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Basic Studies on Fabrication and Characterization of Organic-Inorganic Hybrid Particles

機能性有機-無機複合粒子の調製と評価に関する基礎的研究

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長崎大学大学院 生産科学研究科
木村 秀一
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Acknowledgements
1. Introduction

1.1. Background

Recently, nanometer- or micrometer-sized combined particles have been put into practical use as one of important materials in industrial fields, for fabrications of paints, medical agents, cosmetics, toners, graphical elements, food products, etc. [1-3]. Consequently, special attentions have been focused on developments of combined particles with innovative microstructure and properties, so as to fabricate a final product with excellent performance, and therefore, many studies about combined particles have been reported [4-20].

The combined particles are classified into several types from their microstructure. A capsule is one of the combined particles and is well known. The capsule is formed from a core material and a shell material. The core material can be selected freely, irrespective of solid, liquid and gas states. For example, in the case of a hollow microsphere, the core material is air and the shell material is a solid material such as polymers, metals and ceramics. It is also possible to fabricate a capsule with multicore structure. These capsules with core and shell (core/shell) structure have effective and unique advantages. One of the effective and unique advantages is a protection effect for a core material. The core material is not exposed directly to external environment such as heat, force, a solvent and an enzyme because it is protected by the shell material. Therefore, the capsules formed from a medical agent as a core material and biodegradable plastics as a shell material have been utilized as an important materials for a drug delivery system (DDS). Another effective and unique advantage is the surface modification effect for a core material. The surface properties of a core material can be modified by coating a shell material.

Besides these advantages of combined particles, our special attentions have been focused on another potential advantage, namely, an excellent dispersibility effect of the core material inside a composite fabricated from the combined particles. Generally, properties of polymer-based products have been often improved by the addition of functional fillers for the sake of practical use. Mechanical mixing by a biaxial extruder [22-25], a dispersion mixer or a kneader is the commonest method for mixing the functional fillers with a polymer matrix [26-31]. However, conventional mechanical mixing is rather a time-consuming and skilled process for achieving homogenous distribution of functional fillers inside the final products. For example, segregation of functional fillers inside the final products due to insufficient mixing may lead to poor thermal and mechanical properties. Thus, a key point to achieve homogenous distribution of functional fillers inside the final products within a short time is to fabricate the final product by employing micrometer-sized
polymer-based combined particles containing highly dispersed functional fillers as a raw material, without binders, if possible.

A lot of techniques to fabricate such combined particles have been investigated. Their fabrication techniques are divided into three main branches, i.e. physical (mechanical), chemical and physicochemical techniques. For example, a mechanochemical method [32-34] and a hybridization method [35] as a physical (mechanical) technique, an interfacial polycondensation polymerization method [36-37], an suspension polymerization method [38-39], and a miniemulsion polymerization method [40-41] as a chemical technique, and a complex coacervation method [42-44], a membrane emulsification method [45-50] and a solvent evaporation method [51-69] as a physicochemical technique are well known nowadays.

Details of these techniques are as follows.

Fig. 1-1  A schematic illustration of the mechanofusion system.
Mechanochemical method

The combined particles are formed by a dry coating technique known as mechanofusion (MF). Fig. 1-1 shows a schematic illustration of the MF system. It consists of a rotating cylindrical chamber in which a fixed rounded inner-piece and a fixed scraper blade are placed. The radius of the inner-piece is smaller than that of the chamber and the clearance space between the inner-piece and the chamber inner wall is adjustable in the range from 1 to 5 mm. The clearance between the scraper blade and the chamber inner wall is much smaller, usually around 0.5 mm. These clearances are adjustable, and are determined by many factors such as powder properties, particle size, the desired properties of the final coated products, and so on. The powder mixture is put inside the chamber. The operation of the MF process is simple, but the mechanism of powder processing within the chamber is very complicated. When the chamber rotates, powder is forced to the chamber wall by centrifugal action. While passing through the converging space of the powder between the round inner-piece and the chamber wall, mechanical interactions, mainly in the form of high shear-rate collisions, take place among the particles as well as among the particles, the solid boundaries of the chamber inner wall and the inner-piece. As the particles come out of the inner-piece region, they adhere to each other and to the chamber wall. The blade serves to scrape off the powder attached to the chamber wall. The sheared powder mixture is then redispersed into the chamber and moves towards the inner-piece region again. The powder continuously undergoes this process of compression, deagglomeration, and frictional shearing while the chamber is rotating. Since the chamber rotates at high speeds, the interactions are intense and a considerable amount of thermomechanical energy may be generated, which can produce in various effects on powder materials. Various operating parameters, such as local temperature and operating time, are controlled and monitored to prevent thermal degradation of particles. The degree of coverage is dependent on the particle size ratio of the core to shell particles (typically the size of host particles is required at least 10 times larger than that of guest particles), the proportion of the guest material, the relative adhesive properties of the host and guest particles, and the energy input from the machine.

Hybridization method

The hybridization method, which is classified into a mechanical technique, is an unique and interesting technique, i.e. a dry granulating technique without using any liquids by utilizing mechanical energy such as compressing, friction and/or shearing forces.

Details of the hybridization system will be described in Chapter 2. The structure of the combined particles fabricated by the hybridization method is a mononuclear, i.e. one core material inside a hybrid particle. It is necessary to keep in mind about selection of raw materials. A key point to achieve strong connection between core and shell materials is compatibility between raw core and shell materials. The compatibility depends on the combination of raw core and shell materials.
materials. Generally, thermoplastic polymers such as polyethylene, polystyrene and polymethylmethacrylate have been employed extensively as raw materials [72-73], either a core or a shell material, to fabricate the combined particle, because the polymer materials, which show low melting temperature and relatively high degree of ductility and elongation, are compatible with hard materials such as metals and ceramics.

Figure 1-2 shows a schematic illustration of models of the structures of the combined particles fabricated by the hybridization method [35]. The combined particles with four kinds of structures are showed in a first stage. The different structures are formed by differences of various operating parameters and/or the proportions of raw materials. An ultimate structure of the combined particles is decided by a subsequent process, which is rearrangement, pulverization, dispersion, stabilization or encapsulation, and almost all the combined particles in the case of Model B and Model D are led to the combined particles with the mononuclear structure.

Interfacial polycondensation polymerization method

The interfacial polycondensation polymerization has been used as a useful method for microencapsulating the liquid phase as a core material. In this microencapsulation process, a reactant A is dissolved in a liquid phase beforehand, and then, the resulting solution (dispersed phase) is added into a continuous phase dissolving a reactant B for preparation of an emulsion. In order to prepare a stable emulsion, few surfactants or polymers are always added to the continuous and/or the dispersed phase. And then, shell material is formed by the chemical reaction between the reactant A and the reactant B on the liquid-liquid interface to fabricate the combined particles with a core/shell structure.

