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Effect of Cement on Properties of Inverted Emulsions and Polymers from Vinyl Monomers with Acid Anhydride-Adducted Polypropylene Glycol

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ABSTRACT

Adduct polymer (PPGMA) prepared from polypropylene glycol and maleic anhydride was found to give stable inverted emulsions when mixtures of cement, water, and vinyl monomers were vigorously stirred in the presence of PPGMA. In this case, the carboxyl groups of PPGMA were neutralized with metal ions generated from the cement into neutralized PPGMA which acts as an effective W/O type emulsifier. The inverted emulsions containing cement gave a new type of polymer-cement composites by polymerization of the vinyl monomers and also by hardening of the cement. Water-free composites were easily obtained by removing evaporative water. The effect of cement on the physical properties of the water-free composites was remarkable. Further, the use of mixed fillers of cement and $\text{Al}(\text{OH})_3$ was found to improve the flame-retardant properties of the composites; however, increasing the $\text{Al}(\text{OH})_3$ content in the fillers resulted in a decrease in the physical properties. Generally, the composites have improved resistance to acid media in which the usual foamed hydrated cement is eroded.

INTRODUCTION

It has been reported [1] that a partially neutralized adduct polymer which was prepared by the partial neutralization with MgO of an adduct polymer (PPGMA) from polypropylene glycol (PPG) and maleic anhydride (MA) acts as an effective water-in-oil (W/O) type emulsifier for vinyl monomers such as styrene (St), acrylonitrile (AN), and ethylene glycol dimethacrylate. The emulsifier gives inverted emulsions having very low viscosities. Water-containing polymers obtained by polymerization of the inverted emulsions are characterized by a very high rate of water loss; thus, foamed polymers were easily obtained by removing water.

More recently it has been found [2] that stable inverted emulsions can also be obtained by adding a slurry of CaCO_3 -water into the vinyl monomers in the presence of PPGMA which had not been neutralized. In this case at least part of the carboxyl groups of PPGMA were considered to be neutralized with Ca^{2+} generated from CaCO_3 into partially neutralized PPGMA which acts as an effective W/O type emulsifier.

It was expected that cement also could be used in the above case instead of CaCO_3 , because cement is alkaline. Therefore, in the present study, effects of cement on the formation and properties of the inverted emulsions of vinyl monomers containing PPGMA were investigated. The obtained inverted emulsions containing cement gave a new type of polymer-cement composites by polymerization of the vinyl monomers and also by hardening of the cement. Further, the effects of $\text{Al}(\text{OH})_3$ on flame retardance and other properties of the polymer-cement composites were also investigated.

Polymer-cement composites have usually been classified into the following four groups [3]: 1) Water-retentive grouts and mortars, 2) fiber-reinforced concretes, 3) polymer-impregnated concretes, and 4) polymer latex-modified mortars and concretes. Moreover, of considerable interest to our group are recently reported polymer-modified mortars prepared by two steps; press-molding and steam-curing [4] and polymer-cement foams made by using a polymer emulsion with a cationic initiator as the positive charge introducer on the emulsion particle surface and also by using low cloud point non-ionic surfactant as a foaming agent [5].

EXPERIMENTAL

Materials

The MA-adducted PPG, that is, PPGMA, St, AN, and $\text{Al}(\text{OH})_3$ were the same as those used in the previous study [2]. As the cement, portland cement (obtained from Nihon Cement Co.) was used. Trimethylol-

propane trimethacrylate (TMPT) was of technical grade and used as received.

Preparation of Inverted Emulsions by Using Cement Supernatant

A mixture of cement-water at a 1:2 weight ratio was stirred for 30 min and filtered by suction to obtain a filtrate (cement supernatant). Next, a desired amount of the cement supernatant obtained was added to the monomer solution consisting of St, AN, TMPT, and PPGMA, and the mixture was vigorously stirred to obtain an inverted emulsion. Emulsion stability was estimated by the same way as in the previous studies [1, 2].

In the case of polymerization, 0.05 wt% of vanadyl acetyl acetone (VAA) (as a polymerization accelerator) and 0.5 wt% of benzoyl peroxide (BPO) were added to the inverted emulsion. The mixture was poured into molds and polymerized at 60°C for 4 h to give a water-containing polymer.

Preparation of Polymer-Cement Composites

A fixed amount of a mixture of cement-water or cement-Al(OH)₃-water was added to the vinyl monomers in which 0.05 wt% of VAA had been dissolved, and, after stirring, a desired amount of PPGMA was added. The mixture was vigorously stirred to obtain an inverted emulsion with fillers. The amounts of PPGMA were 10% (based on the monomers) at monomer solution:water ratios of 1:2 and 1:4, and 20% at 1:8.

