Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Matsuda, Hideaki and Saheki, Takashi(1983) 'Effects of $CaCO_3$ and $Al(OH)_3$ on Properties of Inverted Emulsions and Polymers from Vinyl Monomers with Acid Anhydride-Adducted Polypropylene Glycol', Journal of Macromolecular Science, Part A, 20: 2, 271 — 283

To link to this Article: DOI: 10.1080/00222338308069966

URL: http://dx.doi.org/10.1080/00222338308069966

J. MACROMOL. SCI.–CHEM., A20(2), pp. 271-283 (1983)

Effects of $CaCO_3$ and $Al(OH)_3$ 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 a slurry of $CaCO_3$-water was added with stirring into vinyl monomers in the presence of PPGMA. At least part of the carboxyl groups of PPGMA are considered to be neutralized with Ca^{2+} generated from $CaCO_3$ into partially neutralized PPGMA which acts as an effective W/O-type emulsifier. The inverted emulsions containing $CaCO_3$ as filler showed very low viscosities and, on polymerization, gave water-containing polymers which are characterized by a high rate of water loss. The water-free polymers obtained by removing water showed physical properties which generally decrease with an increase in the PPGMA amount, due to a change in cell structure and also to an increase in the plasticizing effect of PPGMA. The use of mixed fillers of $CaCO_3$ and $Al(OH)_3$ was found to impart flame-retardant properties to the polymers without significant changes in the physical properties.

0022-233X/83/2002-0271$3.50/0

INTRODUCTION

Recently it has been found [1] that a partially neutralized adduct polymer 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 (EDM). The emulsifier gives inverted emulsions having very low viscosities. On polymerization, the emulsions are transformed to white solids which are dry to the touch. The water-containing polymers obtained are characterized by a very high rate of water loss.

This partially neutralized adduct polymer, PPGMA(PMg), was prepared by partial neutralization with MgO of the MA-adducted PPG (PPGMA) (PMg means that PPGMA was partially neutralized with MgO). In the present study, first, the addition effect of calcium carbonate ($CaCO_3$) and aluminum hydroxide ($Al(OH)_3$) on the formation and properties of the inverted emulsions of vinyl monomers containing PPGMA were investigated; it was found that stable inverted emulsions could be obtained by adding a slurry of $CaCO_3$-water into the vinyl monomers in the presence of PPGMA which had not been neutralized. Also, the inverted emulsions containing $CaCO_3$ as filler showed very low viscosities and, on polymerization, gave water-containing polymers characterized by a very high rate of water loss. Next, the effect of $Al(OH)_3$ on flame retardance of the water-free polymers with fillers was investigated. Further, properties of the water-free polymers with fillers are also discussed.

EXPERIMENTAL

Materials

The MA-adducted PPG, that is, PPGMA, was prepared according to the method reported in a previous paper [1] by the addition reaction of MA and PPG (molecular weight = 2053, OH value = 0.974 eq/kg) at a mole ratio of 2:1. The conversion of the addition reaction was 86-89%. Also, MA, St, AN, and EDM were the same as those used in the previous study [1]. $CaCO_3$ (Whiton P 30) and $Al(OH)_3$ (Higilite H 31) were obtained, respectively, from Toyo Fine Chemical Co. and Showa Denko Co.

Preparation of Inverted Emulsions

A fixed amount of PPGMA was dissolved in St with stirring at 60°C for 30 min and fixed amounts of AN and EDM were added to it. In this case, 0.1 wt% cobalt naphthenate (as a polymerization accelerator) was added based on the monomer solution. Next, a desired amount of slurry of $CaCO_3$-water, $Al(OH)_3$-water, or $CaCO_3$-$Al(OH)_3$-water was added slowly to the monomer solution with vigorous stirring at room temperature to obtain an inverted emulsion.

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

Preparation of Water-Containing Polymers with Filler

To the inverted emulsion obtained above was added, with stirring at 60°C, 1.0 wt% (based on the monomer solution) of a 55% dimethyl phthalate solution of methyl ethyl ketone peroxide (MEKPO). The mixture was poured into molds and polymerized by heating at 60°C for 4 h to give a water-containing polymer with filler which was dry to the touch.