Suspension polymerization method

A monomer containing a polymerization initiator and a core material (a dispersed phase) is added into a continuous phase, namely water phase containing a stabilizing agent, and then suspended by mechanical force. Polymerization occurs within droplets of the dispersed phase in an oil in water (O/W) emulsion. After polymerization, generally, the resultant combined particles are of multicore structure. Occasionally, a bulk polymerization process was introduced before a suspension polymerization process to prevent the agglomeration of a core material or the separation of a core material from the dispersed phase. This method is named a bulk and suspension two-step polymerization method in the present study. Details of the bulk and suspension two-step polymerization method will be described in Chapter 3.
Miniemulsion polymerization method

A monomer containing a core material (without any polymerization initiators) is added into a continuous phase, namely water phase dissolving a higher concentration of a surfactant. Submicron-size monomer droplets are prepared by using high-force-dispersion devices such as an ultrasonicator and a high-pressure homogenizer. And then, a water-soluble polymerization initiator
is added into the continuous phase to start polymerization. The use of a high water-insoluble compound (hydrophobe) and a surfactant stabilizes small droplets in miniemulsion. The hydrophobes suppress diffusion of monomer component from the droplets to continuous phase and surfactants depress agglomeration of droplets caused by collision. The miniemulsion polymerization provides potential advantages for the encapsulation of inorganic particles in latex particles.

Coacervation method

Microcapsules fabricated by the coacervation are divided into mononuclear and multinuclear microcapsules according to their internal structure. Mononuclear microcapsules are formed when one monomer droplet is encapsulated by the coacervation, while multinuclear microcapsules are formed by aggregation of multiple mononuclear microcapsules. The coacervation process is divided into two types, namely simple and complex, depending on the number of polymeric ingredients. The process of complex coacervation microencapsulation comprises four basic steps: emulsification, coacervation, gelation and hardening. A core material is added into an continuous phase (an oil or a water phase) dissolving a shell material to form a water in oil (W/O) or an O/W emulsion. And then, because a good solvent for the shell material is diluted by adding gradually a poor solvent for the shell material into the continuous phase, the shell material is coacervated, gelated and hardened.

Membrane emulsification method

This technique allows the fabrication of uniform-sized emulsion droplets by permeating a dispersed phase (e.g. an oil phase) into a flowing continuous phase (e.g. an aqueous phase) through a membrane with uniform-sized pores under suitable conditions. The advantages of the membrane emulsification over conventional processes are the low energy consumption and the easy control of droplet size. For the membrane emulsification, Shirasu porous glass (SPG) membranes are potentially suitable membranes due to their uniform-sized pores, a wide range of available mean pore diameter (50 nm to 20 µm) and the possibility of surface modification. With the membrane emulsification using SPG membranes, single and multiple emulsions, namely O/W, W/O, water-in-oil-in-water (W/O/W) emulsions can be prepared.

As for the fabrication of combined particles by SPG membrane emulsification and subsequent suspension polymerization, the oil phase containing a monomer, a polymerization initiator and a core material permeates into the continuous phase through the uniform pores of the SPG membrane by gas pressure. A stabilizer and a surfactant dissolved in the aqueous phase are adsorbed on the surface of the droplets to stabilize them. Then, by elevating temperature beyond the decomposition temperature of the initiator, the suspension polymerization proceeds to form uniform particles.
During the suspension polymerization, the narrow size distribution of the droplets is maintained if the emulsification and polymerization conditions are adequate.

Solvent evaporation method

One of methods for microencapsulating a core material into a water-insoluble polymer is a solvent evaporation method. This technique has been used for fabrication of combined particles for DDS [52-55, 57-59, 61-63]. Details of the solvent evaporation method will be described in Chapter 4.

It is important to select a suitable fabrication technique from view points of the properties of raw materials (e.g. the kind, shape, size, volume, density and composition), application fields, cost [70], processing conditions (e.g. temperature, atmosphere and time), the properties of resultant hybrid particles (e.g. the microstructure, shape and size) and so on. Furthermore, an environmental suitability is also an important factor to select a fabrication technique. Thus, key points are reduction of environmental damage and safeness for human being [71].

1. 2. Aim of the present study

The aim of the present study is to establish the fabrication process and to characterize several kinds of polymer-based hybrid particles containing functional fillers fabricated. These polymer-based hybrid particles were fabricated by three different methods, i.e. a hybridization method, a bulk and suspension two-step polymerization method and a solvent evaporation method. The details of the aim are given in the “Introduction” sections of Chapters 2-5.

1. 3. Concepts

1. 3. 1. Definition of hybrid particles

In the present study, all combined particles fabricated from multiple raw materials are named “hybrid particles”. The hybrid particles include a capsule with core/shell structure and a capsule with multicore structure.

1. 3. 2. Fabrication methods of hybrid particles

A hybridization method, a bulk and suspension two-step polymerization method and a solvent evaporation method are employed in the present paper, so as to fabricate polymer-based hybrid particles with smooth surface and spherical shape.
Details of the hybridization method, the bulk and suspension two-step polymerization method and the solvent evaporation method will be described in Chapters 2, 3 and 4, respectively.

1. 3. 3. Characterization of hybrid particles

Resultant polymer-based hybrid particles, which were fabricated under various conditions, were characterized for shape and particle size, microstructure, thermal and mechanical properties and so on.

1. 4. Outline of the present thesis

As mentioned above, the background, the aim of the present study and the concept are presented in Chapter 1. A fabrication process of polymethylmethacrylate-based hybrid particles containing magnetic materials with core/shell structure by a hybridization method and electromagnetic wave absorption properties and structure of the composites fabricated by employing the resultant hybrid particle are reported in Chapter 2. Chapter 3 presents the results of characterization of polystyrene-based hybrid particles containing hydrophobic Mg(OH)\textsubscript{2} powder fabricated by a bulk and suspension two-step polymerizations method and composites fabricated by employing the resultant hybrid particles. Furthermore, in Chapter 4, fabrication processes and characteristics of polystyrene-based hybrid particles containing hydrophobic Mg(OH)\textsubscript{2} powder or multiple fillers by a solvent evaporation method are reported. Fabrication processes and characteristics of polyethylene-based hybrid particles containing hydrophobic Mg(OH)\textsubscript{2} powder by an environmentally-friendly solvent evaporation method and composites fabricated by employing the resultant hybrid particles are reported in Chapter 5. A general conclusion of the present study is presented in Chapter 6.
References

2. Polymethylmethacrylate/Carbonyl Iron-Ferrite Core/Shell Hybrid Particles and Composites Fabricated from the Hybrid Particles

2.1. Introduction

The present chapter reports about polymethylmethacrylate/carbonyl iron-ferrite core/shell hybrid particles and composites fabricated by employing the resultant hybrid particles. A possibility for an application as an electromagnetic wave absorber will be discussed.

