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Water-Containing Cured Resin from Inverted Emulsion of Unsaturated Polyester Based on Divalent Metal Salt of Mono(hydroxyethyl)phthalate

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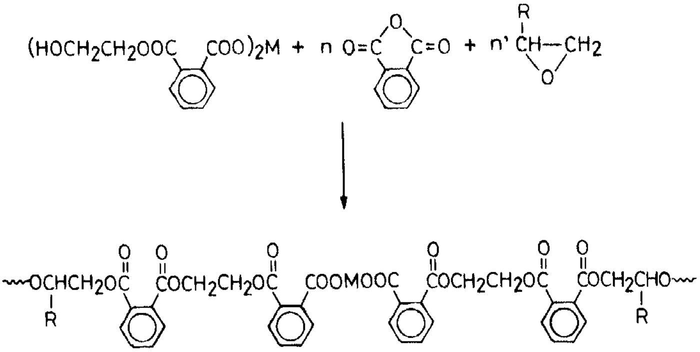
ABSTRACT

Inverted emulsion, i.e., water-in-oil (W/O) type emulsion, was prepared from styrene solution of unsaturated polyester obtained from Mg salt of mono(hydroxyethyl)phthalate, ethylene glycol (EG), maleic anhydride (MA), phthalic anhydride (PA), and propylene oxide (PO). The inverted emulsion was much more stable than that of blank polyester obtained from EG, MA, PA, and PO, and further than the usual inverted emulsion prepared by treating styrene solution of commercial unsaturated polyester with triethanolamine. By polymerization, the inverted emulsion was transformed to a white solid which was dry to the touch. The water-containing cured resin obtained showed considerably higher physical and other properties than those of commercial unsaturated polyester.

INTRODUCTION

It was shown previously [1] that when divalent metal salts of mono(hydroxyethyl)phthalate (HEP), that is, $(HEP-)_2M$ (where HEPdenotes the HEP residue and M is a divalent metal), are used in the (HEP-)$_2$M-phthalic anhydride (PA)-epoxide reactions, metal-containing polyesters containing ionic links are obtained, as shown by Eq. (1), where M = Mg or Ca.


(1)

Further, by applying the above synthetic route to the synthesis of unsaturated polyesters, unsaturated polyesters have been prepared from (HEP-)$_2$M, ethylene glycol (EG), PA, maleic anhydride (MA), and epoxides such as propylene oxide (PO) and butylene oxide (BO) [2]. The unsaturated polyesters obtained were soluble in styrene, and the styrene solutions could be cured to give metal-containing cured resins. Among them, Mg-containing cured resins based on PO showed the best physical properties. In later investigations it was found that the styrene solutions form inverted emulsions, i.e., water-in-oil (W/O) type emulsions, by the addition of water.

Recently, it has been reported [3-5] that various basic compounds act as very effective W/O emulsifiers for unsaturated polyesters. The basic compounds react with the free carboxyl group of the polyester to form in situ polyester salts which act as emulsifying agents. The inverted emulsions are transformed, by polymerization, to white solid resins which are dry to the touch. The water-containing resins obtained have many potential applications [4-6]; among them, the use as a low-cost molding material is particularly attractive.

The styrene solutions of the unsaturated polyesters based on (HEP-)$_2$M contain ionic links and are considered suitable for the preparation of water-containing cured resins. This paper deals with a new type of water-containing cured resins from inverted emulsions of the unsaturated polyester based on (HEP-)$_2$Mg. The preparation of a stable inverted emulsion is also discussed.

EXPERIMENTAL

Synthesis of Unsaturated Polyesters

Polyester $(HEP-)_2Mg$-EG-MA-PA-PO (0.1906:0.8094:4.8:3.2:8.4). In a 1-L flask equipped with a stirrer, thermometer, condenser, and dropping funnel were placed 0.0864 mol of $(HEP-)_2Mg$, 0.367 mol of EG, 2.1763 mol of MA, and 1.4509 mol of PA, and the mixture was stirred at 130°C for 1 h. Next, 2.8564 mol of PO was dropped into the mixture with stirring at 130°C over 1.5 h. After the addition, and adding 0.1 g of hydroquinone (HQ), the mixture was heated to 210°C, at which stirring was continued for 4 h. Then, an additional 0.9522 mol of PO was added at 160-170°C over 1 h. After the addition, the mixture was further stirred for 30 min at the same temperature. The polyester thus obtained (MP-03) showed an acid value of 7.59. The viscosity of the solution in 30% styrene was 4320 cP.