Measurements

The time dependence of the water content of the water-containing polymers with filler was determined from specimens measuring 1.27 × 1.27 × 12.7 cm which were cut from the resins. Differential thermal analyses (DTA) were carried out with a Shimazu thermal analyzer DT-20 B at a heating rate of 10°C/min in air. Infrared (IR) spectra were determined with a Shimazu IR-400 instrument.

Thermogravimetric analyses (TGA) and physical properties determinations of water-free polymers obtained by removing water were carried out by the same methods as in a previous article [1]. Flame retardance was determined according to ASTM D 635-68.

RESULTS AND DISCUSSION

Preparation and Properties of Inverted Emulsions with Filler

In the present study the following monomer system was selected: St-AN-EDM (3:1:1) (weight ratio). Figure 1 shows the phase separation curves for the inverted emulsions of monomer solution-water-$CaCO_3$ (1:1:2) with various amounts of PPGMA. The temperature was 60°C. The monomer solution refers to the mixture of the vinyl monomers and PPGMA. The amounts of PPGMA are expressed by percentages based on the weight of monomers. Inverted emulsions could be obtained at PPGMA amounts above 6% even if large amounts of $CaCO_3$ were contained as filler in the system.

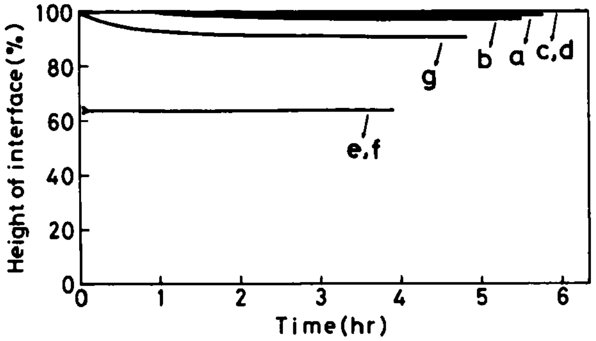

FIG. 1. Separation curves for emulsions of monomer solution-water-$CaCO_3$ (1:1:2). (a) 6% PPGMA; (b) 10% PPGMA; (c) 14% PPGMA; (d) 18% PPGMA; (e) without PPGMA; (f) 10% PPG; (g) monomer solution-water-$Al(OH)_3$ (1:1:2) with 10% PPGMA. Percentages are based on the weight of monomers. 60°C.

The stability of the emulsions generally increases with an increase in the PPGMA amount. Emulsions with 14 to 18% PPGMA are very stable. Blank emulsions without PPGMA collapse immediately after preparation. Also, PPG was tested for comparison with the result that the emulsion with 10% PPG collapsed immediately after preparation. This indicates that the presence of carboxyl groups in the emulsifier is essential for the preparation of inverted emulsions. Further, the system containing $Al(OH)_3$ instead of $CaCO_3$ was tested. As shown by Curve g in Fig. 1, the emulsion began to separate immediately after preparation, but complete separation of water did not occur. Thus, $Al(OH)_3$ is less effective in keeping the emulsions stable.

From the above it is considered that at least part of the carboxyl groups of PPGMA are neutralized with Ca^{2+} generated from $CaCO_3$ into partially neutralized PPGMA which acts as an effective W/O type emulsifier. Thus, the in-situ formation of the emulsifier is commercially advantageous. $Al(OH)_3$ is an amphoteric hydroxide, and partial neutralization of the carboxyl groups in PPGMA with $Al(OH)_3$ is considered possible. However, it seems that the Al carboxylate group in PPGMA does not satisfy the following requirements thoroughly: for forming inverted emulsions, the polarity of the hydrophilic backbone of the emulsifier dissolved in the monomer must be stronger than that of the monomer, while the lipophilic affinity of the emulsifier to the monomer must be stronger than its hydrophilic affinity to water. On the other hand, PPGMA containing the Ca carboxylate group is considered to satisfy these requirements well.