To the inverted emulsion obtained above was added, with stirring, 0.5 wt% of BPO. The mixture was poured into molds and polymerized at 60°C for 4 h. This was then cured under moist atmosphere (40°C, 95% RH) for 7 d to give water-containing polymer-cement composites.

Measurements

Determinations of physical properties and flame retardance, thermogravimetric analyses (TGA), and differential thermal analyses (DTA) were carried out by the same methods as in the previous articles [1, 2].

Resistances to chemical attack were determined as follows: specimens of 1.27 × 1.27 × 2.54 cm were immersed in 300 g of solvent at 23°C. After 7 d the specimens were separated from the solvent phase, washed with water, and, after rapid surface drying, subjected to the determination of change in size. The change in size was expressed as the average of change in length and change in width. Changes in weight and com-

pressive strength were determined for the specimens which were dried to constant weight.

RESULTS AND DISCUSSION

Effect of Cement on Formation and Properties of Inverted Emulsions

It was found that, when mixtures of cement, water, and vinyl monomers were vigorously stirred in the presence of PPGMA, stable inverted emulsions containing cement could be obtained. In this case the carboxyl groups of PPGMA were considered to be neutralized with metal ions generated from the cement into neutralized PPGMA which acts as an effective W/O type emulsifier. To confirm this, preparation and properties of inverted emulsions by using a cement supernatant obtained from a cement-water mixture were investigated. The following monomer system was selected in this work: St-AN-TMPT (3:1:1) (weight ratio). By vigorously stirring the mixtures of the cement supernatant and the vinyl monomers in the presence of PPGMA, inverted emulsions could be obtained.

Figure 1 shows phase separation curves for the inverted emulsions of monomer solution-cement supernatant at various weight ratios. The monomer solution refers to the mixture of the vinyl monomers and PPGMA. The inverted emulsions were stable at least for 1 d at 23°C and for 1 h at 60°C. Figure 2 shows the relationship between water content and viscosity for the emulsions. The increase in water content resulted in a remarkable increase in viscosity. Interestingly,

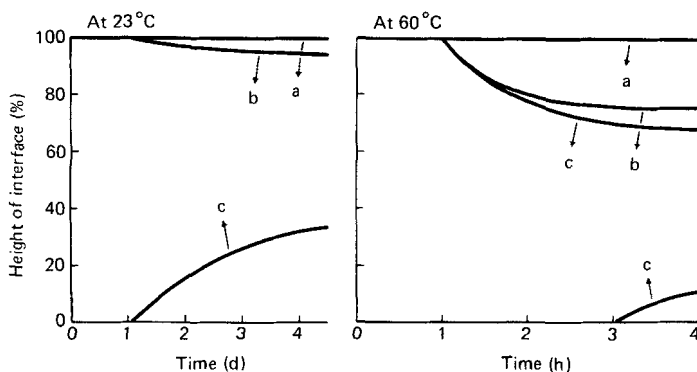


FIG. 1. Separation curves for emulsions of monomer solution-cement supernatant at weight ratios of (a) 1:2, (b) 1:4, and (c) 1:8. Amounts of PPGMA were 10% (based on the monomers) at monomer solution:cement supernatant ratios of 1:2 and 1:4, and 20% at 1:8.

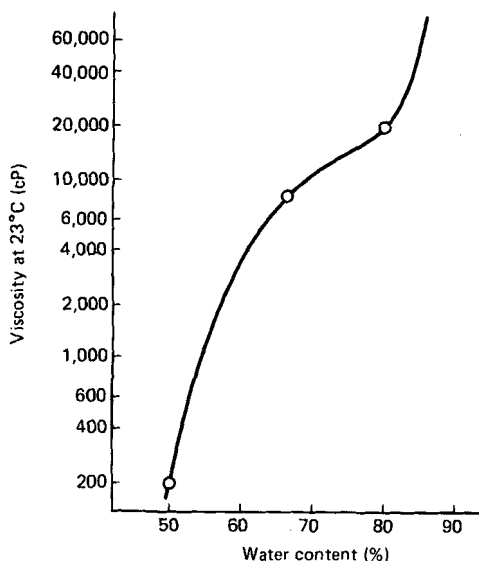


FIG. 2. Relationship between water content and viscosity at 23°C for emulsions of monomer solution-cement supernatant. Amounts of PPGMA were 10% (based on the monomers) at monomer solution: cement supernatant ratios of 1:1, 1:2, and 1:4, and 20% at 1:8.

the emulsion at a water content of 50% was of the O/W type, and the viscosity was very low. However, the increase in water content led to the formation of an inverted emulsion, and the viscosity at 89% water was extremely high (above 100,000 cP). It should also be noted that the viscosities of these inverted emulsions were much higher than those of the inverted emulsions prepared in the previous study [1].