Blank Polyester EG-MA-PA-PO (1:4.8:3.2:8.4). In a flask of the same type as above were placed 0.4757 mol of EG, 2.2836 mol of MA, 1.5224 mol of PA, 3.25 g of trimethylbenzylammonium chloride as a catalyst, and 0.1 g of HQ, and the mixture was stirred at 100°C for 1 h. Next, 3.9962 mol of PO was dropped slowly into the mixture with stirring at 100-120°C over 4 h. After dropping, the mixture was further stirred at the same temperature for 1 h. The blank polyester (MP-B) thus obtained showed an acid value of 1.71. The viscosity of the solution in 30% styrene was 1040 cP.

Preparation of Inverted Emulsions

A fixed amount of water was added slowly to the styrene solution of unsaturated polyester at 40°C with stirring to give an inverted emulsion.

The emulsion stability was estimated from the rates of phase separation of the emulsions. Separation curves were obtained by reading the change of the height of the interface between the separated phases in a test tube.

For comparison, a commercial, casting purpose, unsaturated polyester (Estar C 1510, styrene content = about 35%) was also used; inverted emulsion was prepared by the reported method [5] using triethanolamine (TEA).

Preparation of Water-Containing Cured Resins

To the styrene solution of unsaturated polyester, 1 wt% of 2% styrene solution of cobalt naphthenate was added, and then a fixed amount of water was slowly added to the solution at 40° C with stirring to give an inverted emulsion. Next, the inverted emulsion thus obtained was cured by heating at 60° C for 4 h with methyl ethyl ketone peroxide (MEKPO) initiator to give a dry-to-the-touch resin containing water.

In the case of the Estar C 1510 emulsion for comparison, benzoyl peroxide (BPO) was used as initiator [5].

Determination of Physical and other Properties

Heat distortion temperature (HDT) was determined according to ASTM-D 648-56 (fiber stress = 4.6 kg/cm^2), tensile strength to ASTM-D 638-68, flexural strength to ASTM-D 790-66, and compressive strength according to ASTM-D 695-69. Resistance to chemical attack was determined according to ASTM-D 543-67.

Time dependence of water content of water-containing cured resins was determined for the specimens of 12.5-13.5 × 1.27 × 1.27 cm which were cut from the cured resins.

RESULTS AND DISCUSSION

Stability of Inverted Emulsions

It was found in the previous study [2] that the unsaturated polyester obtained from the $(HEP-)_2Mg$-EG-MA-PA-PO system with an Mg content of 0.3% gave a cured resin with the best balance of physical properties. Therefore, as shown in the experimental section, the Mg-containing system in which the MA/PA molar ratio is 3/2 and the Mg content is 0.3% was selected for the preparation of unsaturated polyester for water-containing cured resins. This polyester will be denoted as MP-03. The solution of MP-03 in 35% styrene (resin solution) was used for the preparation of inverted emulsions and water-containing cured resins. Also, the blank polyester was prepared as described in the experimental section; this will be denoted as MP-B. The solution of MP-B in 30% styrene was used for the investigation.

On the other hand, it has been found [3-5] that a stable inverted emulsion can be formed when pK_a' values of the bases are above 6 and the base concentrations are higher than some critical values; in this observation, triethanolamine (TEA) was studied in detail and was found to be a very effective W/O emulsifier. Therefore, using a commercial, casting purpose, unsaturated polyester resin solution (Estar C 1510, styrene content = about 35%), an inverted emulsion was prepared as a reference emulsion, using TEA.