Figure 2 shows the viscosity characteristics at 23°C of the inverted emulsions containing $CaCO_3$ as filler. A previous study [1] disclosed that PPGMA(PMg) gave inverted emulsions whose viscosities were

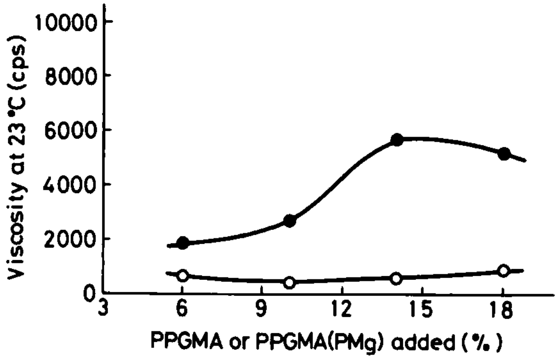

FIG. 2. Effect of amount of PPGMA or PPGMA(PMg) added to monomers on viscosity at 23°C for inverted emulsions of monomer solution-water-$CaCO_3$ (1:1:2). (○) PPGMA; (●) PPGMA(PMg).

much lower than those of the usual inverted emulsions prepared by von Bonin et al. [2-4] and of inverted emulsions from unsaturated polyester salts [5, 6]. For comparison, $CaCO_3$-containing inverted emulsions were prepared in the presence of PPGMA(PMg) and their viscosities were determined. It was found that even they have much higher viscosities than the $CaCO_3$-containing emulsions prepared in the presence of PPGMA. Thus, PPGMA is characterized by the fact that it imparts very low viscosities to the emulsions.

Polymerization and Time Dependence of Water Content of Polymers Obtained

The inverted emulsions containing $CaCO_3$ could be polymerized with a radical-type initiator such as MEKPO to give dry-to-the-touch polymers containing water. In order to get information on the possibility of copolymerization of the maleate groups in PPGMA with the vinyl monomers, the St-AN-EDM (3:1:1) system was polymerized in the presence of 12% PPGMA using the same initiator as above at room temperature for 24 h and at 60°C for 4 h. Similarly, for comparison, the polymerization was conducted in the presence of 12% succinic anhydride (SA)-adducted PPG (PPGSA) obtained from PPG and SA at a mole ratio of 1:2. After the polymerizations, the products were subjected to Soxhlet extraction with acetone. The results were as follows: the PPGMA-containing system gave an Extract A in 53% yield based on the amount of added PPGMA, and the PPGSA-containing one gave an Extract B in 112% yield based on the added PPGSA.

Figure 3 shows the IR spectra of the two extracts. They are essentially identical, and the absorption band at 1730 cm^{-1} (carboxyl

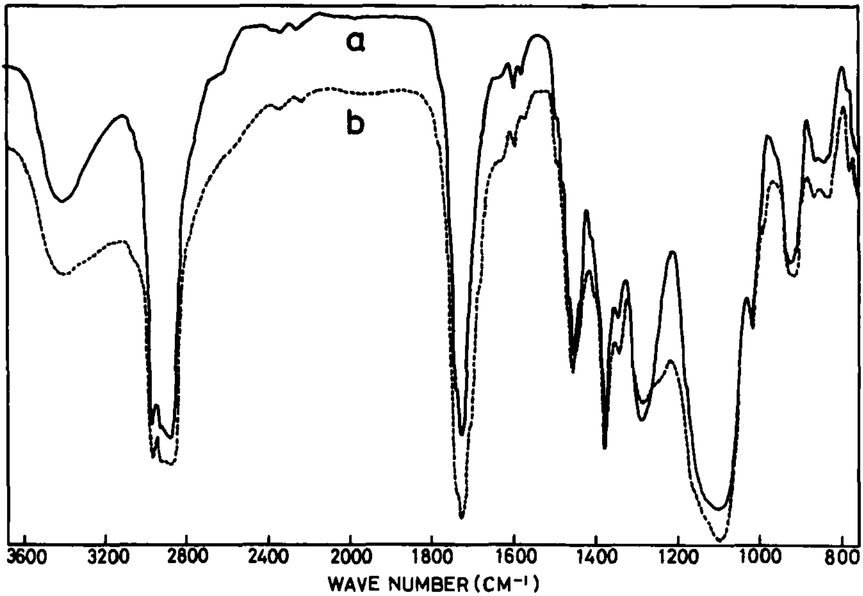

FIG. 3. Infrared spectra of (a) Extract A and (b) Extract B.

