

Fire-Retarding Polypropylene with Magnesium Hydroxide

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Synopsis

Four types of magnesium hydroxide with different particle and crystallite sizes and different degrees of agglomeration were added at amounts up to 60% by weight to polypropylene to obtain a series of composites. The burning characteristics, tensile yield strength, flexural modulus, notched Izod impact strength, and melt flow index of the resulting composites were measured. Magnesium hydroxide coated with sodium stearate was found to give an increased melt flow index and impact strength to the composites as compared to values obtained with uncoated magnesium hydroxide. Incorporation of not less than about 57% by weight of magnesium hydroxide made the composite nonflammable, but at the same time considerably reduced its impact, flexural, and tensile yield strengths. As the amount of magnesium hydroxide filler was increased, the tensile yield strength and flexural strength of the composite proportionally decreased while the flexural modulus increased. The impact strength reached a maximum value when the amount of incorporation was 30% by weight. The lower the degree of agglomeration of the magnesium hydroxide filler and the greater the crystallite size within the range to about $2\mu\text{m}$, the better were the mechanical properties of the composite.

INTRODUCTION

Polypropylene is made nonflammable generally by the joint use of organohalogen-type fire retardants and antimony trioxide. This method, however, poses such problems as toxicity of fire retardants, corrosion during molding, and emission of smoke and toxic fumes in molding and fires. Much attention has been paid, therefore, to such fire retardants as aluminum hydroxide and magnesium hydroxide, which are nontoxic and avoid the above-mentioned difficulties. These fire retardants tend to decrease the amount of fumes generated during combustion.¹

Aluminum hydroxide, however, begins to dehydrate at about 180°C or higher and is hence unusable for such thermoplastic resins as polypropylene whose molding temperatures are at least about 200°C .

Magnesium hydroxide, on the other hand, begins to dehydrate at about 340°C or higher and, therefore, is suitable for developing heat stability in thermoplastic resins, but it suffers from poor dispersibility. We assume the poor dispersibility to be ascribable to a small crystallite size and to a high degree of agglomeration.

Accordingly, we have filled polypropylene with each of four different types of magnesium hydroxide, including novel magnesium hydroxides which have larger crystallite sizes and lower degrees of agglomeration, to study the relationships between the physical properties and characteristics of the magnesium hydroxide filler and the burning characteristics and mechanical properties of the resulting composites.

EXPERIMENTAL

Magnesium hydroxide types S-1 and S-2 are marketed articles (products of Kyowa Chemical Industry Co.), and types S-3 and S-4 are novel articles prepared by us.

Specific surface areas for all types were determined by the BET method from the adsorption of N_2 at the liquefying temperature of N_2 .

X-ray powder diffraction patterns were recorded on a Philips x-ray diffractometer using $CuK\alpha$ radiation filtered by Ni. The scanning speed was $1/4^\circ/\text{min}$. A half-maximum breadth (B) and the instrumental breadth (b) determined using high-purity silicon were employed to give a true half-maximum breadth (β) from the following equation:

$$B = b + \beta$$

The $K_{\alpha 2}$ peaks were resolved by Jones' method.² Crystallite sizes (ϵ) were calculated by using Scherer's equation³:

$$\epsilon = \beta \cos \theta / \lambda$$

where λ = wavelength. Electron micrographs were taken by the transmission method with a Nihon Denki JEM-T 7S-type electron microscope after the sample was dispersed in ethyl alcohol for about 5 min using ultrasonic waves.

Electron scanning photomicrographs of the cut surfaces and of the fractured surfaces of various composites were obtained, after evaporating treatment of gold, with a Nihon Denshi JSM-T-20-type scanning microscope.

DTA and TGA diagrams were recorded in air for 100–120-mg samples with a Rigaku Denki DG-CIH unit at a heating rate of $5^\circ\text{C}/\text{min}$.