It has been reported [5] that cement supernatants are alkaline and contain metal ions such as Na^+ , K^+ , and Ca^{2+} . The alkalinity of the cement supernatant in this work was 61 meq/L. Hence, in the above emulsions, because the metal ions were in much excess over the carboxyl groups in PPGMA, the carboxyl groups were considered to have been completely neutralized with the metal ions. It is apparent that the concentration of excess unreacted metal ions increased with an increase in the water content in the emulsion.

In order to obtain some information on the effect of excess unreacted metal ions on the viscosity of the emulsions, some model emulsions were prepared from the monomer solution (with 10% PPGMA) and water in the presence of varying amounts of NaOH or CaO. It was found that the NaOH-based emulsions with 67% water were of the O/W type and the viscosities were 25 cP at a NaOH/COOH equivalent ratio of 1:1 and 192 cP at 1.5:1, whereas the CaO-based emulsions with 67%

water were of the W/O type and the viscosities were 294 cP at a CaO/COOH ratio of 1:1 and 10,240 cP at 1.5:1. Thus, it seems that, when PPGMA is completely neutralized, generation of Ca carboxylate groups is necessary for the formation of a W/O type emulsion. Meanwhile, because of the higher hydrophilicity of Na carboxylate groups of PPGMA, the existence of a high concentration of the Na carboxylate groups in the system would lead to the formation of a O/W type emulsion. Interestingly, for the CaO-based emulsions, the existence of excess Ca^{2+} caused a remarkable viscosity increase. Further, by adding a 50% excess amount of NaOH to the CaO-based emulsions which had been prepared at CaO/COOH = 1:1, the viscosity increased markedly from 294 to 13,300 cP. It can be concluded that the excess amounts of metal ions remaining after neutralization are necessary for the remarkable viscosity increase of the inverted emulsions.

From the above model experiments it is inferred that in the inverted emulsions of monomer solution-cement supernatant, the carboxyl groups in PPGMA were neutralized preferentially with Ca^{2+} and the remaining excess metal ions, such as Na^+ , K^+ , and Ca^{2+} , caused the remarkable viscosity increase. In the inverted emulsions with 67% water, partial formation of a multiple W/O/W type emulsion was observed. This is probably due to partial formation of the Na and/or K carboxylate groups. However, the systems of monomer solution-water (1:2)-cement gave stable inverted emulsions containing cement. In the emulsions containing cement, $\text{Ca}(\text{OH})_2$ is considered to exist in abundance in order to neutralize the carboxyl groups completely. It is known [6] that, by the addition of a small amount of methacrylic acid (MAA) into unhydrated cement suspension in aqueous or nonaqueous media, Ca methacrylate is formed by reaction of MAA with $\text{Ca}(\text{OH})_2$ in the cement particles. Further, polymerization in this monomer-cement composite by high dose rate electron-beam irradiation has also been investigated [7].

The inverted emulsions containing various amounts of cement were easy to handle for casting.

Preparation and Properties of Polymer-Cement Composites

The inverted emulsions containing cement could be polymerized with a radical-type initiator such as BPO. Polymerization at 60°C for 4 h gave dry-to-the-touch polymers containing water and cement. It is known [8, 9] that, in the presence of water, cement gradually hardens by hydration reactions of cement component compounds to produce a "cement gel" comprising chemical species of high specific surface area. Strength development in conventional cement compositions is said to be intimately associated with formation of the cement gel and the accompanying increase in surface area [10]. For a typical portland cement, after 24 h the extent of the cement hydration was reported to be about 38% [11]. For poly(vinylidene, vinyl chloride)- and poly-

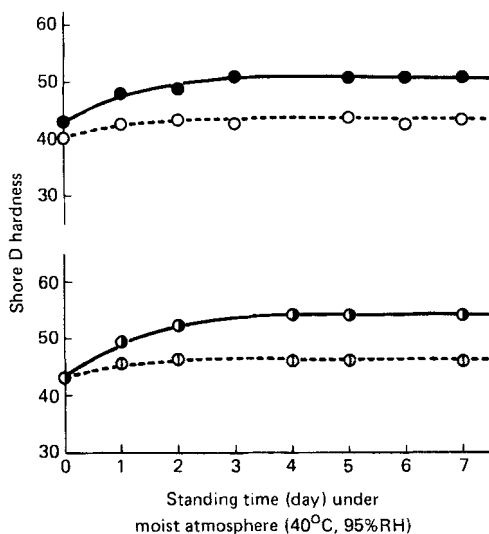


FIG. 3. Effect of standing under moist atmosphere (40°C , 95% RH) on Shore D hardness for water-containing polymers obtained by polymerization at 60°C for 4 h of inverted emulsions of monomer solution-water-cement or CaCO_3 . (●) Resin-water-cement at a weight ratio of 1:2:1; (○) resin-water- CaCO_3 at 1:2:1; (⊙) resin-water-cement at 1:2:2; (⊖) resin-water- CaCO_3 at 1:2:2.

acrylic-modified compositions, the extent of cement hydration was about 22 to 38% after 2 h and about 43 to 52% after 7 d [12]. Therefore, the above dry-to-the-touch polymers containing water and cement were further allowed to stand under moist atmosphere (40°C , 95% RH).