The stability of inverted emulsions was estimated by the rate of

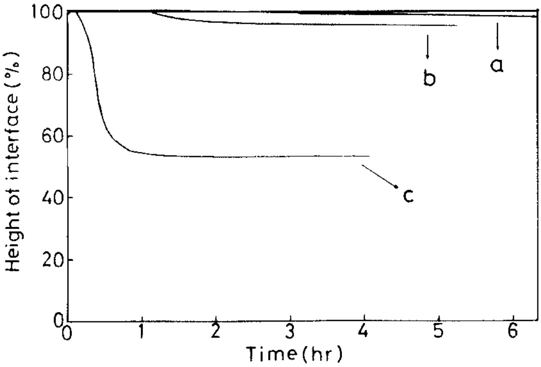


FIG. 1. Separation curves of inverted emulsions of unsaturated polyester resin solutions at 60°C. (a) MP-03; (b) Estar C 1510 with TEA (0.55 mmol/g); (c) blank polyester (MP-B). Weight ratio of resin solution:water = 1:1.

phase separation of the emulsion. Figure 1 shows phase separation curves at 60°C of the inverted emulsions prepared at a weight ratio of resin solution:water = 1:1. The blank emulsion (of MP-B) not containing Mg collapsed within 30 min. Thus the MP-B polyester was found to be unsuitable for preparation of emulsion. In contrast to this emulsion, the emulsion of MP-03 did not collapse for at least 3 hr and even after 3 h the phase separation was extremely small or almost negligible. In case of the reference emulsion (of Estar C 1510) which was prepared at a TEA concentration of 0.55 mmol/g of resin solution (far above the critical concentration), phase separation occurred after about 1 h.

Figure 2 shows the time dependence of viscosity at 23°C of the inverted emulsions containing 50% water. The emulsion of MP-03 was very stable for more than 20 days, the viscosity remaining almost unchanged. Meanwhile, the reference emulsion (of Estar C 1510) showed a marked decrease of viscosity with time and became impractical for use as the inverted emulsion after 5 days, even though the initial viscosity was much higher than that of the Mg-containing emulsion. It is worthy of note that the difference of emulsion stabilities appears more clearly at room temperature.

Thus the emulsion of MP-03 was found to be much more stable than the usual inverted emulsion at both room and higher temperatures. This very high stability of the Mg-containing emulsion is considered to assure the subsequent curing of the emulsion under a wide range of polymerization conditions. The polymerization is considered to be completed long before the collapse of the inverted emulsions.

It has been considered that for obtaining stable inverted emulsions

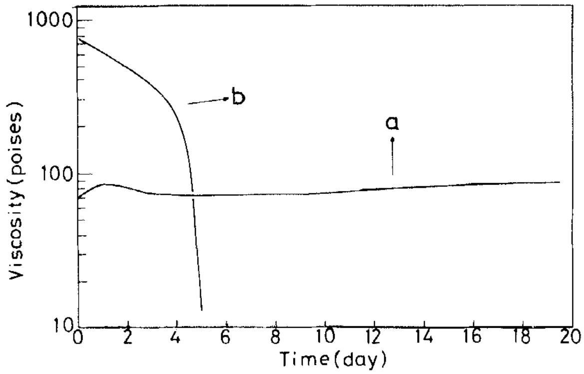


FIG. 2. Time dependence of viscosity at 23°C of inverted emulsions of unsaturated polyester resin solutions. (a) MP-03; (b) Estar C 1510 with TEA (0.55 mmol/g). Weight ratio of resin solution:water = 1:1.

of unsaturated polyesters of high molecular weight, high viscosity, and high polarity, both the hydrophilic and lipophilic affinities of W/O emulsifier must be strong. The Mg-salts of the polyester itself seem to satisfy these requirements thoroughly. The Mg-salts are considered to accumulate at the water-resin solution interface, stabilizing the inverted emulsions.

It has been known [3, 4, 7, 8] that the mechanism of polymerization in inverted emulsion is not very different from that of ordinary radical polymerization. The polymerization proceeds in the resin solution phase. The inverted emulsion obtained in the present study could be cured by using a radical-type initiator such as MEKPO to give a dry-to-the-touch resin containing water.