The composites were prepared as follows: Pellets of polypropylene homopolymer, trade name Noblen MH-4, produced by Mitsubishi Petrochemical, were mixed with pellets of magnesium hydroxide about 3 mm in diameter which had been coated with 3% sodium stearate. The mixture was melt-kneaded twice at about 220°C by a vented extruder with a screw diameter of 30 mm, a product of Thermoplastic ($L/D = 28$). The resulting pellets were dried at 120°C for 2 hr and then molded at about 230°C by an injection molding machine (produced by Japan Steel Works, V14-65 type) to form test pieces.

Properties of the test pieces were measured by the following methods: burning characteristics, UL-94 VE (1/8 in.); density, JIS K-7112; tensile yield strength, JIS K-7113; flexural modulus, JIS K-7203; flexural strength, JIS K-7203; notched Izod impact strength, JIS K-7110; melt flow index, JIS K-6758.

RESULTS AND DISCUSSION

Thermal Properties of Magnesium Hydroxide

The DTA and TGA data for the $Mg(OH)_2$ samples S-3 are shown in Figure 1. According to the figure the reaction in which $Mg(OH)_2$ endothermically decomposes to release water and form magnesium oxide begins at about 340°C , reaches its peak at about 430°C , and ends at about 490°C . As noted from this, the foaming, or silver streaks on the molded articles due to release of water, does not occur until about 340°C is reached; hence, $Mg(OH)_2$ has good thermal stability even when used as a filler in polypropylene.

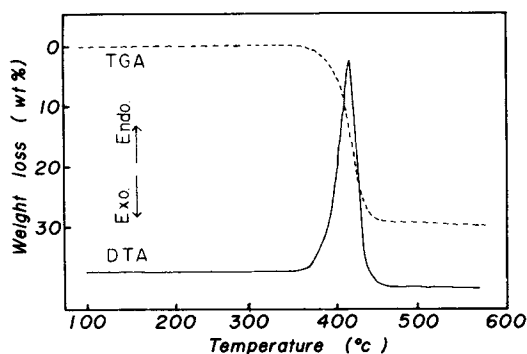


Fig. 1. DTA and TGA analysis of magnesium hydroxide.

The amount of heat absorption of $\text{Mg}(\text{OH})_2$ accompanied by dehydration is 10.7 kcal/mole, or 184 cal/g, when measured by DSC. That of aluminum hydroxide is 70 kcal/mole.¹

From the above results, it is seen that $\text{Mg}(\text{OH})_2$ meets the requirements as a fire retardant for thermoplastics, namely, the requirement of being thermally stable up to 300°C, the temperature necessary for molding, and of decomposing endothermically at a temperature nearest to the decomposition temperature (about 300–400°C) of the resins.

Physical Properties of Magnesium Hydroxide

Four types of $\text{Mg}(\text{OH})_2$ were selected which were different from each other in the crystallite size and the dispersibility. The physical properties of the respective $\text{Mg}(\text{OH})_2$ are tabulated in Table I.

TABLE I
Physical Properties of Magnesium Hydroxide

Property	Types of magnesium hydroxide			
	S-1	S-2	S-3	S-4
BET, m ² /g	16	11	9.4	1.4
Crystallite size, Å				
ϵ_{001}	326	581	679	1870
ϵ_{100}	1088	948	2880	17500
Particle size distribution, wt %				
>1 μm	2.7	18.9	77.2	27.1
1–2 μm	7.8	23.8	19.5	30.6
2–3 μm	15.0	14.9	3.2	26.5
3–6 μm	22.5	30.2	0.1	15.8
6–10 μm	24.1	6.7		
10–15 μm	15.7	5.5		
<15 μm	12.2			
Average particle size \bar{x} ; μm	7.4	2.9	0.4	1.9
\bar{x}/ϵ_B	46.5	12.6	1.48	1.04
\bar{x}/ϵ_{001}	227	49.9	17.7	10.2
\bar{x}/ϵ_{100}	68.0	30.6	1.74	1.09

^a ϵ_B denotes mean particle size derived from BET.