Figure 3 shows the effect of standing under moist atmosphere on Shore D hardness for the water-containing polymers. For comparison, data for corresponding reference dry-to-the-touch polymers containing water and CaCO_3 , obtained by the same polymerization condition, are also shown. For the cement-containing systems, the hardness increased significantly with standing time under moist atmosphere, whereas little increase was observed for the CaCO_3 -containing systems. This is considered due mainly to cement hardening of the former systems. Thus, it was found that the inverted emulsions containing cement can give water-containing polymer-cement composites by polymerization of the vinyl monomers and also by hardening of the cement.

The water-containing polymer-cement composites thus cured for 7 d under moist atmosphere after the polymerization were subjected to various properties determinations. Also, the polymer-cement composites are characterized by the property of very high rate of water loss, indicating that the water droplets in the system are highly connected

TABLE 1. Effect of Cement on Physical Properties of Water-Free Polymers from Inverted Emulsions of Vinyl Monomers with PPGMA

Weight ratio of components in inverted emulsions				Physical properties of water-free polymers					
Vinyl monomers	PPGMA	Water	Cement	Specific gravity	HDT ($^{\circ}$ C)	Flexural strength (kg/cm^2)	Compressive strength (kg/cm^2)	Impact strength ($\text{kg}\cdot\text{cm}/\text{cm}$)	Shore D hardness
				\bar{a}	\bar{b}	\bar{a}	\bar{b}	\bar{a}	\bar{b}
100	10	220 ^a	-	0.63	93	74	86	1.2	50.5
100	10	220	110	1.00	102	112	135	2.8	64.3
100	10	220	220	0.20	72	26	31	0.6	27.3
100	10	440 ^a	-	0.72	89	54	66	0.8	48.8
100	10	440	220	0.10	\bar{b}	2	3	\bar{b}	5.0
100	20	960 ^a	-	0.52	88	12	21	0.3	20.3
100	20	960	480						

^aCement supernatant was used.

^bSamples were too brittle to be subjected to physical properties determinations.

with one another. By removing evaporative water at 60°C to constant weight, water-free polymer-cement composites were easily obtained.

Table 1 shows the effect of cement on the physical properties of the water-free polymers. For comparison, data for blank water-free polymers without cement are also shown. The blank polymer from monomer solution-cement supernatant at a ratio of 1:2 was too brittle to be subjected to physical properties determinations because of the partial formation of multiple W/O/W type emulsion. However, by incorporating cement into this system, a remarkable improvement in physical properties was observed. Thus, the effect of cement on the physical properties clearly appears. A similar tendency was also observed for other systems. The physical properties of the cement-containing systems showed a tendency to decrease in value with an increase in the initially added water.

Effects of $\text{Al}(\text{OH})_3$ on Flame Retardance and Physical Properties of Polymer-Cement Composites

The water-free polymer-cement composites with a high cement content have good flame retardance. However, the flame retardance became poor with a decrease in the cement content. The previous study [2] indicated that $\text{Al}(\text{OH})_3$ has a remarkable effect in imparting flame-retardant properties to water-free polymers containing CaCO_3 . $\text{Al}(\text{OH})_3$ has been reported to also be a most effective flame retardant filler for polyvinyl chloride [13], phenol resins [13], epoxy resins [13, 14], and unsaturated polyester resins [13, 15]. Therefore, the effects of $\text{Al}(\text{OH})_3$ on the flame retardance and the physical properties of the polymer-cement composites were investigated.

Figure 4 shows the effect of $\text{Al}(\text{OH})_3$ on Shore D hardness for the water-containing polymer-cement composites. For comparison, data for the polymers immediately after the polymerization are also shown. The effect of curing under moist atmosphere on the hardness appeared over a wide range of $\text{Al}(\text{OH})_3$ contents, especially so for the resin-water-fillers (1:8:4) series, again indicating the effect of cement hardening. For the resin-water-fillers (1:2:2) series, above about 75% $\text{Al}(\text{OH})_3$, both cured and uncured samples exhibited very poor hardness due to less stable inverted emulsion because of the very low alkali concentration. For the former series, above about 75% $\text{Al}(\text{OH})_3$, cement containing inverted emulsions could not be obtained. Also, the composites containing $\text{Al}(\text{OH})_3$ easily lost evaporative water to give water-free composites.

