Research Letter

Characterizations of Polystyrene-Based Hybrid Particles Containing Hydrophobic Mg(OH)$_2$ Powder and Composites Fabricated by Employing Resultant Hybrid Particles

Shuichi Kimura,[1, 2] Takeo Hyodo,[3] Yasuhiro Shimizu,[3] and Makoto Egashira[3]

[1] *Graduate School of Science and Technology, Nagasaki University, 1-14 Bunkyo-machi, 852-8521 Nagasaki, Japan*
[2] *Advanced Material R&D Center, Yazaki Parts Co., Ltd., 1500 Mishuku, Susono, 410-1194 Shizuoka, Japan*
[3] *Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-machi, 852-8521 Nagasaki, Japan*

Correspondence should be addressed to Shuichi Kimura, d705019b@stcc.nagasaki-u.ac.jp

Polystyrene (PS)-based hybrid particles containing a large amount of Mg(OH)$_2$ powder treated with methylhydrogen polysiloxane (MHS) were fabricated by a bulk and subsequent suspension two-step polymerization method. All the particles fabricated showed spherical shape and their particle sizes were about 500 μm, irrespective of the additive amount of the Mg(OH)$_2$ powder modified with MHS (ST-1). The actual content of ST-1 powder incorporated inside each kind of hybrid particle was almost the same as that in the raw mixture, and agglomeration of ST-1 powder was hardly observed inside the hybrid particles. The compressive strength of the hybrid particles remained almost unchanged, even when the ST-1 powder content increased from 10 to 50 phr. Furthermore, a composite fabricated by employing the hybrid particles achieved homogenous distribution of ST-1 powder and showed a higher oxygen index than that of a composite fabricated by directly mixing of PS pellets and ST-1 powder.

1. INTRODUCTION

Polystyrene (PS) is one of the important thermoplastic resins in industrial fields, such as electrical and household products areas. However, its poor flame retardancy limits free practical uses in various areas. An environmentally friendly approach to solve poor flame retardancy is to add an alternative halogen-free flame retardant, such as magnesium hydroxide, Mg(OH)$_2$, powder. It is well known that this approach is easy and effective for general crystalline polymers, such as polyethylene or polypropylene [1].

Mechanical mixing by a twin screw extruder or a two-roll mill is the simplest and commonest method [2] for mixing the Mg(OH)$_2$ powder with a PS matrix. However, conventional mechanical mixing is rather a time-consuming and skilled process for achieving homogenous distribution of Mg(OH)$_2$ powder inside the final products. For example, segregation of Mg(OH)$_2$ powder inside the final products due to insufficient mixing may lead to poor mechanical properties. Thus, a key point to achieve homogenous distri-

bution of Mg(OH)$_2$ powder inside the final products within a short time is to use micrometer-sized PS-based hybrid particles containing a large amount of Mg(OH)$_2$ powder as a raw material. This method also enables us to make a complex shape and a tailored design and control of properties of products by changing the kinds and contents of functional fillers. However, the microstructure and properties of these PS-based hybrid particles and composites fabricated by employing the resultant PS-based hybrid particles have not been investigated satisfactorily yet.