Physical and Other Properties of Water-Containing Cured Resins

Table 1 shows the physical properties of water-containing cured resins prepared at a weight ratio of unsaturated polyester resin solution:water = 1:1. The water-containing cured resin of MP-03 showed considerably higher physical properties than the water-containing cured resin of the reference polyester (Estar C 1510); the flexural and compressive strengths were especially much higher. Thus the difference of stabilities of the inverted emulsions is well reflected in these physical properties.

Figure 3 shows the effect of water content on physical properties of the water-containing cured resin of MP-03. The tensile, flexural, and compressive strengths decrease with an increase in the water content. The values at about 70% water content are about one-third

TABLE 1. Physical Properties of Water-Containing Cured Resins Prepared at a Weight Ratio of Unsaturated Polyester Resin Solution: Water = 1:1

Properties	Water-containing cured resin based on MP-03	Water-containing cured resin basded on reference polyester[a]
Heat distortion temperature (°C)	76	47
Tensile strength (kg/cm^2)	140	104
Flexural strength (kg/cm^2)	262	114
Compressive strength (kg/cm^2)	227	123

[a] Reference polyester of Estar C 1510.

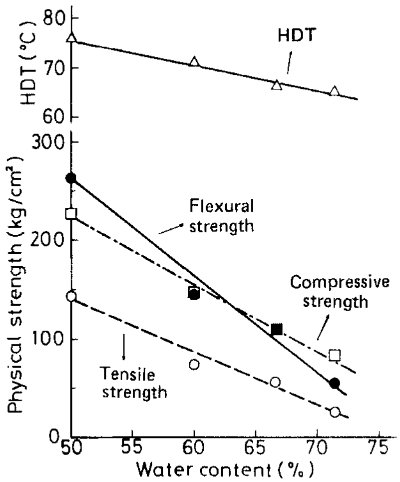


FIG. 3. Effect of water content on physical properties of water-containing cured resins based on MP-03.

TABLE 2. Resistance to Chemical Attack of Water-Containing Cured Resins Prepared at a Weight Ratio of Unsaturated Polyester Resin Solution:Water = 1:1

	Water-containing cured resin based on MP-03				Water-containing cured resin based on reference polyester[a]			
Chemical	Appearance[b]	Change in length (%)	Change in width (%)	Change in weight (%)	Appearance[b]	Change in length (%)	Change in width (%)	Change in weight (%)
Distilled water	U	+0.4	+0.1	+0.25	U	+0.4	+0.3	+3.23
10% NaCl	U	0.0	0.0	-0.20	U	-0.8	-0.9	+0.55
10% NaOH	U	0.0	0.0	-0.75	SY, SH	-4.8	-4.4	-9.92
30% H_2SO_4	U	-0.4	-0.3	-2.05	SR, SH	-3.6	-2.6	-12.38
95% Ethanol	SR	-1.2	-0.6	-6.87	SR	-2.8	-2.7	-13.02
Benzene	CR	+2.0	+0.3	+2.01	S, CR	+4.4	+3.4	+15.26
Acetone	S, SC	+6.0	+5.8	+13.42	D	-	-	-
$ClCH_2CH_2Cl$	S, CR	+7.6	+7.2	+44.42	S, CR	+12.1	+11.9	+54.34

[a] Reference polyester of Estar C 1510.

[b] U = unaffected, SY = sample became slightly yellow, SR = surface of sample became slightly rough, S = sample was swollen, CR = sample cracked, SC = sample slightly cracked, SH = sample slightly shrinked, D = disintegrated.