Figure 5 shows the effect of $\text{Al}(\text{OH})_3$ on the time required to extinguish flame and burning rate for the water-free polymer-cement composites. The composites with the lowest fillers content were combustible, except when the $\text{Al}(\text{OH})_3$ content in the fillers was high; the composites containing only cement exhibited a burning rate of 6.6 cm/min. With an increase in the $\text{Al}(\text{OH})_3$ content, the burning rate decreased markedly and above 75% $\text{Al}(\text{OH})_3$ content in the fillers the burning rate

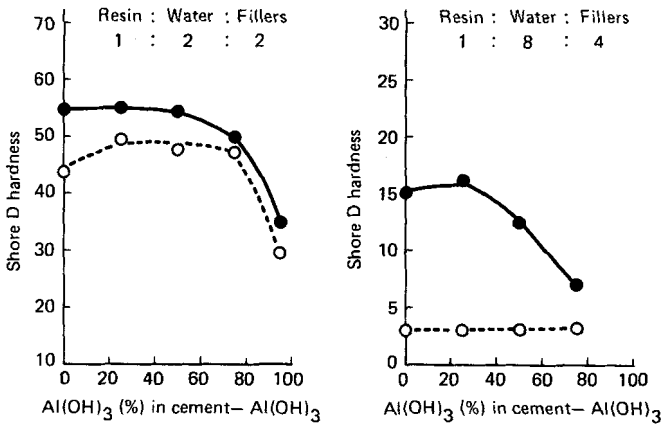


FIG. 4. Effect of $\text{Al}(\text{OH})_3$ on Shore D hardness for water-containing polymer-cement composites based on inverted emulsions of vinyl monomers with PPGMA. (○) Immediately after polymerization; (●) after curing for 7 d under moist atmosphere (40°C , 95% RH). Fillers = cement- $\text{Al}(\text{OH})_3$.

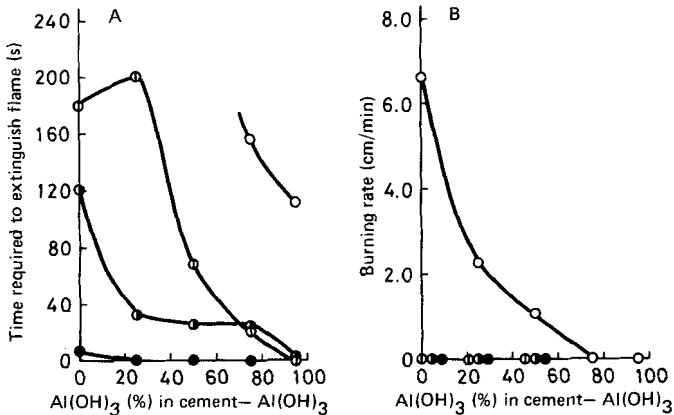


FIG. 5. Effect of $\text{Al}(\text{OH})_3$ on (A) time required to extinguish flame and (B) burning rate for water-free polymer-cement composites from inverted emulsions of monomer solution-water-fillers at weight ratios of (○) 1:2:1, (◐) 1:2:2, (◑) 1:4:2, and (●) 1:8:4. Fillers = cement- $\text{Al}(\text{OH})_3$.

was zero cm/min. Other composites were self-extinguishing and their burning rates were zero cm/min. The composites with the highest fillers content extinguished flame immediately after the withdrawal of a flame when the $\text{Al}(\text{OH})_3$ content was above 20%. The composites from monomer solution-water-fillers (1:2:2) showed longer self-extinguishing times than those from monomer solution-water-fillers (1:4:2), though the specific gravities were higher in the former than in the latter. This is considered to be due to the fact that the former contained a larger amount of combustible resin per unit volume than the latter.

The samples whose resin portion had been burned were easy to break by external force. Therefore, the resin portion seems to have formed a continuous phase.

Figures 6 and 7 show the effect of $\text{Al}(\text{OH})_3$ amount in the fillers on the physical properties for the water-free polymer-cement composites. For the water-free polymers containing CaCO_3 - $\text{Al}(\text{OH})_3$, variation in the $\text{Al}(\text{OH})_3$ content in the fillers brought about no significant changes in the physical properties up to 75% $\text{Al}(\text{OH})_3$ content [2]. Meanwhile, for the composites of this work, increasing the $\text{Al}(\text{OH})_3$ content in the fillers resulted in a decrease in the physical properties, especially so for the flexural and compressive strengths. This is considered due mainly to the decrease in the contribution of cement hardening to the properties with a decrease in the cement content. The remarkable decrease in the properties, as observed