The crystallite sizes listed in the table were determined by x-ray diffraction. Those in the $\langle 001 \rangle$ direction correspond to the thickness and those in the $\langle 100 \rangle$ direction correspond to the diameter of the $\text{Mg}(\text{OH})_2$ crystallites.

Furthermore, the crystallite size in the $\langle 100 \rangle$ direction and the dispersibility were directly observed by a transmission electron microscope (Fig. 2). However,

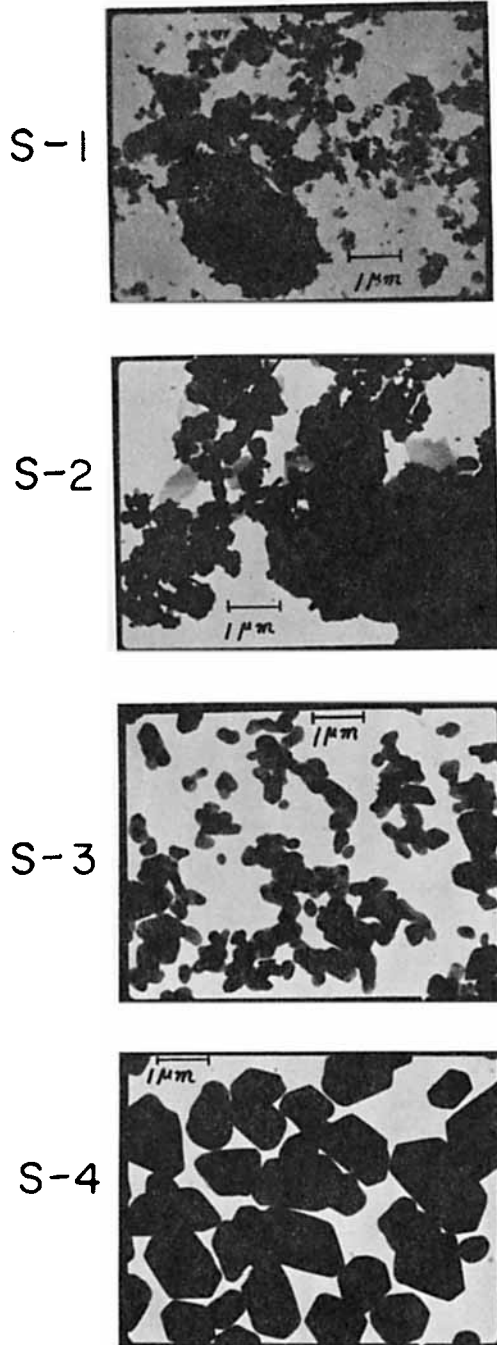


Fig. 2. Electron micrographs of magnesium hydroxide S-1 to S-4.

an electron microscope is unsuitable for precise measurement of dispersibility because of its high magnification, thus making the field of vision narrow. Also, particle size distribution determined by the photoextinction method does not clarify how many crystallites are agglomerated because the results obtained thereby are concerned with the average particle size.

In view of these facts, the ratio between the average particle size (\bar{x}) determined by the photoextinction method and the crystallite size (ϵ) determined by x-ray diffraction, i.e., \bar{x}/ϵ_{001} or \bar{x}/ϵ_{100} , was used to express dispersibility. An alternative method was to use the ratio of the average particle size (\bar{x}) to the crystallite size (ϵ_B) calculated from the BET specific surface area.

Table I shows that the crystallite size increases and the BET specific surface area decreases in the order S-1, S-2, S-3, S-4.