group) and the strong shoulder band at 1740 cm^{-1} (ester linkage) are noteworthy. However, they showed no distinct bands at about 1640 cm^{-1} (double bonds of vinyl monomers and maleate group) and at about 2250 cm^{-1} (CN group). The weak band at 1600 cm^{-1} (phenyl ring) suggests the presence of small amounts of low molecular weight soluble polymers based on St. Hence, the major part of Extract A is considered to be PPGMA whose double bonds (maleate groups) have copolymerized with St, and the remainder would be St-based low molecular weight soluble polymers. The length of the poly-St block bound to PPGMA would be very short. Moreover, concentrations of unreacted vinyl monomers and maleate groups, if any, would be very low based on the above IR spectra. At least half of the added PPGMA is supposed to have been bound to the network polymer matrix, judging from the yield of Extract A. As described in the experimental section, the degree of addition of MA to PPG in the addition reaction was 86-89%, and the emulsifier contained small amounts of hydroxyl-terminated PPGMA and possibly unreacted PPG. Therefore, these hydroxyl-terminated polymers are considered to have been preferentially extracted. This seems to be reflected in the broad band around 3400 cm^{-1}, characteristic of the hydroxyl group. Meanwhile, almost all the added PPGSA is considered to have been recovered unreacted in Extract B, and at least about 11% of Extract B would be St-based low molecular weight soluble polymers. The reac-

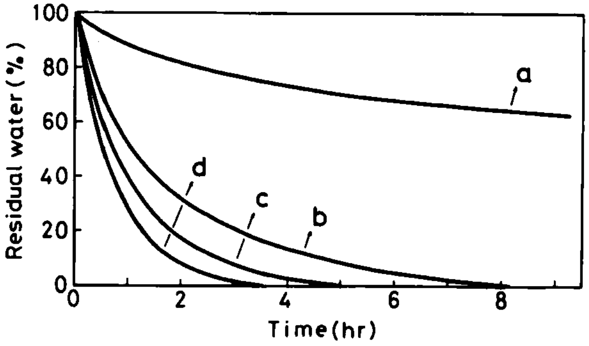

FIG. 4. Time dependence of water content for water-containing polymers from inverted emulsions of monomer solution-water-$CaCO_3$ (1:1:2). (a) 6% PPGMA; (b) 10% PPGMA; (c) 14% PPGMA; (d) 18% PPGMA. 60°C. Percentages are based on the weight of monomers.

tivity ratio in the copolymerization of St (M_1) with monoethyl maleate (M_2) has been reported to be $r_1 = 0.13 \pm 0.01$ and $r_2 = 0.035 \pm 0.01$ at 60°C [7].

From the above it is considered that, in the polymerization of the inverted emulsions, the double bonds of the maleate groups in PPGMA have taken part in the copolymerization with the vinyl monomers, especially St, to an appreciable extent. This eliminates its bleeding out, one of its peculiarities.

Figure 4 shows the time dependence at 60°C of the water content of polymers obtained from the inverted emulsions of monomer solution-water-$CaCO_3$ (1:1:2). Water escapes from the polymers. The loss of water is very slow for the material with 6% PPGMA; however, increasing the PPGMA amount leads the water loss to become much more rapid, indicating that the water droplets in the polymers with filler become much more connected with one another with an increase in the PPGMA amount. All the samples, except for one, lose almost all the water within about 8 h at 60°C. Thus, very high rates of water loss are observed. This tendency is similar to that observed for the water-containing polymers prepared in the presence of PPGMA(PMg) at a monomer solution:water ratio of 1:1 [1]. The presence of $CaCO_3$ as filler seems to have less influence on the cell structure than the emulsifier amount. The advantageousness for obtaining water-free foamed materials is still retained in the water-containing polymers with $CaCO_3$ as filler.

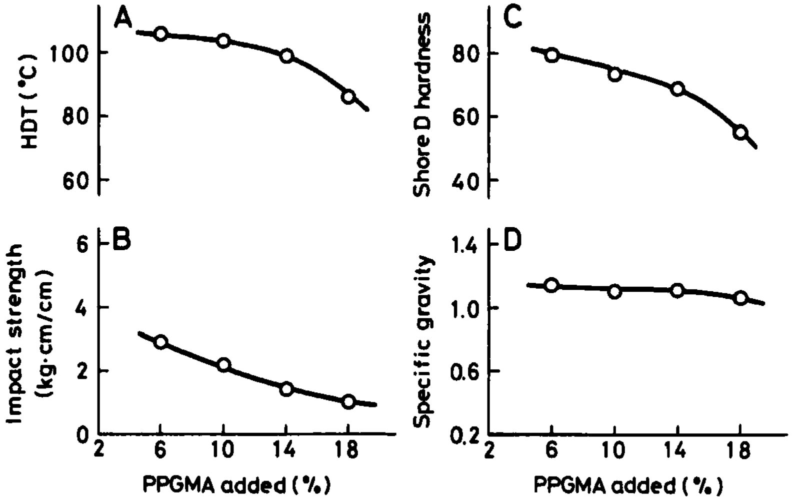

FIG. 5. Effect of amount of PPGMA added to monomers on (A) HDT, (B) impact strength, (C) Shore D hardness, and (D) specific gravity for water-free polymers from inverted emulsions of monomer solution-water-$CaCO_3$ (1:1:2).