2.1.1. Electromagnetic wave absorber

Recently, various kinds of devices, which utilize electromagnetic waves in the range of GHz, have been put into practical use. Those include cellular telephones, wireless LAN systems, central processing units for computers, satellite-based broadcasting, and so on. In accordance with a rapid and wide spread of the use of these devices, especially for cellular telephones, electromagnetic interference (EMI) is getting serious problems today. Therefore, development of electronic devices having electromagnetic compatibility (EMC) is becoming very important. The electromagnetic compatible devices can be defined as those emitting outside no harmful electromagnetic wave and protecting from the harmful electromagnetic waves generated from other devices. To achieve sufficient EMC, a variety of electromagnetic wave absorbers have already been used inside various kinds of commercial devices, but development of more prominent electromagnetic wave absorbers is still highly requested in various fields.

2.1.2. Potential advantages of core/shell hybrid particles

Generally, the electromagnetic wave absorbers consist of a polymer and a magnetic material [74-78]. A mechanical mixing such as an electrothermal roll or a twin screw extruder is one of simple and common methods for preparation of electromagnetic wave absorbers. After the mechanical mixing, the resultant composites are formed into a suitable shape such as a sheet. However, conventional mechanical mixing is rather a time-consuming and skilled process for achieving homogenous dispersion of fillers. For example, segregation of magnetic materials inside of the composites due to insufficient mixing may degrade quality of electromagnetic wave absorption properties.

Thus, a key point to achieve homogenous dispersion of magnetic material in final products within
a short time is to use polymer-based hybrid particles containing magnetic materials in micrometer size as a raw material [79-80]. The resultant composites fabricated by employing the hybrid particles, without binders such as polymers or rubbers, may have uniform and homogeneous distribution of magnetic materials. Furthermore, other potential advantages of the use of these hybrid particles are simplicity for making a complex shape and a tailored design and/or control of absorption properties of electromagnetic wave absorbers by changing the kind and content of magnetic materials [81-85]. However, fabrication processes and morphology of these polymer-based hybrid particles containing magnetic materials and properties of composites fabricated by employing the resultant hybrid particles have not been investigated satisfactorily yet.

2.1.3. Aim

The aim of this chapter is to establish fabrication processes and morphology of polymethylmethacrylate (PMMA)-based hybrid particles by a hybridization method, which belongs to a mechanical technique among fabrication techniques of hybrid particles, and then to investigate the electromagnetic wave absorption properties of the composites fabricated by employing the resultant hybrid particles.
2. 2. Experimental

2. 2. 1. Materials

Carbonyl iron powder (mean particle size (MPS): 7 μm, Toda Kogyo Co., Ltd.) spherical in shape and Mn-Zn ferrite powder (MPS: 1.8 μm, Toda Kogyo Co., Ltd.) as core materials and PMMA microspheres (MPS: 0.4 μm, Soken Chemical and Engineering Co., Ltd.) as a shell material were employed.

2. 2. 2. Fabrication of core/shell hybrid particles by a hybridization method

Carbonyl iron powder or mixed powder (1 : 1 in volume) of carbonyl iron and Mn-Zn ferrite was coated with an equal volume of PMMA microspheres by a hybridization system in laboratory atmosphere at room temperature. The use of the hybridization system (NHS-0, Nara Machinery Co., Ltd.) is one of methods to modify the surface of particles, in order to granulate uniformly or to combine several particles. External views and a schematic illustration of the movement of the hybridization system are shown in Fig. 2-1. The hybridizer consists of a rotor, a flow path and a sample holder. Mixed powder of carbonyl iron and PMMA or mixed powder of carbonyl iron, ferrite and PMMA was input from the entrance and was allowed to circulate continuously through a flow path and a rotor with a help of pressure of air flowing. Powders were then combined each other in the rotor by mechanical energy such as shearing, friction and compressing forces generated by the rotating blades. These combined powders were collected from the vent. The rotation condition of a rotor was 10000 rpm for 5 min. Then, these combined particles, which will be referred to as hybrid particles, were subjected to heat treatment at 433 K for 7.2×10^3 s, to prepare the smooth surface of the hybrid particles with core (carbonyl iron or carbonyl iron-ferrite)/shell (PMMA) structure, as shown in Fig. 2-2.

For comparison, a mixture of carbonyl iron particles and PMMA particles (1 : 1 in volume) was prepared by using a blender at 10000 rpm for 1.8×10^2 s.

2. 2. 3. Fabrication of composites from core/shell hybrid particles

These hybrid particles and a mixed powder of carbonyl iron and PMMA (carbonyl iron/PMMA mixture) were molded into a cylinder shape with a thick wall (7 mm in outer diameter and 3 mm in inner diameter) at 433 K for 7.2×10^3 s. A schematic illustration of the cylinder and an external view of a metallic mold are shown in Figs. 2-3 and 2-4, respectively. The resultant cylinders, which will be referred to as a composite, were cut into predefined lengths (1-10 mm in length, that is
the composite thickness) and then were subjected to the measurements of the electromagnetic wave absorption properties.

Fig. 2-1 (a) and (b) External views and (c) a schematic illustration of the movement of the hybridization system used.
Fig. 2-2 A schematic illustration of a cross section of a hybrid particle fabricated by the hybridization method.

Fig. 2-3 A schematic illustration of the shape and size of a composite in a cylindrical shape fabricated by employing the resultant hybrid particles.
2. 2. 4. Scanning electron microscopic observation

Shapes and surface regions of the hybrid particles and a surface region and a cross sectional view of a composite were observed by a scanning electron microscopy (SEM, S-2250N, Hitachi High-Technologies Corp.) shown in Fig. 2-5(a). To reduce the charging effect of the hybrid particles, the surfaces of the hybrid particles were coated with Au under vacuum by using an ion sputtering apparatus shown in Fig. 2-5(b), before being subjected to SEM observation.
2. 2. 5. Measurement of electromagnetic wave absorption properties

The cylindrical composite cut into predefined lengths was set either a 2 mm or 5 mm sample holder shown in Fig. 2-6(a), depending upon the length of the composites. Thereafter, these composites were subjected to the measurements of scattering parameters (S-parameter), i.e. reflection ($S_{11}$ parameter) and transmission ($S_{21}$ parameter) of a transverse electric and magnetic wave, by using a network analyzer (8710B, Hewlett-Packard Co., Ltd.) shown in Figs. 2-6(b) and 2-6(c), in a frequency range of 0.05-13.50 GHz. Then, the real and imaginary components of the complex permeability ($\mu_r^* = \mu_r' - j\mu_r''$) and permittivity ($\varepsilon_r^* = \varepsilon_r' - j\varepsilon_r''$) values were calculated from the S-parameters ($S_{11}$ and $S_{21}$) measured by using two-port technique, shown in Fig. 2-7(a). Electromagnetic wave absorption properties were evaluated by reflection loss (RL) values. Using the obtained values of the complex permittivity and complex permeability, it is possible to calculate a simulated RL (RL(s)) and to design the optimum composite thickness. The RL(s) values were derived from the following equations,
\[
\Gamma = \log_{10} \left( \frac{Z_{in} - Z_0}{Z_{in} + Z_0} \right),
\]

where \( Z_{in} \) is the input impedance of composites, \( Z_0 \) is the characteristic impedance of free space and \( \lambda \) is the wavelength. The situation with a RL value of less than -20 dB means adequate electromagnetic wave absorption conditions at a specific microwave frequency, and is then called a matching situation. The composite thickness and the specific frequency in the matching situation were defined as matching thickness and frequency, respectively.