Dispersibility improves in the order S-4 > S-3 > S-2 > S-1 in any of the two methods. \bar{x}/ϵ_{100} , \bar{x}/ϵ_{001} , and \bar{x}/ϵ_B , however, show different values from each other, particularly in S-1 and S-2, for the following reasons: The BET specific surface area does not include the area occupied by micropores having diameters smaller than that of the N_2 molecule. Hence, ϵ_B is estimated at a value greater than its actual value, and thus, as agglomeration proceeds, \bar{x}/ϵ_{100} or \bar{x}/ϵ_{001} should be larger than \bar{x}/ϵ_B . In fact, in expressing the dispersibility of $Mg(OH)_2$, it is appropriate to use \bar{x}/ϵ_{100} .

From the above results, it is understandable that S-3 and S-4 are markedly different from S-1 and S-2 in crystallite size and dispersibility. This is apparent from the electron micrograph of Figure 2 as well.

Physical Properties of Magnesium Hydroxide-Polypropylene Composite

Without a surface treatment on the $Mg(OH)_2$ pellets, the extruder will receive

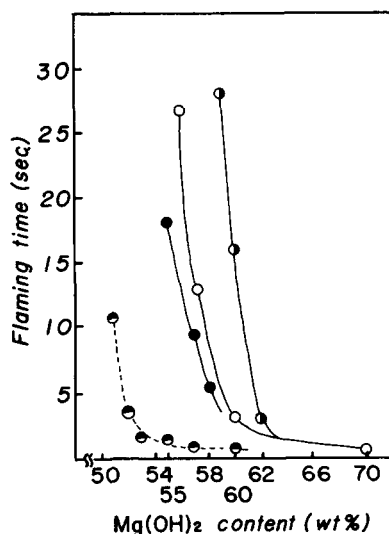


Fig. 3. Relationship between magnesium hydroxide content and time required for flame extinction: (○) S-3 on first contact with flame; (●), (○), and (●) S-1, S-3, and S-4, respectively, on second contact with flame.

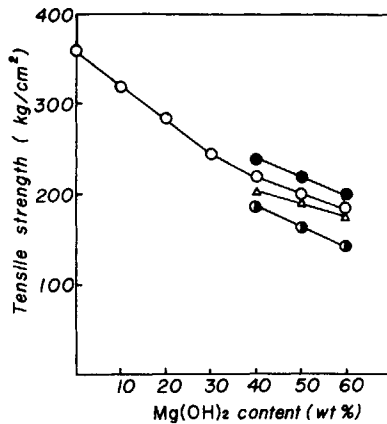


Fig. 4. Relationship between magnesium hydroxide content and tensile yield strength: (○) S-1; (Δ) S-2; (○) S-3; (●) S-4.

high torque, and an extruded strand will be brittle and break easily, thus making its working properties very poor. Also, because of the poor flow properties of the product, injection molding sometimes becomes impossible. These drawbacks have been eliminated by coating $\text{Mg}(\text{OH})_2$ with 3% sodium stearate by chemisorption in an aqueous medium.

Figure 3 illustrates the flaming time on second contact with flame of the composites against the incorporated amount of $\text{Mg}(\text{OH})_2$. According to the figure when the amount of $\text{Mg}(\text{OH})_2$ incorporated exceeds 61% for S-1, 58% for S-3, and 57% for S-4, the flaming time on second contact with flame is 10 sec or shorter; this is indicative of so-called nonflammability.

The flaming time changes sharply with a slight change in the incorporated amount of $\text{Mg}(\text{OH})_2$, no matter what the type of $\text{Mg}(\text{OH})_2$ is. This is characteristic of the composite. The reason why the flaming time shortens in the order S-1 > S-3 > S-4 is that the better the dispersibility of $\text{Mg}(\text{OH})_2$ in polypropylene, the more evenly the heat of combustion of the resin is absorbed homogeneously by the endothermic decomposition of $\text{Mg}(\text{OH})_2$.