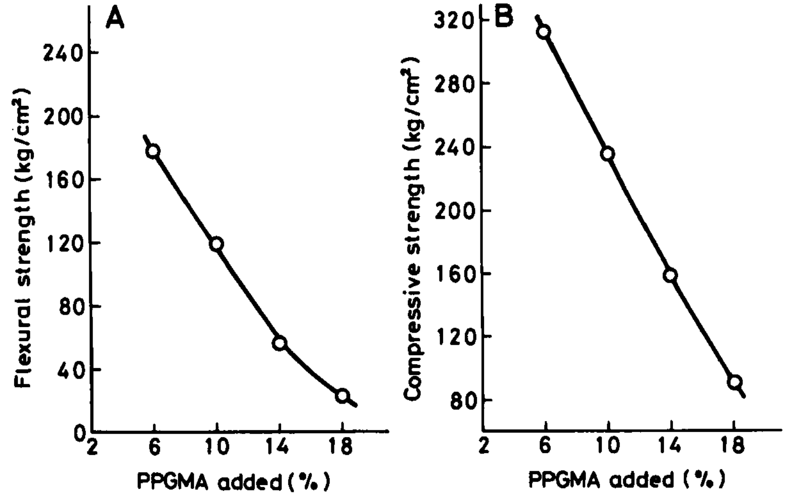

FIG. 6. Effect of amount of PPGMA added to monomers on (A) flexural and (B) compressive strengths for water-free polymers from inverted emulsions of monomer solution-water-$CaCO_3$ (1:1:2).

Physical Properties of Water-Free Polymers with $CaCO_3$ as Filler

Figures 5 and 6 show physical properties of the polymers after the removal of water (water-free polymers with $CaCO_3$ as filler). The water-free polymers obtained showed specific gravities of 1.05-1.14. The physical properties generally decrease with an increase in the PPGMA amount, especially so for flexural and compressive strengths, due to the change in cell structure and also to an increase in the plasticizing effect of PPGMA. As is obvious when compared with the previously reported water-free polymers from the emulsions at a monomer solution:water ratio of 1:1 [1], the addition of $CaCO_3$ as filler results in a decrease in the impact and flexural strengths and in an increase in the Shore D hardness. Meanwhile, HDT is little influenced. In the case of compressive strength, the addition of $CaCO_3$ results in a remarkable increase in the strength at low (6%) PPGMA amount, but the reverse trend is observed at high (18%) PPGMA amount. It is noteworthy that the compressive strength at 6% PPGMA is close to that [8] of concrete (316 kg/cm^2).

Effect of $Al(OH)_3$ on Flame Retardance and Physical Properties

In an attempt to impart flame retardance to plastics, active investigations have been conducted on the development of new types of inorganic filler materials which, when blended with polymers, can act as diluent of expensive polymers and, at the same time, suppress ignition, spreading out of flame, and quantity of smoke due to endothermic reaction by decomposition of the filler materials. Among inorganic filler materials, $Al(OH)_3$ has been reported to be a most effective flame retardant filler [9]. For instance, it has become applied in the fields of polyvinyl chloride [9], phenol resins [9], epoxy resins [9, 10], and unsaturated polyester resins [9, 11]. $Al(OH)_3$ is known to generate 34.5% of H_2O by its decomposition. It is said that $Al(OH)_3$ undergoes a rapid dehydration decomposition above about 200°C and, at the same time, absorbs great quantities of heat, resulting in a flame retardation of plastics containing it.