On the other hand, an actual (experimental) RL (\( RL(a) \)) value was calculated from the \( S_{11} \) parameter measured by using one-port technique (see Fig. 2-7(b)) at a particular composite thickness for the composite terminated with a metal at its rear face. In this case, \( RL(a) \) values are calculated by the following equation.

\[
RL(a) = 20 \log |S_{11}| \quad \text{(4)}
\]

The \( RL(a) \) values measured with one-port technique were compared with the \( RL(s) \) values obtained with two-port technique.

Fig. 2.7  Schematic illustrations of measurement techniques used for a network analyzer. (a) Two port technique and (b) one port technique.
2. 3. Results and discussion

2. 3. 1. Morphology of core/shell hybrid particles

Figures 2-8(a) and 2-8(c) show SEM images of as-prepared PMMA/carbonyl iron and PMMA/carbonyl iron-ferrite hybrid particles, respectively. It is obvious that the surface of large particles is covered with a plenty of small particles in both the cases. By referring to the difference in particle size among carbonyl iron (MPS: 7 μm), ferrite (MPS: 1.8 μm) and PMMA (MPS: 0.4 μm), it is reasonable to consider that carbonyl iron particles and mixture of carbonyl iron and ferrite particles are coated with small PMMA particles by the hybridization method employed. These coated PMMA particles were intended to be converted into a smooth and uniform coating layer on the surfaces of carbonyl iron particles and the mixture of carbonyl iron and ferrite particles, in order to make a core/shell structure, by subsequent heat treatment at 433 K. This attempt could be achieved to a certain extent after the heat treatment, as shown in Figs. 2-8(b) and 2-8(d), since the calcined hybrid particles still showed a rough surface.

One may expect that the thickness of the PMMA layer on the surface of the heated hybrid particles can be controlled by the amount of PMMA particles in the mixture of raw materials. However, excess addition of PMMA, e.g. core : shell = 3 : 7 in volume, resulted in agglomeration of only PMMA particles and/or cohesion among hybrid particles under the experimental conditions employed (the data is not shown here). In addition, the excess addition of PMMA directly means a decrease in the content of magnetic materials, and then is considered to result in poor electromagnetic wave-absorption properties. Therefore, the results obtained with the raw materials with the composition of core : shell = 1 : 1 in volume are reported in the present study.

2. 3. 2. Internal morphology of composites

Figures 2-9(a) and 2-9(b) show external views of the PMMA/carbonyl iron hybrid composite after molding of the hybrid particles into the cylindrical shape at 433K. The hybrid composite could maintain its cylindrical shape after the molding without the addition of another binder. The carbonyl iron/PMMA hybrid composite also exhibited enough mechanical strength, and no cracks were observed after its molding. These features are suitable for the measurement of electromagnetic wave absorption properties. The surface and fracture surface of the hybrid composites shown in Fig. 2-9(c) and 2-9(d) revealed uniform and homogeneous distribution of carbonyl iron in the PMMA matrix due to the unique fabrication process of the composite.

2. 3. 3. Electromagnetic wave absorption property
Fig. 2-8  SEM images of hybrid particles before and after heat treatment at 433 K for $7.2 \times 10^3$ s. (a) As-prepared PMMA/carbonyl iron, (b) heated PMMA/carbonyl iron, (c) as-prepared PMMA/carbonyl iron-ferrite, and (d) heated PMMA/carbonyl iron-ferrite.
Fig. 2-9  (a), (b) External views and SEM images of (c) the surface and (d) the fracture surface of a molded PMMA/carbonyl iron composite (composition of raw materials, core(carbonyl iron) : shell(PMMA) = 1 : 1 in volume).
Figures 2-10(a) and 2-10(b) show the real ($\varepsilon'$) and imaginary part ($\varepsilon''$) of complex permittivity and the real ($\mu'$) and imaginary part ($\mu''$) of complex permeability, respectively, for the three composites molded from the following particles: a PMMA/carbonyl iron mixture, PMMA/carbonyl iron hybrid particles, and PMMA/carbonyl iron-ferrite hybrid particles. Values of complex

Fig. 2-10 Variations in (a) complex permittivity and (b) complex permeability with frequency for PMMA/carbonyl iron mixture composite (△: real part, ▲: imaginary part), PMMA/carbonyl iron hybrid composite (○: real part, ●: imaginary part) and PMMA/carbonyl iron-ferrite hybrid composite (□: real part, ■: imaginary part).
The permittivity and complex permeability of these composites varied with the kind of raw particles. The smaller values in $\varepsilon_r'$ and $\mu_r'$ of the composite molded from the PMMA/carbonyl iron mixture (hereafter it will be referred to as the PMMA/carbonyl iron mixture composite) may be attributed to a higher content of pores (values in $\varepsilon_r'$ and $\mu_r'$ of air is ca. 1) in the composite than that of the composite molded from the PMMA/carbonyl iron hybrid particles (the PMMA/carbonyl iron hybrid composite). In addition, the smaller values in $\varepsilon_r'$ and $\mu_r'$ of the PMMA/carbonyl iron-ferrite hybrid composite than that of the PMMA/carbonyl iron hybrid composite are attributed to the fact that the values in $\varepsilon_r'$ and $\mu_r'$ of ferrite is lower than those of carbonyl iron. On the other hand, the $\varepsilon_r''$ and $\mu_r''$ values were not zero for all the composites in the most frequency range studied. In addition, each composite had an individual material constant (complex permittivity and complex permeability) at a specific frequency, and therefore each composite showed specific electromagnetic wave absorption properties in different frequency ranges.

