in 30% styrene (cP)
M-2-2-PO[b]	PO	86	40	0.17	0.30	1096
M-2-2-BO[b]	BO	77	35	0.41	0.30	2210
M-2-2-GM[b]	GM	85	35	0.34	0.30	1020

[a] PO = Propylene oxide. BO = Butylene oxide. GM = Glycidyl methacrylate.

[b] Composition of polyesters before addition of epoxide corresponds to that of M-2-2 in Table 3.

Physical Properties

The metal-cpntaining unsaturated polyesters in Table 3 and 4 were soluble in styrene, and the styrene solutions of the polyesters (resins solutions) were cured in the manner described in the experimental section. The physical properties of the cured polyester resins are summarized in Table 5. The M-1 series of polyester resins was flexible and showed comparatively poor physical properties, but the impact strengths were excellent. This tendency is considered due mainly to the oxygen-ether group in the DEG used as a glycol component.

On the other hand, in case of the M-2 series of polyester resins, generally good physical properties were observed. It is obvious by comparing the polyesters having similar acid values that the impact and compressive strengths have a tendency to increase with an increase in $(HEP-)_2M$ content (metal content), and no major difference was observed in the heat distortion temperature (HDT). The tensile and flexral strengths showed maximum values at a Mg content of 0.32% (M-2-2 polyester). Rockwell hardness showed the highest value at a Mg content of 1.07% (M-2-4 polyester); thus the effect of introducing metal clearly appears in this case. However, to a great extent increasing the metal content reduces the tensile and flexural strengths (M-2-4 polyester). On comparing polyesters with the same metal content, the polyesters with lower acid values showed higher HDT (M-2-2 vs M-2-2', and M-2-3 vs. M-2-3'). It has been shown that HDT is improved as the length of the unsaturated polyester chain is increased. In summary of the results described above, polyesters with a Mg content of 0.32% have excellent physical properties.

As for the epoxide adducts, the addition of PO and BO reduces the HDT, Rockwell hardness, and compressive strength, indicating that terminal hydroxypropyl and hydroxybutyl groups have a plasticizing effect. However, the M-2-2-PO resin has high tensile and flexural strengths. Addition of GM increases the HDT, tensile strength, and Rockwell hardness due to an increase in the cross-linking density of the cured resin.

Resistance to Chemical Attack

As shown in Table 6, the metal-containing cured resins were generally unaffected in external appearance by 30% H_2SO_4, 95% ethanol and benzene. In 10% NaOH, most of cured resins became slightly yellow, but the cured resin of M-2-2-GM was unaffected. All cured resins were disintegrated by acetone, except for the M-2-3 resin (Mg content of the polyester = 0.85%) which was slightly disintegrated (corners of the sample were slightly disintegrated).

TABLE 5. Physical Properties of Cured Polyester Resins (70% Polyester-30% Styrene)

Polyester	Mg in polyester (%)	Heat distortion temp (°C)	Tensile strength (kg/cm^2)	Flexural strength (kg/cm^2)	Rockwell hardness	Impact strength [(kg)(cm)/cm]	Compressive strength (kg/cm^2)
M-1-B	-	29	293	-	103	2.57	396
M-1-1	0.16	22	279	-	103	2.89	305
M-1-2	0.32	26	293	-	110	2.14	522
M-1-3	0.53	22	218	-	104	2.27	302
M-1-4	0.85	27	265	-	108	1.66	473
M-1-5	1.04	22	216	-	103	1.53	378
M-2-B	-	92	538	712	117	0.93	1572
M-2-1	0.17	78	544	971	116	0.89	1626
M-2-2	0.32	81	605	1259	117	1.11	1613
M-2-2'	0.32	85	618	1264	117	1.29	1480
M-2-3	0.85	79	518	977	116	1.26	1721
M-2-3'	0.85	91	471	873	117	1.23	1476
M-2-4	1.07	85	305	552	119	1.28	1695
M-2-2-PO	0.30	67	716	1173	114	1.23	1344
M-2-2-BO	0.30	78	601	758	115	1.17	1402
M-2-2-GM	0.30	85	742	1133	118	1.19	1455

TABLE 6. Resistance of Cured Polyester Resins (70% Polyester-30% Styrene) to Chemical Attack

Reagent	Change in weight (%) and external appearance[a] (in parenthesis)						
	M-2-B	M-2-2	M-2-2'	M-2-3	M-2-3'	M-2-2-PO	M-2-2-GM
30% H_2SO_4	+0.26(UA)	+0.23(UA)	+0.22(UA)	+0.39(UA)	+0.91(UA)	+0.34(SW)	+0.27(UA)
10% NaOH	-0.36(SY)	+0.17(SY)	-0.37(SY)	-0.58(SY)	-0.61(SY)	-1.69(SY)	0 (UA)
95% Ethanol	+1.45(UA)	+0.86(UA)	+0.30(UA)	+1.20(UA)	0 (UA)	+2.10(SW)	+0.37(UA)
Acetone	- (DI)	- (DI)	- (DI)	- (DI)	- (SD)	- (DI)	- (DI)
$ClCH_2CH_2Cl$	+0.64(UA)	- (DI)	+2.00(UA)	- (DI)	+2.29(UA)	- (DI)	+1.20(UA)
10% NaCl	+0.25(UA)	+0.50(SW)	+0.50(UA)	+0.74(SW)	+0.63(UA)	+0.73(SW)	+0.52(UA)
Benzene	-0.04(UA)	+0.98(UA)	0 (UA)	+0.09(UA)	0 (UA)	+0.14(UA)	+0.19(UA)
Distilled water	+0.54(UA)	+0.70(SW)	+0.59(UA)	+1.01(SW)	+0.66(UA)	+1.08(SW)	+0.69(UA)

[a] UA = Unaffected. SY = Sample became slightly yellow. SW = Surface of sample became slightly white. SD = Sample was slightly disintegrated. DI = Sample was disintegrated.