Figure 4 shows that the tensile yield strength decreases in proportion to an increase in the incorporated amount of $\text{Mg}(\text{OH})_2$. A look at the influence of the type of $\text{Mg}(\text{OH})_2$ in the region where the incorporated amount of $\text{Mg}(\text{OH})_2$ is

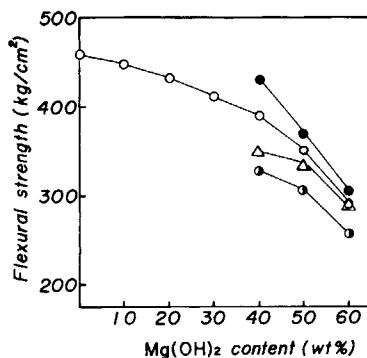


Fig. 5. Relationship between magnesium hydroxide content and flexural strength: (○) S-1; (Δ) S-2; (○) S-3; (●) S-4.

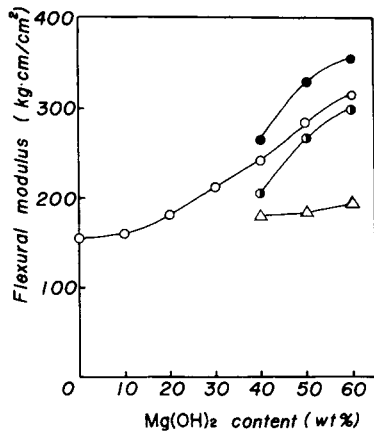


Fig. 6. The relation between magnesium hydroxide content and the flexural modulus. S-1 (●), S-2 (Δ), S-3 (○), S-4 (●).

40 to 60% shows that a reduction in the tensile yield strength occurs in the order S-4 > S-3 > S-2 > S-1. The tensile yield strength when S-3 is incorporated in an amount of 50% corresponds to about 57% of the base polypropylene.

According to Figure 5, the flexural strength shows little reduction until the amount of incorporation of Mg(OH)₂ reaches 20%, but its reduction becomes relatively great when that amount exceeds 20%. However, the flexural strength when the amount of incorporation of S-3 is 50% accounts for about 76% of the base polypropylene, and hence, its reduction is not so great as in the case of the tensile yield strength. The flexural strength reduction according to the type of Mg(OH)₂ is least for S-4, less for S-3, little for S-2, and greatest for S-1.

In Figure 6, the flexural modulus, in contrast to flexural strength, increases with an increase in the amount of incorporation of Mg(OH)₂, and its increase is greater when the amount of incorporation exceeds 20%. The flexural modulus at an S-3 incorporation of 50% corresponds to about 1.7 times the flexural modulus of the base polypropylene. A look at the influences of the type of Mg(OH)₂ shows that the flexural modulus follows the order S-4 > S-3 > S-1 > S-2.

In Figure 7, the notched Izod impact strength is the highest when the amount

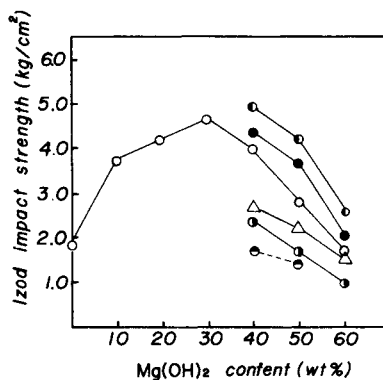


Fig. 7. Relationship between magnesium hydroxide content and notched Izod impact strength: (●) S-1; (Δ) S-2; (○) S-3; (●) S-4; (●) S-3 uncoated; (●) S-3 coated with sodium oleate.

of $\text{Mg}(\text{OH})_2$ incorporated is 30% but is lower than that of the base polypropylene when that amount is 60%. It is interesting that the impact strength at 30% filler is about 2.4 times that of the base polypropylene. Concerning the effect of the type of $\text{Mg}(\text{OH})_2$ on impact strength, the order in which an increase in impact strength is obtained is $\text{S-4} > \text{S-3} > \text{S-2} > \text{S-1}$.