Minimum RL(s) values are compared with actually observed ones (RL(a)) as a function of composite thickness for the three composites, PMMA/carbonyl iron mixture composite, PMMA/carbonyl iron hybrid composite and PMMA/carbonyl iron-ferrite hybrid composite, as shown in Fig. 2-11. As for the both hybrid composites, the values of minimum RL(s) agreed well with RL(a) over the almost whole thickness range studied, as shown in Figs. 2-11(b) and 2-11(c). In contrast, such a good agreement was not achieved for the case of the PMMA/carbonyl iron mixture composite, as shown in Fig. 2-11(a). Therefore, the good agreements observed for the hybrid composites may arise from uniform and homogeneous distribution of magnetic materials in the PMMA polymer matrix due to the unique fabrication process of hybrid particles. Furthermore, the minimum RL(a) values less than -30 dB were observed in a wide thickness range for these two hybrid composites (see Figs. 2-11(b) and 2-11(c)), in comparison with those for the PMMA/carbonyl iron mixture composite (see Fig. 2-11(a)).

Figure 2-12 shows the frequency dependence of RL(a) for the two hybrid composites having different thicknesses. As for the PMMA/carbonyl iron hybrid composite, the matching situation could be achieved in a frequency range of 1.7 to 5.0 GHz when the composite thickness was below 5.00 mm. In the case of the PMMA/carbonyl iron-ferrite hybrid composite, on the other hand, similar RL(a) was observed in a frequency range of 4.3 to 13.5 GHz, which was a wider and higher frequency region than that observed for the PMMA/carbonyl iron hybrid composite. Thus, the addition of ferrite was found to be useful for achieving a large absorption in a wide frequency range, especially for higher frequency values. Thus, by employing these composites fabricated, it is possible to fabricate the final products, which require excellent electromagnetic wave absorption property at a specific frequency in the frequency range from 1.73 to 13.1 GHz.

Variations in frequency at the minimum RL(a) with the composite thickness measured for both series of hybrid composites are shown in Fig. 2-13. The frequency at the minimum RL(a) tended to
increase with decreasing the composite thickness in both series of hybrid composites. From these relationships, we can design an appropriate thickness of an electromagnetic wave absorber so as to be suitable for a specific frequency.

Fig. 2-11 Variations in minimum RL(s) (solid line) and RL(a) values (○) of three kinds of composites with composite thickness. (a) PMMA/carbonyl iron mixture composite, (b) PMMA/carbonyl iron hybrid composite, and (c) PMMA/carbonyl iron-ferrite hybrid composite.
Fig. 2-12  Frequency dependence of RL(a) of (a) PMMA/carbonyl iron hybrid composites and (b) PMMA/carbonyl iron-ferrite hybrid composites having different thicknesses.
Fig. 2-13 Variations in frequency at the minimum RL(a) with composite thickness measured for (a) PMMA/carbonyl iron hybrid composite and (b) PMMA/carbonyl iron-ferrite hybrid composite.
2. 4. Conclusions

The surface of carbonyl iron powder or a mixture of carbonyl iron and ferrite was coated with PMMA microspheres by a hybridization method to make hybrid powders, and then electromagnetic wave absorption properties of the composites fabricated by employing the resultant hybrid powders have been investigated. As for the PMMA/carbonyl iron hybrid composite, the reflection loss less than -20 dB could be achieved in a frequency range of 1.7 to 5.0 GHz when the composite thickness was below 5.00 mm. In the case of the PMMA/carbonyl iron-ferrite hybrid composite, a similar reflection loss was observed in a frequency range of 4.3 to 13.0 GHz. Thus, the addition of ferrite was found to be useful for achieving a large absorption in a wide frequency range, especially for higher frequency values. Both the good agreement between simulated and observed values for the minimum RL and the good electromagnetic wave absorption properties confirmed advantages of utilizing the hybrid particles fabricated by the hybridization method. Namely, it is considered that composites with uniform and homogeneous distribution of magnetic materials in a polymer matrix are suitable for electromagnetic wave absorbers. These results enable us to make a tailored design and/or control of absorption properties of electromagnetic wave absorbers by employing the hybrid composites.
References

3. (Polystyrene-Maleic Anhydride)/Mg(OH)\textsubscript{2} Hybrid Particles and Composites Fabricated from the Hybrid Particles

3. 1. Introduction

The present chapter reports about fabrication processes and characterizations of \{polystyrene (PS)-maleic anhydride (MA)\}/magnesium hydroxide (Mg(OH)\textsubscript{2}) hybrid particles and composites fabricated by employing the resultant hybrid particles.

(PS-MA)/Mg(OH)\textsubscript{2} hybrid particles are fabricated by a unique method, i.e., a bulk and suspension two-step polymerization, which is classified into a chemical technique among fabrication techniques of hybrid particles. The details of the bulk and suspension two-step polymerization will be explained in Section 3.2.2

3. 1. 1. Potential advantages of polystyrene-based hybrid particles

PS is one of important thermoplastic resins in industrial fields, such as electrical and household products areas. However, it needs to improve its poor flame retardancy for practical use in various areas. An environmentally-friendly approach to solve poor flame retardancy is to add an alternative halogen-free flame retardant, such as Mg(OH)\textsubscript{2}, aluminum hydroxide (Al(OH)\textsubscript{3}) and hydrotalcite (e.g., Mg\textsubscript{6}Al\textsubscript{2}(CO\textsubscript{3})(OH)\textsubscript{16} $\cdot$ 4H\textsubscript{2}O) powder [86]. It is well known that this approach is easy and effective for general crystalline polymers, such as polyethylene or polypropylene [87]. However, it is difficult to apply this approach to PS. An addition of Mg(OH)\textsubscript{2} powder to the PS matrix results in poor mechanical properties, i.e. decreases in impact strength, compressive strength and so on, even if the additive amount is small. As a result, the improvement of flame retardancy of PS by the addition of Mg(OH)\textsubscript{2} can not be achieved. Therefore, numerous efforts have been directed to developing a technique to enhance the additive amount of Mg(OH)\textsubscript{2} powder to the PS matrix without deteriorating its mechanical properties, in order to improve the flame retardancy.

Key points to enhance the additive amount of Mg(OH)\textsubscript{2} may be affinity between Mg(OH)\textsubscript{2} powder and the PS matrix and dispersibility of Mg(OH)\textsubscript{2} powder in the PS matrix. Therefore, we propose a surface modification of Mg(OH)\textsubscript{2} powder with methylhydrogen polysiloxane (MHS) and an introduction of MA into the PS polymer chains, to achieve excellent affinity between Mg(OH)\textsubscript{2} powder and the PS matrix and excellent dispersibility of Mg(OH)\textsubscript{2} powder.

On the other hand, from a viewpoint of improvement of the work environment, the use of a large amount of submicron-sized Mg(OH)\textsubscript{2} powder is not environmental-friendly because of flying of the
powder in all directions during the mixing process. Thus, to improve the work environmental, the use of PS-based hybrid particles containing a large amount of monodispersed Mg(OH)$_2$ powder with micrometer size as a raw material may be an effective method. This method also enables us to make a complex shape and a tailored design and control of properties of products by changing the kind and content 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 [89].