In the present study, therefore, our efforts have been directed to establishing a fabrication process and characterization of the PS-based hybrid particles containing a large amount of Mg(OH)$_2$ powder modified with methylhydrogen polysiloxane (MHS) by a bulk [3] and suspension [4] two-step polymerization method. Furthermore, microstructure and properties of the PS-based composites fabricated by employing a mixture of PS polymer and Mg(OH)$_2$ powder modified with MHS or PS-based hybrid particles have been investigated.
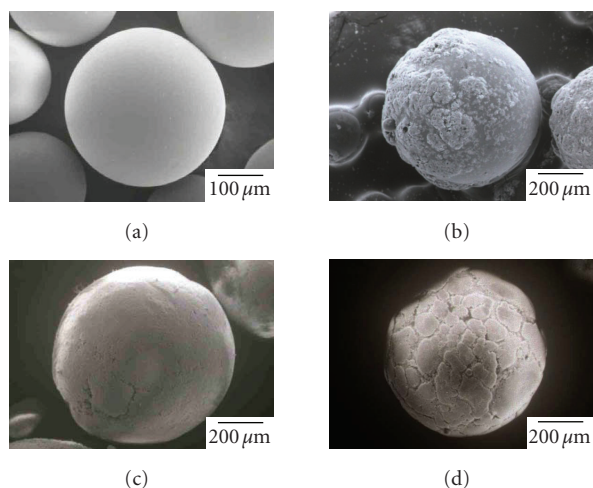
Figure 1: SEM images of (a) PSM particle, (b) 10(ST-1)-PSM, (c) 30(ST-1)-PSM, and (d) 50(ST-1)-PSM hybrid particles.
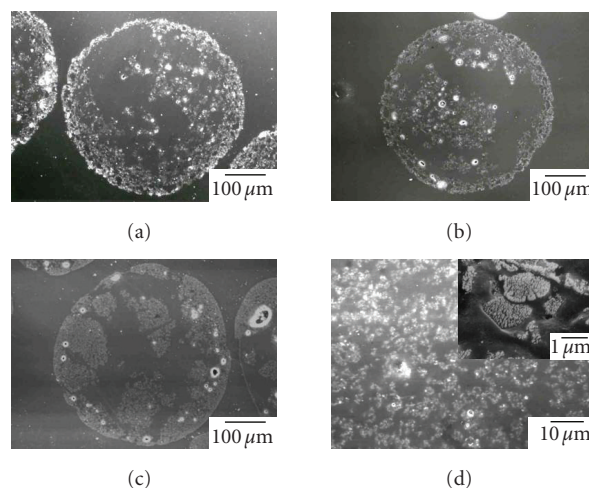

Figure 2: Cross-sectional views of (a) 10(ST-1)-PSM, (b) 30(ST-1)-PSM and (c), and (d) 50(ST-1)-PSM hybrid particles.

2. EXPERIMENTAL

2.1. Materials and fabrication of PS-based hybrid particles

$Mg(OH)_2$ powder (Konoshima Chemical Co., Ltd.) with a mean particle size of ca. $0.6\,\mu m$ was used as a filler for the PS-based flame retardant hybrid particles. Prior to fabricating hybrid particles, the surface of $Mg(OH)_2$ powder was treated with methylhydrogen polysiloxane (MHS, Dow Corning Toray Co., Ltd.) in the following manner, in order to change the surface properties from hydrophilic to hydrophobic so as to enhance the affinity of the treated powder with the PS matrix and then to achieve homogenous distribution in the PS matrix. A given amount of MHS was mixed with isopropyl alcohol (IPA, 1:5 in weight), and the mixture was sprayed to the $Mg(OH)_2$ powder in a general mixer while stirring at 1740 rpm for 0.9 ks. The amount of MHS used for the surface modification was controlled to be 1 wt% of $Mg(OH)_2$ powder. Then, the resultant powder was subjected to the heat treatment at 423 K for 7.2 ks under vacuum, in order to remove IPA and proceed with a chemical reaction between $Mg(OH)_2$ powder and MHS. This hydrophobic MHS-treated $Mg(OH)_2$ powder will be referred to as ST-1 powder.

PS-based hybrid particles were fabricated by a bulk and suspension two-step polymerization method. A mixture of styrene monomer (SM, Wako Pure Chemical Industries, Ltd.), 2, 2′-azobisisobutyronitrile (AIBN, Wako Pure Chemical Industries, Ltd.) as a radical initiator for polymerization, divinylbenzene (DVB, Kishida Chemical Co., Ltd.) as a cross-linking agent, maleic anhydride (MA, Kanto Chemical Co., Inc.) for copolymerizing with SM, and ST-1 powder was used as a starting material. The composition of the mixture was 1 part of AIBN, 10 parts of DVB, 5 parts of MA, x (x = 10, 30, 50) parts of ST-1 powder, and 100 parts of SM on a basis of weight of chemicals. The bulk polymerization was first carried out aiming at increasing the viscosity of a dispersed phase, that is, the mixture of SM, AIBN, DVA, MA,