The water-free polymers containing $CaCO_3$ as filler are combustible, even if the $CaCO_3$ amounts are high. Therefore, the effects of $Al(OH)_3$ on the flame retardance and the physical properties of the polymers with $CaCO_3$ as filler were investigated. Figure 7 shows the effect of $Al(OH)_3$ on the time required to extinguish flame and burning rate for the water-free polymers from the inverted emulsions of monomer solution-water-fillers (1:2:2). The polymer containing only $CaCO_3$ is combustible and exhibits a burning rate of 1.4 cm/min. Meanwhile, the polymer containing $Al(OH)_3$-$CaCO_3$ (1:3) is self-extinguishing and the

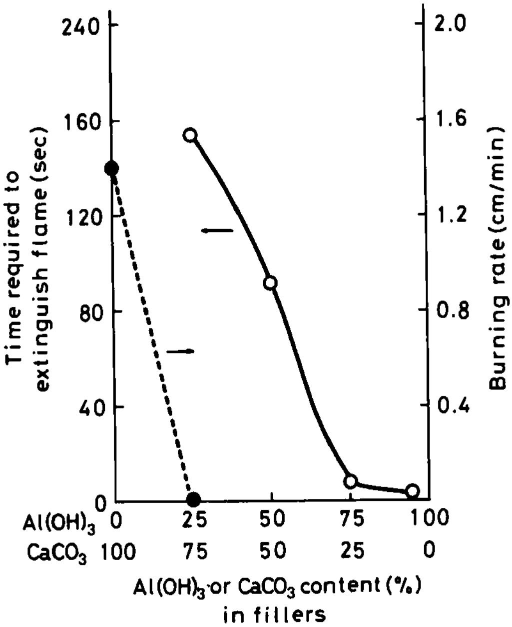

FIG. 7. Effect of $Al(OH)_3$ or $CaCO_3$ content in fillers on time required to extinguish flame and burning rate for water-free polymers from inverted emulsions of monomer solution-water-fillers (1:2:2). Amount of PPGMA = 10% based on monomers.

time required to extinguish flame is about 155 s. With a further increase in the $Al(OH)_3$ content in the fillers, the self-extinguishing time decreases markedly. Above 75% $Al(OH)_3$ content in the fillers the samples extinguish flame within about 8 s after the withdrawal of a flame. Thus, a remarkable effect is observed at 75% $Al(OH)_3$ content in the fillers.

Figures 8 and 9 show the effect of $Al(OH)_3$ amount in the fillers on the physical properties for the water-free polymers from the inverted emulsions of monomer solution-water-fillers (1:2:2). The variation in the $Al(OH)_3$ content in the fillers brings about no significant changes in the physical properties up to 75% $Al(OH)_3$ content, above which the physical properties decrease, especially so for the flexural and compressive strengths. It is noteworthy that the impact strength shows a tendency to increase with an increase in the $Al(OH)_3$ content up to 75% $Al(OH)_3$ content. The inferior physical properties observed at 95% $Al(OH)_3$ content in the fillers are considered to be attributed to the less stable inverted emulsion because of the very low $CaCO_3$ concentration. Thus, the use of mixed fillers of $Al(OH)_3$ and $CaCO_3$ was found to impart the flame-retardant properties to the polymers without significant changes in the physical properties.

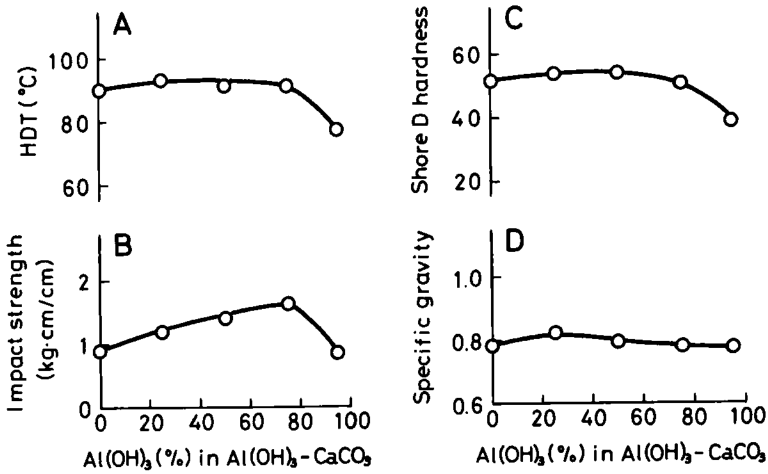

FIG. 8. Effect of Al(OH)$_3$ content in Al(OH)$_3$-CaCO$_3$ (fillers) on (A) HDT, (B) impact strength, (C) Shore D hardness, and (D) specific gravity for water-free polymers from inverted emulsions of monomer solution-water-fillers (1:2:2). Amount of PPGMA = 10% based on monomers.