By the way, there are some fabrication techniques to fabricate PS-based hybrid particles [90-91]. Therefore, to select a relevant technique to fabricate the PS-based hybrid particles designed, it is important to investigate a relationship between a fabrication technique and properties of the hybrid particles fabricated.

3. 1. 2. Aim

Our efforts have been directed to establishing a fabrication process and characterization of the flame retardant PS-based hybrid particles containing a large amount of monodispersed Mg(OH)$_2$ powder modified with MHS by a bulk [92] and suspension [93] two-step polymerization method. Furthermore, microstructure and properties of composites fabricated by employing the resultant hybrid particles have been also investigated.
3. 2. Experimental

3. 2. 1. Materials

Mg(OH)\textsubscript{2} powder (Konoshima Chemical Co., Ltd.) with a mean particle size of ca. 0.6 µm as a filler and MHS (Dow Corning Toray Co., Ltd.) as a surface treatment agent for the Mg(OH)\textsubscript{2} powder were used in preparing the flame retardant PS-based hybrid particles. 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 crosslinking agent, maleic anhydride (MA, Kanto Chemical Co., Inc.) for copolymerizing with SM and polyvinyl alcohol (PVA, Wako Pure Chemical Industries, Ltd.) as a dispersion stabilizer were used as starting materials.

Prior to fabricating hybrid particles, the surface of Mg(OH)\textsubscript{2} powder was treated with MHS by the procedure shown in Fig. 3-1, by employing an experimental assembly shown in Fig. 3-2, 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)\textsubscript{2} powder in a general mixer while stirring at 1740 rpm for 0.9 ks. The conditions to spray a mixture of MHS and IPA are listed in Table 3-1.

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<table>
<thead>
<tr>
<th>Electromagnetic valve (EV)</th>
<th>LVM11-5A (SMC corp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EV switching condition (EV driving frequency)</td>
<td>40 times per second (40 Hz)</td>
</tr>
<tr>
<td>EV driving time</td>
<td>0.6 ks</td>
</tr>
<tr>
<td>Inside diameter of a spray nozzle</td>
<td>220 µm</td>
</tr>
<tr>
<td>Gas medium</td>
<td>air</td>
</tr>
<tr>
<td>Gas pressure</td>
<td>20 kPa</td>
</tr>
</tbody>
</table>

The amount of MHS used for the surface modification was controlled to be 1 wt% of Mg(OH)\textsubscript{2} powder. Then, the resultant powder was subjected to the heat treatment at 423 K for 7.2 ks under
vacuum by a vacuum drier (DP23, Yamato Scientific Co., Ltd.) shown in Fig. 3-3, in order to remove IPA and achieve 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.

3. 2. 2. Fabrication of hybrid particles by a bulk and suspension two-step polymerization method

PS-based hybrid particles containing ST-1 powder were fabricated by a bulk and suspension two-step polymerization
method. Schematic illustration and the procedure of the bulk and suspension two-step polymerization process are shown in Figs. 3-4 and 3-5. The bulk polymerization was carried out aiming at making the subsequent suspension polymerization processing time as short as possible. An introduction of the bulk polymerization process prevents the agglomeration of a core material or the separation of a core material from the dispersed phase, i.e. the mixture of a monomer, a radical initiator, a crosslinking agent and a core material in the suspension polymerization because the viscosity of the dispersed phase in deionized water containing a dispersion stabilizer (continuous phase) starts to increase immediately in the suspension polymerization. A relationship between the viscosity of the dispersed phase and the moving velocity of a core material in the dispersed phase was presented by following a Stokes equation,
\[ v = 2a^2 \Delta \rho g / 9 \eta \]  

(5)

where \( v \) is the moving velocity of the core material in the dispersed phase, \( a \) is the radius of the core material, \( \Delta \rho \) is the density difference between the core material and the dispersed phase, \( g \) is the apparent gravity and \( \eta \) is the viscosity of the dispersed phase. Consequently, an increase of the viscosity of the dispersed phase leads to a decrease in the moving velocity of filler.

The viscosity of the dispersed phase can be controlled by changing the processing time of the bulk polymerization, i.e., the viscosity is elevated gradually as the processing time of the bulk polymerization. Fig. 3-6 shows variations in viscosity of the dispersed phase, i.e. the mixture of SM, AIBN, DBV and ST-1 powder, with the processing time of the bulk polymerization at 313, 323 and 333 K. The detailed composition of the dispersed phase was 100 parts of SM, 1 part of AIBN, 10 parts of DVB and \( x \) (\( x = 10, 30, 50 \)) parts of ST-1 powder on a basis of weight of chemicals. Viscosity measurements of the dispersed phase were carried out by using a viscotester (VT550, Thermo Fisher Scientific, Inc) shown in Fig. 3-7. The shear rate used was 300 s\(^{-1}\). The measurement data were stored to a computer at the condition of 1 plot/min.

Abrupt increases in viscosity of the dispersed phase were observed after certain periods of the bulk polymerization process and the period shortened with a rise in bulk polymerization temperature. The bulk polymerization temperature had an obvious effect on the starting point of abrupt increase in viscosity. In addition, the increasing rate of viscosity became faster with a rise in bulk polymerization temperature (from 313 K to 333 K). These differences are anticipated to arise from changes in increasing rate of molecular weights.

The bulk polymerization temperature of 313 K is a time-consuming condition and the increasing rate of viscosity under the condition of 333 K is

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**Bulk and suspension two-step polymerization method**

- **Styrene monomer (SM)**
- **2,2'-azobisisobutyronitrile (AIBN)**
- **Divinylbenzene (DVB)**
- **Maleic anhydride (MA)**
- **ST-1 (10, 30, 50 phr)**
- **Mixing under ultrasonic wave irradiation**
- **Bulk suspension polymerization** 323 K, 7.2 ks, 150 rpm
- **Suspension polymerization** 343 K, 14.4 ks, 150 rpm
- **In deionized water dissolving polyvinyl alcohol**
- **Filtration, washing and drying**
- **BS-PS particles**
- **BS-x(ST-1)-PSM hybrid particles (x = 10, 30, and 50)**

Fig. 3-5 Procedure of a bulk and suspension two-step polymerization method.
Fig. 3-6  Variations in viscosity of the dispersed phase, i.e. the mixture of SM, AIBN, DBV and ST-1 powder, with the processing time of the bulk polymerization at 313, 323 and 333 K.

too high to form an O/W emulsion in the subsequence suspension polymerization. Furthermore, if the viscosity of the dispersed phase increases abruptly in the bulk polymerization process, irregular shaped and millimeter-sized droplets will be generated in subsequent suspension polymerization
process. Form these results, the bulk polymerization process, hereafter, was carried out at 323 K for 120 min to obtain the dispersed phase having appropriate condition for the subsequent suspension polymerization.