and ST-1 powder, in the subsequent suspension polymerization, so as to prevent the agglomeration of ST-1 powder or the separation of ST-1 powder from the dispersed phase. The mixture was premixed by an ultrasonic generator (24 kHz, 110 W) for 0.6 ks, and thereafter it was subjected to bulk polymerization at 323 K while stirring at a speed of 2.5 rps. The resulting viscous liquid was gradually dropped into the water dissolving 1.3 wt% polyvinyl alcohol kept at 343 K and then was subjected to suspension polymerization for 14.4 ks while stirring at a speed of 2.5 rps. After the suspension polymerization, the resultant particles were collected by filtration under reduced pressure, washed sufficiently with deionized water, and dried at 353 K for 7.2 ks. The particles thus fabricated were referred to as x(ST-1)-PSM (x = 10, 30, 50) hybrid particles, depending upon the additive amount of ST-1 powder. For reference, the suspension polymerization was done by employing the same raw mixture, but without ST-1 powder. Then, the resultant particles were simply expressed as PSM particles.

2.2. Fabrication of composite sheets from PS-based hybrid particles

PS-based composite sheets fabricated by employing ST-1 powder or 50(ST-1)-PSM hybrid particles were prepared to estimate the dispersion level of ST-1 powder, mechanical strength, and oxygen index. ST-1 powder or 50(ST-1)-PSM hybrid particles were incorporated into PS polymer by using a two-roll mill at 403 ± 5 K for about 900 seconds. The composites obtained were then compression molded into a form of sheet at 453 K for 240 seconds under an applied pressure of 0.46 MPa and subsequently at 453 K for 120 seconds at 2.4 MPa. Thereafter, the compressed sheets were cooled down to room temperature within 300 seconds under the same pressure, and those resultant composite sheets were cut into a predefined shape suitable for tensile testing. For reference, a PS sheet without any ST-1 powders was also prepared by a similar procedure.

TABLE 1: Properties of PS sheet and composite sheets fabricated by a mixture of PS pellets and ST-1 powder and a mixture of PS pellets and 50(ST-1)-PSM hybrid particles.

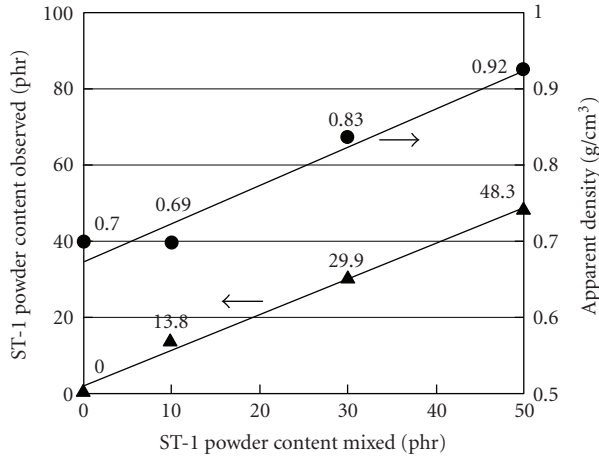| Sample | Composition (g) | | | | Total ST-1 content (wt%) | Elongation (%) | Oxygen index |
| | PS | ST-1 | 50(ST-1)-PSM hybrid particle | | | | |
			PS (observed)	ST-1 (observed)			
PSC-1	120.0	0.0	0.0	0.0	0.0	11.8 (10.0–16.8)	18.0
PSC-2	148.3	38.6	0.0	0.0	20.0	8.2 (6.4–8.9)	19.0
PSC-3	50.0	0.0	98.3	38.6	20.0	7.9 (6.0–8.9)	20.1

FIGURE 3: Variations in the observed content of ST-1 powder in x(ST-1)-PSM hybrid particles and their apparent density with the mixed content of ST-1 powder. Data for PSM particles is also indicated.

2.3. Characterization

The shape and cross-section of the hybrid particles were observed by scanning electron microscopy (SEM, S-2250N, Hitachi High-Technologies Corp.). The PSM particles and the x(ST-1)-PSM hybrid particles were fired at 1273 K at a heating rate of 20 deg/min under flowing air (flow rate: 100 ml/min) and the amounts of MgO left behind were measured to confirm the contents of ST-1 powder in the hybrid particles.