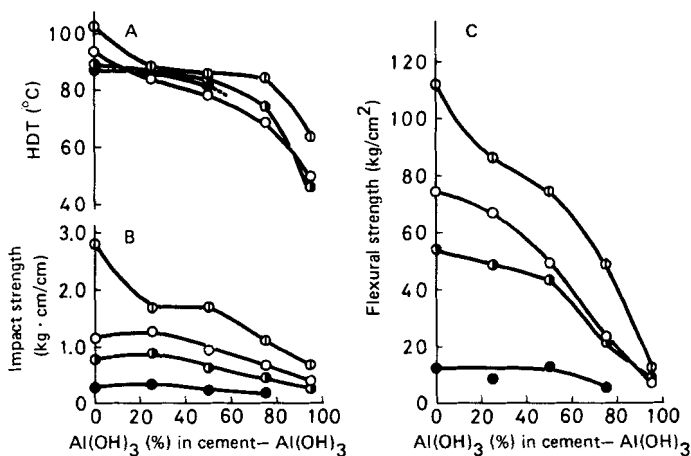


FIG. 6. Effect of $\text{Al}(\text{OH})_3$ on (A) HDT, (B) impact strength, and (C) flexural strength for water-free polymer-cement composites from inverted emulsions of monomer solution-water-fillers at weight ratios of (○) 1:2:1, (◻) 1:2:2, (◻) 1:4:2, and (●) 1:8:4. Fillers = cement- $\text{Al}(\text{OH})_3$.

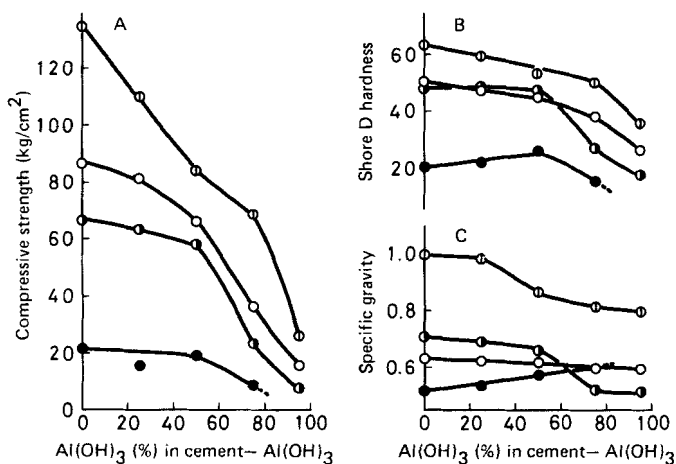


FIG. 7. Effect of $\text{Al}(\text{OH})_3$ on (A) compressive strength, (B) Shore D hardness, and (C) specific gravity for water-free polymer-cement composites from inverted emulsions of monomer solution-water-fillers at weight ratios of (○) 1:2:1, (◐) 1:2:2, (◑) 1:4:2, and (●) 1:8:4. Fillers = cement- $\text{Al}(\text{OH})_3$.

above 75% $\text{Al}(\text{OH})_3$ content, is attributed to the less stable inverted emulsions. For the composites with the highest fillers content, no significant changes in the properties were observed over a wide range of $\text{Al}(\text{OH})_3$ contents because of the very low initial strengths.

Thermal Properties of Polymer-Cement Composites

Figure 8 shows the TGA and DTA curves of representative water-free polymer-cement composites from the inverted emulsions of monomer solution-water-fillers (1:4:2). The composite containing only cement began to decompose markedly above about 300°C , and the plateau observed above 520°C in the TGA curve corresponds to the weight fraction of cement contained. Its DTA curve exhibited two main exothermic peaks, probably due to degradations occurring via oxidative modes.

On the other hand, in the TGA curve of the composite containing cement- $\text{Al}(\text{OH})_3$ (1:1), a first remarkable weight loss began above about 270°C and a second remarkable weight loss above about 320°C . The DTA curve exhibited a large endothermic peak at about 320°C , which correlates well with the first remarkable weight loss, indicating that this is due mainly to the dehydration decomposition of $\text{Al}(\text{OH})_3$. The second remarkable weight loss is attributed to decomposition of the polymer matrix, and the plateau above about 520°C corresponds to the sum of the weight fractions of Al_2O_3 produced and the contained cement.

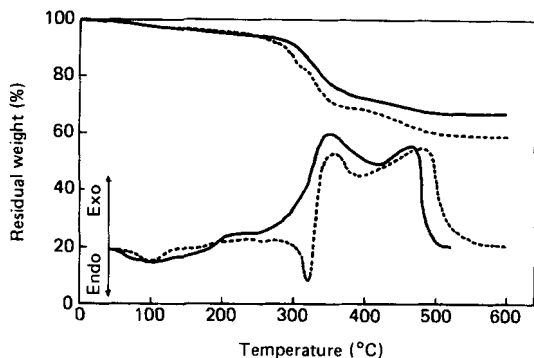


FIG. 8. TGA and DTA curves of water-free polymer-cement composites from inverted emulsions of (—) monomer solution-water-cement (1:4:2) and of (---) monomer solution-water-cement- $\text{Al}(\text{OH})_3$ (1:4:1:1).