In Figure 8, the melt index tends to increase approximately in proportion to the increase in the amount of incorporation of $\text{Mg}(\text{OH})_2$ until this amount reaches 50% but tends to rapidly decrease when the amount exceeds 50%. The melt index at 50% filler is about 2.6 times that of the base polypropylene and is more than 10 times that obtained when uncoated S-3 is employed. Regarding the effect of the type of $\text{Mg}(\text{OH})_2$ on the melt index, the increase in the melt index is in the order $\text{S-4} > \text{S-3} > \text{S-2} > \text{S-1}$.

When the amount of incorporation of $\text{Mg}(\text{OH})_2$ is 40%, the density is 1.19. When the amount is 50%, the density is 1.30. When the amount is 60%, the density is 1.41.

To confirm the state of dispersion of $\text{Mg}(\text{OH})_2$ in polypropylene, electron scanning microphotographs of the fracture surfaces of the composites having $\text{Mg}(\text{OH})_2$ incorporated in an amount of 50% were taken and are shown in Figure 9.

With S-1, large agglomerates with a maximum size of about $15 \mu\text{m}$ are observed, including large agglomerates with an average particle size of about $4 \mu\text{m}$. Also, many voids are recognized between $\text{Mg}(\text{OH})_2$ and the matrix. With S-2, agglomerates with a maximum particle size of about $5 \mu\text{m}$ are seen, but many particles with a size of less than $1 \mu\text{m}$ are present, with agglomerates smaller and voids less, on the whole, than in the case of S-1. In the case of S-3, a small number of agglomerates with a size of about 1 to $2 \mu\text{m}$ are observed, but most of particles are $0.5 \mu\text{m}$ or less in size; this indicates much better dispersion than in the case of S-1 or S-2. In the case of S-4, there are practically no agglomerates, and the size of the dispersed particles equals that of the crystallites, i.e., about 2 to $3 \mu\text{m}$.

From the above results, the dispersibility of $\text{Mg}(\text{OH})_2$ in polypropylene is in the order $\text{S-4} > \text{S-3} > \text{S-2} > \text{S-1}$. Accordingly, voids between the matrix and $\text{Mg}(\text{OH})_2$ are the fewest for S-4, the second fewest for S-3, the third fewest for

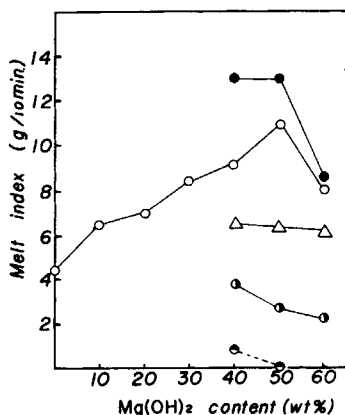


Fig. 8. Relationship between magnesium hydroxide content and melt index: (●) S-1; (Δ) S-2; (○) S-3; (●) S-4; (○) S-3 uncoated.