Apparent densities of the PSM particles and the x(ST-1)-PSM hybrid particles were measured with a gas pycnometer (Accupyc 1330, Shimadzu Corp.) by using their dry powders. Compressive strengths of the PSM particles and the x(ST-1)-PSM hybrid particles were measured with a microcompression testing machine (MCT-W500, Shimadzu Corp.) under conditions of a maximum load of 4500 mN, a loading rate of 69 mN/s and diameter of an indenter with a flat surface of 500 μmϕ. Particle sizes of the hybrid particles used for the measurements were under 500 μm. Compressive strength was calculated by the following equation:

$$S_c = \frac{2.8P}{\pi d^2}, \qquad (1)$$

where S_c is a compressive strength, P is a load at the fracture, and d is a particle diameter.
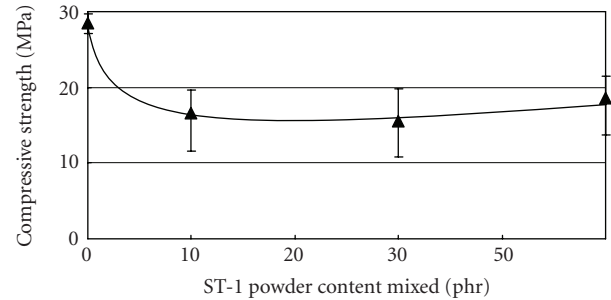

FIGURE 4: Variation in compressive strength of x(ST-1)-PSM hybrid particles with mixed contents of ST-1 powder.

The fracture surfaces of the composite sheets, which were prepared at room temperature, were also observed by SEM. Flame retardancy of the composite sheets was evaluated with the oxygen index, which is defined by the JIS K 7201, measured with a D-type instrument (Toyo seiki Seisakusho, Co., Ltd.). The specimen size subjected to this test was $3 \times 6.5 \times 80$ mm. The composite sheets were then subjected to tensile tests along with the direction of roll milling of the sheets by using a tensile test machine (Strograph, Toyo Seiki Seisaku-sho, Ltd.) at a crosshead speed of 50 mm min^{-1} according to the JIS K 6551 method. During these tensile tests, elongations of the composite sheets were also measured. The experimental results were evaluated with the average value of five measurements for each specimen.

3. RESULTS AND DISCUSSION

It was revealed that ST-1 powder showed hydrophobic nature, since a contact angle value between a droplet of deionized water and a tablet of ST-1 powder was 120.7°. The high hydrophobicity can be attributed to the introduction of a lot of methyl groups by chemical reaction between the hydroxyl groups on the surface of ST-1 powder and MHS and physical adsorption of MHS.

Figure 1 shows SEM images of the surfaces of the PSM particle and x(ST-1)-PSM hybrid particles. Cross-sectional views of x(ST-1)-PSM hybrid particles are shown in Figure 2. It is obvious that all these hybrid particles are sphere in shape with a particle size of about 500 μm, although the surfaces of x(ST-1)-PSM hybrid particles are rather rough, as shown in Figures 1(b), 1(c), and 1(d). From the cross-sectional views, it was confirmed that the ST-1 powder was involved in the

particles, irrespective of the amount of ST-1 powder, and the dispersion level of ST-1 powder was a micrometer order (see Figure 2(d)), although a fraction of the ST-1 powder existing in the surface region of particles was rather high.

Observed contents of ST-1 powder in x(ST-1)-PSM hybrid particles and their apparent densities are plotted against the mixed content of ST-1 powder, as shown in Figure 3. For reference, data for PSM particles is also plotted. The apparent density of x(ST-1)-PSM increases almost linearly with increasing the ST-1 content. This is due to the larger density of $Mg(OH)_2$ than that of PS. On the other hand, observed ST-1 powder contents in the hybrid particles were almost equivalent to the mixed ones, for example, the observed content was 48.3 phr for 50(ST-1)-PSM hybrid particles. Such a good agreement between the mixed and the observed content of ST-1 powder is considered to arise from the combined effect of the following three factors: (1) limitation of the separation of ST-1 powder from the dispersed phase by an increase in its viscosity, (2) a good affinity between hydrophobic ST-1 powder and PS matrix induced by the surface modification with MHS, and (3) a chemical bonding with a dehydration between remaining surface hydroxyl groups on the ST-1 powder and MA incorporated in the PS chains.