Moreover, both composites exhibited a slight weight loss even below about 250°C . They showed a weak endotherm in the range from 50 to 180°C . It is known [10, 11] that hydrated cement includes the so-called "gel water" within the gel pores. The samples, which had been kept at 60°C for 24 h to remove the gel water, were subjected to the above thermal analyses. Hence, the slight weight loss is considered due mainly to loss of hydrated water and partly to loss of the gel water which had not been thoroughly removed.

Resistance to Chemical Attack of Polymer-Cement Composites

Table 2 shows the resistance to chemical attack of the water-free polymer-cement composites. They were unaffected in external appearance by 10% NaOH, 10% NaCl, and water, and dimensional changes were negligible. In 30% H_2SO_4 and 5% HCl, however, the samples became white; in the former, small size increase and considerable weight gain were observed and those with the highest cement content cracked.

It is noteworthy that the size increase and the weight gain in 30% H_2SO_4 became remarkable with an increase in the fillers content, especially so for the composites containing cement only. This is considered due mainly to formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the composite by reactions of H_2SO_4 with cement component compounds. Meanwhile, in 5% HCl they showed a weight decrease which became remarkable with an increase in the fillers content, especially so for the composites containing cement only. However, dimensional changes were negligible. Cement is well known to be disintegrated by the acid. In 10% NaOH they generally showed weight gain of about 6 to 16%. It is considered

TABLE 2. Resistance to Chemical Attack of Water-Free Polymer-Cement Composites from Inverted Emulsions of Monomer Solution-Water-Fillers

Weight ratio of monomer solution: water: fillers	Fillers	Change in size (A) and change in weight (B)											
		30% H ₂ SO ₄		5% HCl		10% NaOH		10% NaCl		Water			
		A (%)	B (%)	A (%)	B (%)	A (%)	B (%)	A (%)	B (%)	A (%)	B (%)		
1:2:1	Cement	1.6	21.8	0.5	-7.7	0.1	16.0	0.1	1.6	0.1	1.6	0.1	-0.8
	Cement- Al(OH) ₃ (1:1)	0.7	19.4	0.5	-2.9	0.1	5.8	0.1	0.4	0.1	0.4	0.0	0.0
1:4:2	Cement	3.2	47.4	-0.1	-22.7	0.0	10.3	0.0	1.9	0.2	1.9	0.2	-0.9
	Cement- Al(OH) ₃ (1:1)	1.1	31.5	-0.1	-4.4	0.1	7.6	0.1	1.5	0.1	1.5	0.1	0.0
1:8:4	Cement	9.0	88.7	-0.4	-44.3	0.2	14.4	0.0	0.4	0.2	0.4	0.2	-0.4
	Cement- Al(OH) ₃ (1:1)	1.4	45.5	-0.3	-27.4	0.3	1.4	0.1	1.1	0.1	1.1	0.2	-1.4

that the absorbed NaOH in the composite could not be removed during drying. In 10% NaCl and water, weight changes were, respectively, small and negligible.

As shown in Table 3, the composites with the lowest or medium fillers content generally exhibited considerable increase in the compressive strength in acid media, especially in 30% H_2SO_4 . Meanwhile, the composite with the highest cement content showed a remarkable compressive strength decrease in acid media. The decrease in 30% H_2SO_4 might be attributable to breakdown of the polymer matrix due to the growth of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in the composite; the decrease in 5% HCl is due to the removal of cement by its disintegration.

In 10% NaOH, 10% NaCl, and water, all of the composites exhibited a significant compressive strength increase, especially in 10% NaOH. Hydration proceeded further in these aqueous media, particularly in 10% NaOH. The remarkable strength increase in 10% NaOH reflected the further advance of hydration. It is known [3, 10, 11, 16] that while tricalcium silicate and beta-dicalcium silicate, which comprise about three fourths of the weight of cement, hydrate very slowly, the remaining fraction, consisting chiefly of tricalcium aluminate and tetracalcium aluminoferrite, hydrates much more rapidly, being essentially complete within 7 d.

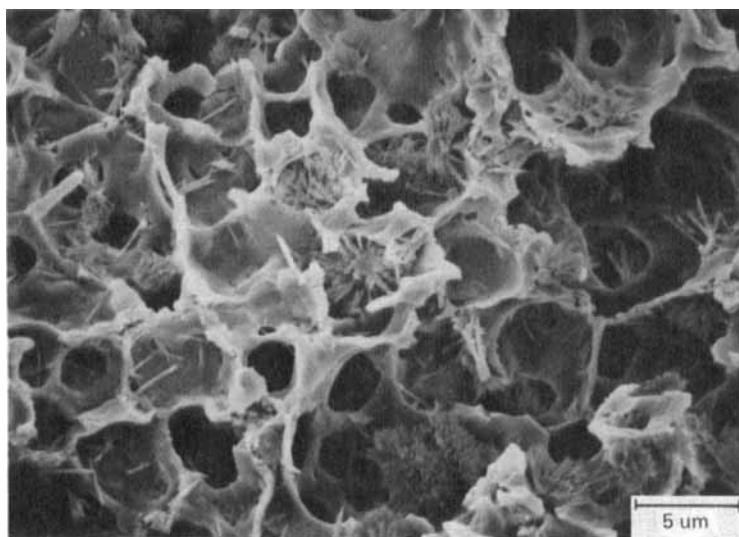
In summary, the above polymer-cement composites, except for those with low polymer content, have improved resistance to acid media in which usual, foamed hydrated cement is eroded, one of their peculiarities. In addition, the use of mixed fillers of cement and $\text{Al}(\text{OH})_3$ leads to further improved resistance.