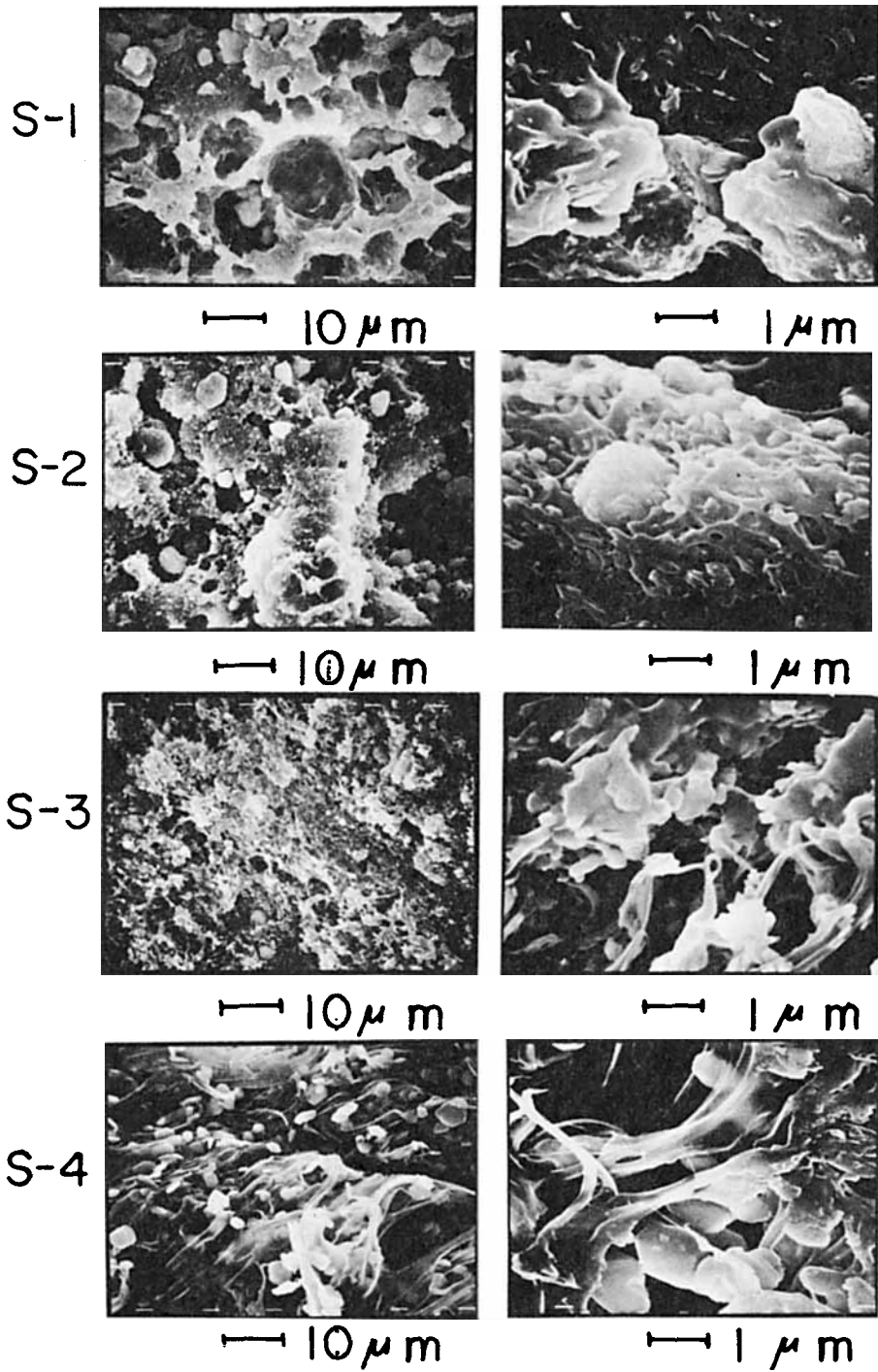


Fig. 9. Electron scanning microphotographs of the fractured surface of polypropylene filled with 50% magnesium hydroxide.

S-2, and the most for S-1. Since the dispersibility of $Mg(OH)_2$ is the same in alcohol and in polypropylene, a mere knowledge of its dispersibility in alcohol enables its dispersibility in resins to be anticipated.

The results shown in Figures 4-7 are quite similar to the results for a composite^{3,4} of $CaCO_3$ and rigid PVC or GP-PS. This is considered to be due to a similarity in crystal shape between $Mg(OH)_2$ and $CaCO_3$. That is, the crystals of both are platelike crystals having a small aspect ratio. On the other hand, when a composite^{5,6} is prepared from polypropylene, for example, with glass fibers or mica having a crystal shape of a high aspect ratio, the composite exhibits different behavior in that its tensile yield and flexural strength increase but its notched Izod impact strength decreases.