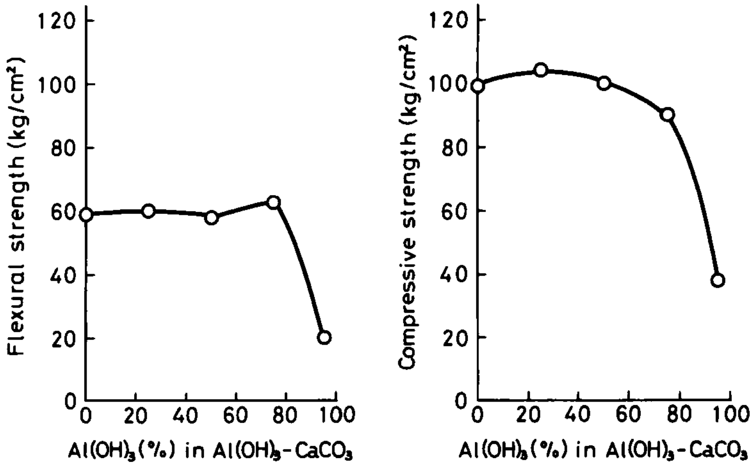

FIG. 9. Effect of Al(OH)$_3$ content in Al(OH)$_3$-CaCO$_3$ (fillers) on (A) flexural and (B) compressive strengths for water-free polymers from inverted emulsions of monomer solution-water-fillers (1:2:2). Amount of PPGMA = 10% based on monomers.

Thermal Properties of Water-Free Polymers with Fillers

Figure 10 shows the TGA and DTA curves of representative water-free polymers from the inverted emulsions of monomer solution-water-fillers (1:2:2). The polymer containing only $CaCO_3$ begins to decompose rapidly above about 300°C and the plateau observed above 480°C in the TGA curve corresponds to the weight fraction of $CaCO_3$ initially added. Its DTA curve shows two exothermic peaks, probably due to degradations occurring via oxidative modes.

On the other hand, in the TGA curve of the polymer containing $Al(OH)_3$-$CaCO_3$ (3:1), gradual weight loss begins above about 180°C and the first remarkable weight loss begins above 280°C; the second remarkable weight loss is above about 320°C. It is noteworthy that the DTA curve shows two endothermic peaks, a small one at 235°C and a large one at 300°C. The major endothermic peak at 300°C correlates well with the first remarkable weight loss, indicating that the weight loss is due mainly to the dehydration decomposition of $Al(OH)_3$. At 310°C the residual weight is 77%. The second remarkable weight loss is attributable to decomposition of the polymer matrix and the plateau above about 540°C corresponds to the sum of the weight fractions of produced Al_2O_3 and the added $CaCO_3$.

$Al(OH)_3$ is said to have the following peculiarities [9]: the endotherm heat of $Al(OH)_3$ is largest (470 cal/g) among this type of hydrate compounds and, in addition, it exhibits the endothermic effect immediately before the heat decomposition of plastics. Such peculiarities seem to be reflected in the thermal properties of the $Al(OH)_3$-containing polymer in Fig. 10.

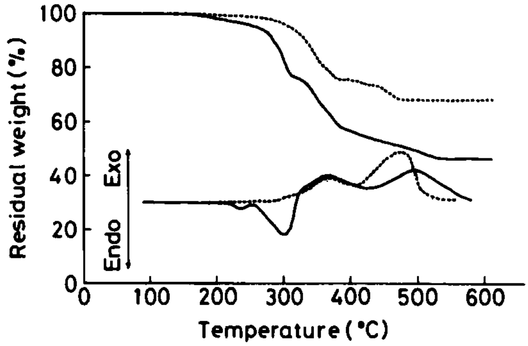

FIG. 10. TGA and DTA curves of water-free polymers. (--) Polymer from inverted emulsion of monomer solution-water-$CaCO_3$ (1:2:2); (—) polymer from inverted emulsion of monomer solution-water-$CaCO_3$-$Al(OH)_3$ (1:2:0.5:1.5). Amount of PPGMA = 10% based on monomers.

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Accepted by editor December 12, 1982
Received for publication January 12, 1983