From these results, the hybrid particles were fabricated as follows. The detailed composition of the dispersed phase, i.e. a mixture of SM, AIBN, DVB, MA and ST-1 powder, 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 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 by employing a general mixer (Tornado PM-203, As One Corp.) shown in Fig. 3-8. The resulting viscous dispersed phase 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 hybrid particles were collected by filtration under reduced pressure, washed sufficiently with deionized water, and dried at 353 K for 7.2 ks by an electric drier. The hybrid particles thus fabricated were referred to as BS-x(ST-1)-PSM (x = 10, 30, 50), 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 BS-PSM. Furthermore, to investigate the additive effect of MA, the suspension polymerization was also done by employing the same raw mixtures, but without MA powder. Then, the resultant particles were expressed as BS-x(ST-1)-PS (x = 10, 30, 50) and BS-PS (no addition of ST-1 powder), respectively.
3. 2. 3. Fabrication of composites from hybrid particles

PS-based composite sheets fabricated by employing BS-50(ST-1)-PSM hybrid particles were prepared to estimate the mechanical strength and oxygen index. The procedure of the fabrication process of the composite sheets is shown in Fig. 3-9. BS-50(ST-1)-PSM hybrid particles was incorporated into PS polymer, by using a two-roll mill (Testing Mills, Ikeda Inc.) shown in Fig. 3-10, at 403 ± 5 K for about 900 s. The composite obtained was then compression molded into a form of sheet at 453 K for 240 s under an applied pressure of 0.83 MPa by a hot press (MP-2F, Toyo Seiki Co., Ltd.) shown in Fig. 3-11, and subsequently heated at 453 K for 120 s at 2.4 MPa. Thereafter, the compressed sheet was cooled down to room temperature within 300 s under the same pressure, and the resultant composite sheet (PSC-3) was cut into a predefined shape suitable for tensile testing. For reference, a PS sheet without any ST-1 powder (PSC-1) and a composite sheet from a mixture of PS pellets and ST-1 powder (PSC-2) were also prepared, according to the procedure shown in Fig. 3-9.

3. 2. 4. Characterization of hybrid particles

The contact angle of a droplet of deionized water against a pellet of ST-1 powder was measured in order to investigate the hydrophobic property of the resultant ST-1 powder.

The shape of ST-1 powder was observed by SEM. The shapes of the BS-PS and BS-PSM
particles and the shapes and cross sections of the BS-x(ST-1)-PSM hybrid particles were also observed by SEM. The cross sections of the BS-x(ST-1)-PSM hybrid particles were polished by a buffing machine (S5629, Marumoto Struers Co., Ltd.) shown in Fig. 3-12. Energy dispersive X-ray spectrometric analysis (EDX, EMAX-5770Q, Hitachi High-Technologies Corp.) was performed to observe the dispersion state of ST-1 particles inside the hybrid particles. The fracture surfaces of the composite sheets were also observed by SEM.

The BS-PSM particles and the BS-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) by a muffle furnace (KPG-80, Denken Co., Ltd.) shown in Fig. 3-13. The amounts of MgO left behind were measured to confirm the content of ST-1 powder in the hybrid particles.

Mg(OH)₂ powder, ST-1 powder, the BS-PSM particles and the BS-50(ST-1)-PSM hybrid particle were examined with a Fourier transform infrared spectrometer (FT-IR; FT/IR-680, JASCO Corp.) shown in Fig. 3-14, at room temperature using a KBr method at a 4 cm⁻¹ resolution.

Thermal properties of the BS-PSM particles and the BS-x(ST-1)-PSM hybrid particles were studied by thermogravimetric (TGA) and differential thermal (DTA) analyses (DTG-50, Shimadzu Corp.) shown in Fig. 3-15, at a heating and cooling rate of 20 deg/min under flowing air (flow rate: 100 ml/min). Furthermore, glass-transition temperature of the BS-PSM particles and the BS-x(ST-1)-PSM hybrid particles was also investigated by a differential scanning calorimetry (DSC, DSC-50, Shimadzu Corp.) shown in Fig. 3-16 at a heating rate of 10 deg/min under flowing N₂ (flow rate: 20 ml/min). All the specimens were preheated at 573 K at a heating and cooling rate of 10 deg/min under flowing N₂ (flow rate: 20 ml/min). The preheating was performed in order to remove any impurities on the surface of the specimens.
Apparent densities of the BS-PSM particles and the BS-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 BS-PSM particles and the BS-x(ST-1)-PSM hybrid particles were measured with a micro-compression testing machine (MCT-W500, Shimadzu Corp.) shown in Fig. 3-17, under conditions of a maximum load of 4500 mN, a loading rate of 69 mN/sec and a diameter of 500 µm of an indenter with a flat surface. Particle sizes of the hybrid particles used for the measurements were under 500 µm. Compressive strength was calculated by the following equation [94],

\[
S_c = \frac{2.8P}{\pi d^2}
\]

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

3. 2. 5. Characterization of composites

Flame retardancy of the composite sheets was evaluated with the oxygen index, which is defined by JIS K 7201, measured with a D-type instrument (Toyo Seiki Seisaku-sho, Co., Ltd.) shown in Fig. 3-18. The specimen size cut by a punching machine (SDL-200, Dumbbell Co. Ltd.) shown in Fig. 3-19 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.) shown in Fig. 3-20, 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.

Furthermore, apparent densities of the composite sheets were measured with a densimetry assembly (a precision balance; AUX-320, Shimadzu Corp., a densimetry kit; SMK-401, Shimadzu Corp.) shown in Fig. 3-21. Apparent densities were calculated by the following equation according to Archimedes’ principle,
\[ \rho = \frac{W_a}{W_a - W_l} \rho_l \]  (7)

where \( \rho \) is the apparent density, \( W_a \) is the weight of sample in air, \( W_l \) is the weight of sample in water and \( \rho_l \) is the density of water.

Fig. 3-19 An external view of a punching machine.

Fig. 3-20 An external view of a tensile test machine.