According to Figure 4, the tensile yield strength decreases in proportion to the increase in the incorporated amount of $Mg(OH)_2$. This tendency agrees with the behavior of the model proposed by Nielsen⁷ in which there is no adhesion between the filler and the polymer matrix. This means that the tensile yield strength of the $Mg(OH)_2$ -polypropylene composite is proportional to the effective volume of polypropylene without including the volume occupied by $Mg(OH)_2$, because no chemical bonding exists between $Mg(OH)_2$ and polypropylene.

The absence of strong adhesion between $Mg(OH)_2$ and polypropylene can be seen from Figure 9 as well.

Therefore, surface coating with sodium stearate enhances the compatibility with the resin but does not afford a chemical bonding between the filler and matrix. If S-4 is surface coated with sodium oleate having unsaturated groups, the melt index is somewhat inferior, the tensile yield strength and flexural strength show a little increase, and the notched Izod strength at a filler concentration of about 50% shows a 1.7-fold increase as compared with use of sodium stearate. This is a good indication that $Mg(OH)_2$ and polypropylene have been bonded chemically via oleic acid. This is also proof that the chemical bonding between the filler and the matrix is effective for improvement of the physical properties.

Concerning the effect of the physical properties of $Mg(OH)_2$ on the composite, all of the data including tensile yield strength, flexural strength, flexural modulus, notched Izod impact strength, melt index, and flame retardancy, excluding part of the flexural modulus, are in the order S-4 > S-3 > S-2 > S-1. This tendency is in agreement with the tendency to be exhibited when the crystallite size of $Mg(OH)_2$ increases and agglomeration decreases. When the crystallite size is larger than that of S-4, however, a further improvement in the physical properties is not observed.

From the foregoing it can be said that the larger the crystallite size within the range of up to about $2 \mu m$ and the less the agglomeration of the crystallites, the better the particles are dispersed in the resin, thus increasing the effective volume of the resin and improving the mechanical properties of the composite. This can be confirmed from Figure 9, which shows that polypropylene resin has been drawn when using S-4 or S-3, but no drawing is recognized when using S-1 or S-2.

Further, when glass beads whose agglomeration is almost negligible are filled in a resin, the strengths of the composite such as flexural strength and impact strength increase as the average particle size decreases. When considerable

agglomeration occurs as in the case of using $\text{Mg}(\text{OH})_2$, it would be hasty to judge the properties of the composite only from the average particle size; it is necessary to regard the crystallite size and agglomeration as independent factors.

The reason why the melt index of the composite reaches a value more than two times that of the base resin is that sodium stearate has a lubricating action. The melt index ranking of S-4 > S-3 > S-2 > S-1 is mainly due to the difference in agglomeration.⁹ This is because, although the average particle size of S-3 is not greatly different from that of S-4, S-4 has much less tendency to agglomerate.

Concerning the flame retardancy, it is considered that the better the $\text{Mg}(\text{OH})_2$ disperses in the resin, the fewer the voids become. As a result, the heat of combustion of the resin is transmitted rapidly to $\text{Mg}(\text{OH})_2$ having a low thermal conductivity, thereby causing $\text{Mg}(\text{OH})_2$ to decompose endothermically at low temperatures. It is also considered that the better the degree of dispersion, the more evenly the heat generation of the resin and the heat absorption of $\text{Mg}(\text{OH})_2$ balance throughout the composite.

Improvements in the injection moldability of the composite as well as in the appearance and gloss of the injection-molded product are in the order S-4 > S-3 > S-2 > S-1.

CONCLUSIONS

To render polypropylene flame retardant, it is necessary to incorporate therein at least 57% $\text{Mg}(\text{OH})_2$. The tensile yield, flexural strength, notched Izod impact strength, flexural modulus, melt index, and flame retardancy of the composite are all improved as the crystallite size of $\text{Mg}(\text{OH})_2$ becomes larger in the range of up to about 2 μm and the agglomeration of the particles become less.

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