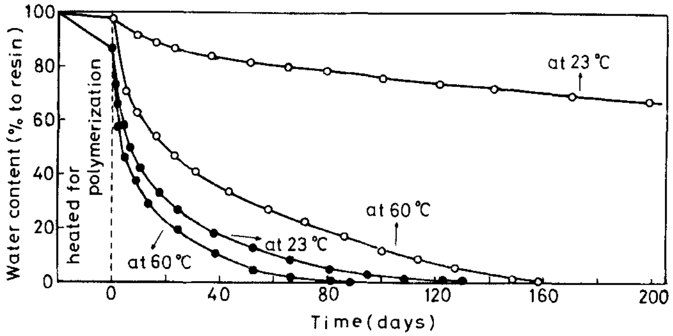


FIG. 4. Time dependence of water content of water-containing cured resins prepared at a weight ratio of unsaturated polyester resin solution:water = 1:1. (○) Water-containing cured resin based on MP-03; (●) water-containing cured resin based on Estar C 1510.

to one-fourth the values at 50% water. In case of the HDT, a marked decrease was not observed; increasing the water content to about 72% reduced the HDT to 65°C (11°C decrease).

The tensile strength at 60% water is close to that [6] of wood (84 kg/cm^2 in the case of No. 2 pine); however, at 50% water the strength is much higher than that of wood. Similarly, the compressive strength at about 72% water is still higher than that [6] of wood (21-63 kg/cm^2).

Although the compressive strength at 50% water is less than that [6] of concrete (316 kg/cm^2), the tensile strength is much higher than that [6] of concrete (21 kg/cm^2) over a wide range of water content in the cured resin.

Table 2 shows the resistance to chemical attack of the water-containing cured resins. The water-containing cured resin of MP-03 was unaffected in external appearance by aqueous chemical solvents such as distilled water, 10% NaCl, 10% NaOH, and 30% H_2SO_4; the dimensional and the weight changes were generally smaller than those of the water-containing cured resin of the reference polyester, which slightly shrinked in 10% NaOH and 30% H_2SO_4.

Against benzene and ethylene dichloride, the former resin showed smaller dimensional and weight changes than the latter resin, especially so against benzene. In acetone, the former resin was swollen and slightly cracked, while the latter resin was disintegrated.

In summary, the water-containing cured resin of MP-03 has considerably better resistance to chemical attack than has the reference polyester.

Figure 4 shows the time dependence of the water content of the water-containing cured resins prepared at a weight ratio of unsaturated polyester resin solution:water = 1:1. At room temperature (at 23°C) the cured resin based on MP-03 retained 68% of initially

TABLE 3. Physical Properties of Water-Containing Cured Resins (based on MP-03) Prepared by Using a Slurry of Gypsum-Water (1:1)

	Amount of added slurry of gypsum-water (1:1)		
Properties	50% to resin	100% to resin	200% to resin
Heat distortion temperature (°C)	78	71	72
Tensile strength (kg/cm^2)	219	116	70
Flexural strength (kg/cm^2)	316	193	119
Compressive strength (kg/cm^2)	492	279	195

added water after about 200 days. However, at 60°C the loss of water was more rapid and the resin lost most of added water after about 160 days. Thus the loss of water is influenced considerably by temperature. On the other hand, the reference cured resin based on Estar C 1510 showed much more rapid loss of water at both room and higher temperatures. It is considered that water droplets in the latter cured resin are more connected with one another than those in the former cured resin. It is also apparent from this that the Mg-salts of the polyester itself act as powerful W/O type emulsifier.

Stable inverted emulsions containing filler can also be prepared by adding a slurry of filler-water into the resin solution with vigorous stirring. They are transformed, by polymerization, to water-containing cured resins with filler. Table 3 shows, as an example, the physical properties of water-containing cured resins prepared by using a slurry of gypsum (calcium sulfate hemihydrate)-water (weight ratio = 1:1). The tensile, flexural, and compressive strengths have a tendency to decrease with an increase in the amount of added slurry. The values at 200% added slurry (to resin) are about one-third to two-fifths the values at 50% added slurry. However, HDT is not affected very much by the amount of added slurry.

Generally, water-containing cured resins are known to shrink because they slowly lose water on aging by transpiration of water vapor through the resin. The rate of water loss depends on sample thickness, surface treatment, initial water content, quality of emulsion, aging temperature, etc. On the other hand, the water-containing cured resins with gypsum showed little shrinkage on aging at both room and high temperatures. That is, the postmolding shrinkage of the water-containing cured resins could be almost eliminated by using fillers such as gypsum.

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