Microscopic Observation of Polymer-Cement Composites

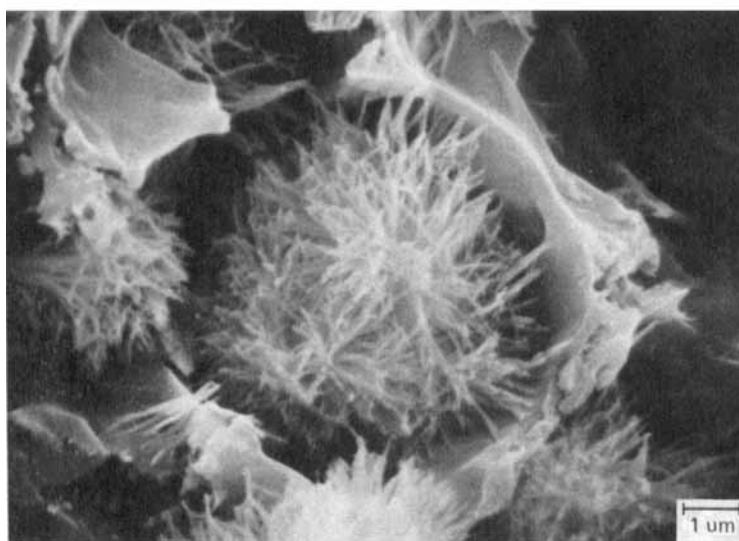
Observation with a light microscope of sample cross sections which were cut from the water-free composites showed that cement particles of about 5×10^{-4} to 5×10^{-3} cm diameter were dispersed in the resin matrix. Areas where such large particles were not observed were further examined with a scanning electron microscope. Figure 9 shows scanning electron micrographs of the cross sections of a representative water-free polymer-cement composite from monomer solution-water-fillers (1:4:2). Figure 9(a) shows that the resin phase has fine cells whose walls were ruptured, probably owing mainly to breakdown of the polymer matrix due to contraction during polymerization. Cement gels have developed through the cell walls. However, considerable amounts of the cement gels are considered to have been removed from the surface during cutting the sample cross section from the composite. Figure 9(b) shows, at higher magnification, the area where the cement gel development has occurred. It is clearly seen that needle-like or plume-like crystals of the cement gels have sprouted out radially from each cement particle through the cell walls. This seems to reinforce the cells to some extent. The same type of cement gel development as

TABLE 3. Influence of Chemical Attack on Compressive Strength for Water-Free Polymer-Cement Composites from Inverted Emulsions of Monomer Solution-Water-Fillers

Weight ratio of monomer solution: water:fillers	Fillers	Change (%) in compressive strength					
		30% H ₂ SO ₄	5% HCl	10% NaOH	10% NaCl	Water	
1:2:1	Cement	+26.0	+10.0	+65.7	+34.9	+14.3	
	Cement- Al(OH) ₃ (1:1)	+36.1	+18.8	+35.8	+6.4	+11.7	
1:4:2	Cement	+30.2	-14.3	+25.9	+8.3	+11.6	
	Cement- Al(OH) ₃ (1:1)	+20.7	+0.6	+54.5	+19.2	+16.2	
1:8:4	Cement	-66.5	-61.8	+159.0	+34.9	+62.7	
	Cement- Al(OH) ₃ (1:1)	-3.2	-49.6	+40.8	+14.4	+12.8	



(a)



(b)

FIG. 9. Scanning electron micrographs of sample cross section of water-free polymer-cement composite from monomer solution-water-cement (1:4:2). (a) At magnification of 3,500 \times ; (b) magnified view (at 10,000 \times) of area where cement gel development has occurred.

this is believed to have occurred at the interface between the above-described large particles and the resin phase. Thus, a bonding effect between the cement particles and the resin phase would have appeared. These structural characteristics of the composite are considered to contribute to some extent to the above-observed improvement in the physical properties. Increasing the $\text{Al}(\text{OH})_3$ content in the fillers resulted in a decrease in these structural characteristics, leading to the decrease in the physical properties.

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