Figure 4 shows variation in compressive strength of x(ST-1)-PSM hybrid particles with the content of ST-1 powder. The compressive strength of PSM particles was ca. 28.5 MPa, and the addition of ST-1 powder led to a decrease in compressive strength. However, almost the same value of the compressive strength was kept even if 50 phr of ST-1 powder was added, that is, 16.6, 15.5, and 18.6 MPa were measured for 10(ST-1)-PSM, 30(ST-1)-PSM, and 50(ST-1)-PSM hybrid particles, respectively. Almost the same compressive strength of x(ST-1)-PSM hybrid particles may arise from low agglomeration of ST-1 powder, less formation of voids inside the hybrid particles (see Figure 2(d)), and a good affinity between hydrophobic ST-1 powder and PS matrix.

Table 1 compares properties of three kinds of PS composite sheets: one without ST-1 powder (PSC-1) and two containing ST-1 (PSC-2) or 50(ST-1)-PSM hybrid particles (PSC-3). Values of elongation of PSC-2 and PSC-3 were almost the same and were lower slightly than that of PSC-1. This is a reasonable phenomenon induced by the addition of ST-1 powder into the PS matrix. However, an oxygen index of 20.1 observed for PSC-3 was higher than those of PSC-1 and PSC-2. This result indicates a potential advantage of the hybrid particles. It is obvious that PSC-3 shown in Figure 5(b) achieves homogenous distribution of ST-1 powder and the number of voids between the ST-1 powder and the PS matrix is smaller than that of PSC-2 shown in Figure 5(a). In addition, a density of PSC-3 was higher than that of PSC-2. Therefore, it is considered that the dense structure of PSC-3 may be one of the reasons for the higher oxygen index.

4. CONCLUSION

PS-based spherical particles with different additive amounts of ST-1 powder were fabricated by a bulk and suspension two-step polymerization method. The actual contents of ST-1 powder incorporated inside the x(ST-1)-PSM
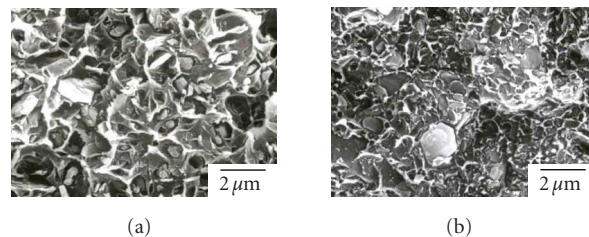

(a)

(b)

FIGURE 5: SEM images of the fracture surfaces of (a) the composite sheet fabricated by a mixture of PS pellets and ST-1 powder (PSC-2) and (b) the composite sheet fabricated by a mixture of PS pellets and 50(ST-1)-PSM hybrid particles (PSC-3).

(x = 10, 30, 50) hybrid particles were almost the same as those in the raw mixtures, and agglomeration of ST-1 powder was hardly observed inside these hybrid particles. The compressive strength of x(ST-1)-PSM hybrid particles remained almost unchanged, irrespective of an increase in the ST-1 powder content. Furthermore, the composite fabricated by employing PS pellets and the 50(ST-1)-PSM hybrid particles achieved homogenous distribution of ST-1 powder and showed a higher oxygen index than that of the composite fabricated by employing PS pellets and ST-1 powder. These features are very attractive as a flame retardant PS material, since we can expect the enhancement of flame retardancy without any vital degradation of mechanical properties.

REFERENCES

[1] U. Hippi, J. Mattila, M. Korhonen, and J. Seppälä, "Compatibilization of polyethylene/aluminum hydroxide (PE/ATH) and polyethylene/magnesium hydroxide (PE/MH) composites with functionalized polyethylenes," *Polymer*, vol. 44, no. 4, pp. 1193–1201, 2003.

[2] S. Chang, T. Xie, and G. Yang, "Effects of polystyrene-encapsulated magnesium hydroxide on rheological and flame-retarding properties of HIPS composites," *Polymer Degradation and Stability*, vol. 91, no. 12, pp. 3266–3273, 2006.

[3] J. Qin, W. Guo, and Z. Zhang, "A kinetic study on bulk thermal polymerization of styrene," *Polymer*, vol. 43, no. 26, pp. 7521–7527, 2002.

[4] B. Platzer, R.-D. Klodt, B. Hamann, and K.-D. Henkel, "The influence of local flow conditions on the particle size distribution in an agitated vessel in the case of suspension polymerisation of styrene," *Chemical Engineering and Processing*, vol. 44, no. 11, pp. 1228–1236, 2005.