TABLE 7. Boiling Water Resistance of Cured Polyester Resins (70% Polyester-30% Styrene)

Polyester	Mg in polyester (%)	Change in thickness (%)	Change in weight (%)	External appearance[a]
M-2-B	-	+0.79	+1.07	UA
M-2-2	0.32	+0.50	+1.79	SW, ND
M-2-2'	0.32	+0.60	+1.64	SW, ND
M-2-3	0.85	+1.59	+2.35	W, ND
M-2-3'	0.85	+0.90	+1.75	SW, ND
M-2-2-PO	0.30	+0.88	+2.25	SE
M-2-2-GM	0.30	+0.66	+1.83	UA

[a] UA = Unaffected. SW = Surface of sample became only slightly white. W = Surface of sample became white. SE = Surface of sample was *only slightly* eroded. ND = Sample showed no deformation.

In ethylene dichloride the M-2-2 and M-2-3 resins with higher acid values, and the M-2-2-PO resin were disintegrated. The M-2-2' and M-2-3' resins with lower acid values, the M-2-2-GM resin, and the blank resin (M-2-B) were unaffected in appearance. Further, in 10% NaCl and distilled water, the surfaces of the samples of the M-2-2, M-2-3, and M-2-2-PO resins became slightly white; the M-2-2', M-2-3' and M-2-2-GM resins and the blank resin (M-2-B) were unaffected in appearance. Thus the effect of reducing the acid values clearly appears. This effect appears most clearly in ethylene dichloride. As for the epoxide adducts, GM is more effective than PO in giving chemical resistance.

Boiling Water Resistance

Table 7 shows the boiling water resistance of the cured polyester resins. The metal-containing cured resins showed higher water absorption than the blank resin (M-2-B). The water absorption increased with an increase in Mg content. Moreover, reducing the acid values showed a tendency to decrease the water absorption. On the other hand, the M-2-2-PO resin showed a higher water absorption than the M-2-2-GM resin. As for external appearance, the surfaces of the samples of the M-2 series resins containing Mg became slightly white or white. The M-2-2-PO resin was only slightly eroded. It is notable that the M-2-2-GM resin was unaffected by boiling water due to high cross-linking density.

All samples of the cured resins showed no deformation.

Thermal Behavior

Figure 1 shows representative TGA and DTA curves in air of the

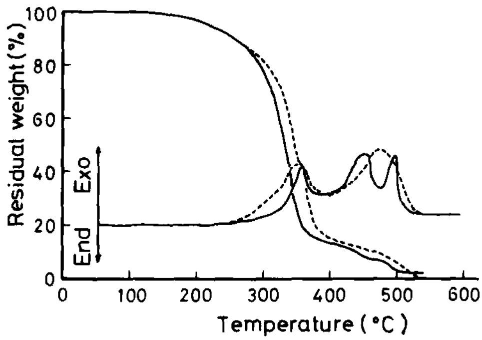


FIG. 1. TGA and DTA curves of cured polyester resins (70% polyester-30% styrene). (——) M-2-3' polyester resin. (--) M-2-B polyester resin.

cured polyester resins. The DTA curve of the M-2-3' resin shows three exothermic peaks, while that of the blank resin (M-2-B) shows two exothermic peaks, probably due to degradations occurring via oxidative modes. In the TGA curves the M-2-3' resin and the blank resin show a 50% weight loss at temperatures of 332 and 347° C, respectively. In the case of the former resin, the plateau observed above about 500° C corresponds to the formation of $CaCO_3$.

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REFERENCES

[1] H. Matsuda, J. Polym. Sci., A-1, 12, 455 (1974).
[2] H. Matsuda, Ibid., A-1, 12, 469 (1974).
[3] H. Matsuda, Ibid., A-1, 12, 2419 (1974).
[4] I. Vancsó-Szmercsányi and E. Vöö, Kunststoffe, 58, 907 (1968).
[5] H. Krämer, K. Conze, and N. Träger, Ibid., 58, 913 (1968).
[6] I. Vancsó-Szmercsányi, Ibid., 60, 1066 (1970).
[7] I. Vancsó-Szmercsányi, Ibid., 58, 25 (1968).
[8] F. B. Alvey, J. Polym. Sci., A-1, 9, 2233 (1971).
[9] I. Vancsó-Szmercsányi, L. K. Maros, and A. A. Zahran, J. Appl. Polym. Sci., 10, 513 (1966).
[10] R. E. Park, R. M. Johnston, A. D. Jesensky, and R. D. Cather, SPE J., 17, 1088 (1961).

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