Fig. 3-21 An external view of a densimetry assembly.
3. 3. Results and discussion

3. 3. 1. Characterization of Mg(OH)$_2$ powder treated with MHS

In general, the surface of untreated Mg(OH)$_2$ powder is covered with hydroxyl groups and therefore shows a hydrophilic nature. This results in a poor affinity with a polymer matrix. Therefore, the surface of Mg(OH)$_2$ powder was treated with MHS so as to change to a hydrophobic nature and to guarantee a good affinity with the PS matrix. During the surface treatment, the hydroxyl groups on the surface of Mg(OH)$_2$ powder is expected to react with MHS. Figs. 3-22(a) and 3-22(b) show a SEM image of ST-1 powder and a photograph of a droplet of deionized water on a tablet of ST-1 powder, respectively. Hexagonal plate-like shape of Mg(OH)$_2$ remained unchanged by the surface modification, as shown in Fig. 3-22(a). It was revealed that ST-1 powder showed a hydrophobic nature, since a contact angle value between a droplet of deionized water and the tablet of ST-1 powder was 120.7° (a contact angle value between the droplet of deionized water and the tablet of untreated Mg(OH)$_2$ powder was 0.0°). The high hydrophobicity is attributed to the introduction of a lot of methyl groups by combined effects of chemical reaction between the hydroxyl groups on the surface of Mg(OH)$_2$ powder and MHS and physical adsorption of MHS. Fig. 3-23 shows FT-IR spectra of (a) untreated Mg(OH)$_2$ and (b) ST-1 powder. The intensity of a peak centered at 3696 cm$^{-1}$, assignable to O-H stretching, remained almost unchanged even after the reaction with MHS. This may indicate that the amount of OH groups reacted is small, in comparison with the total amount of OH groups on the surface. However, the IR spectrum shown in Fig. 3-23(b) revealed Si-H stretching between 2250 and 2100 cm$^{-1}$, Si-CH$_3$ bending between 1280 and 1255 cm$^{-1}$ and Si-O stretching between 1110 and 1000 cm$^{-1}$. The chemical reaction between hydroxyl groups and MHS results in the formation of a new Si-O bond accompanied by evolution of gaseous H$_2$. Although the new
Si-O bond could not be distinguished from the bonds originally existing in the MHS molecule in the FT-IR measurement, formation of gaseous H₂ was confirmed during the reaction. Therefore, it is obvious that the chemical reaction between Mg(OH)₂ and MHS has occurred under the conditions employed in the present study, but the surface of Mg(OH)₂ powder is also expected to be covered with physically adsorbed MHS from the appearance of peaks ascribable to Si-H stretching.

3. 3. 2. Characterization of hybrid particles

3. 3. 2. 1. Microstructures
Figure 3-24 shows SEM images of the surfaces of the BS-PS particles and the BS-PSM particles. It is obvious that both particles are spherical in shape with a particle size of about 200 μm. Fig. 3-25 shows SEM images of the surfaces of the BS-x(ST-1)-PSM hybrid particles. All these hybrid particles are spherical in shape with a particle size of about 500 μm, although the surfaces of the BS-x(ST-1)-PSM hybrid particles are rather rough.

Cross sectional views of the BS-x(ST-1)-PSM hybrid particles and EDX analysis of a cross section of a BS-50(ST-1)-PSM are shown in Fig. 3-26, and a magnified cross sectional view and EDX analysis of the magnified cross section of the BS-50(ST-1)-PSM hybrid particles are shown in Figs. 3-27(a) and 3-27(b), respectively. From the cross sectional views, it was confirmed that ST-1 powder was involved in the particles, irrespective of the amounts of ST-1 powder, and the dispersion
level of ST-1 powder was a micrometer order (see Figs. 3-27(a) and 3-27(b)), although a fraction of the ST-1 powder existing in the surface region of particles was rather high. When the hybrid particles were fabricated only by the suspension polymerization method, almost all ST-1 powder agglomerated in the surface regions. However, adoption of the bulk and suspension two-step polymerization method, i.e. introduction of the bulk polymerization prior to the suspension polymerization, enabled us to fabricate hybrid particles containing ST-1 powder in their interior regions. In addition, since shapes, sizes and microstructures of these hybrid particles are almost the

Fig. 3-25  SEM images of (a) BS-10(ST-1)-PSM, (b) BS-30(ST-1)-PSM and (c) BS-50(ST-1)-PSM hybrid particles.
same, regardless of the amount of ST-1 powder, the bulk and suspension two-step polymerization method adopted in the present study has several flexibilities in designing the composition of polymers, along with nearly homogeneous distribution of ST-1 powder inside the particles.

Figures 3-28(a) and 3-28(b) show the FT-IR spectra of the BS-PSM particles and the BS-50(ST-1)-PSM hybrid particles, respectively. The IR spectra in Figs. 3-28(a) and 3-28(b) reveal C-H stretching around 3000 cm\(^{-1}\), aromatic C-C stretching around 1470 cm\(^{-1}\) and aromatic overtones between 1700 and 2000 cm\(^{-1}\). These peaks are attributed to PS. Moreover, the IR spectrum in Fig. 3-28(b) shows O-H stretching centered at 3696 cm\(^{-1}\). This implies the existence of ST-1 powder.

Observed contents of ST-1 powder in BS-\(x\)(ST-1)-PSM hybrid particles and their apparent
densities are plotted against the mixed content of ST-1 powder in Fig. 3-29. For reference, the data for BS-PSM particles is also plotted in Fig. 3-29. The apparent density of BS-x(ST-1)-PSM increases almost linearly with increasing ST-1 powder content. This is due to the larger density of Mg(OH)$_2$ than that of PS. On the other hand, the observed ST-1 powder contents in the hybrid particles were almost equivalent to the mixed ones, e.g. the observed content was 13.8 phr for BS-10(ST-1)-PSM hybrid particles, 29.9 phr for 30(ST-1)-PSM hybrid particles and 48.3 phr for BS-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) chemical bonding via dehydration between remaining surface hydroxyl groups on ST-1 powder and MA incorporated in the PS chains. Owing to these effects, the separation ratio of ST-1 powder from the PS-MA matrix is anticipated to be kept at a very low level.

Fig. 3-27 (a) A magnified image and (b) EDX analysis (Mg-K$\alpha$) of a cross section of a BS-50(ST-1)-PSM hybrid particle.
Fig. 3-28  FT-IR spectra of (a) BS-PSM particles and (b) BS-50(ST-1)-PSM hybrid particles.
Fig. 3-29 Variations in the observed content of ST-1 powder in BS-x(ST-1)-PSM hybrid particles and their apparent densities with the mixed content of ST-1 powder. Data for PSM particles is also indicated.
3. 3. 2. 2. Thermal properties

TGA and DTA curves of the BS-PSM particle and the BS-x(ST-1)-PSM hybrid particles are shown in Figs. 3-30 and 3-31, respectively. As shown in Fig. 3-30, large two-step weight losses are observed with all the particles. This implies that two components with different molecular weights coexist inside all the particles, probably due to a difference in degree of cross-linkage. As for the weight loss in the high-temperature region, the temperatures of weight loss of the BS-x(ST-1)-PSM hybrid particles (ca. 773-823 K) were lower than that of the BS-PSM particles (ca. 823-873 K). This result may be explained by smaller molecular weights of PS in the BS-x(ST-1)-PSM hybrid particles, in comparison with that in the BS-PSM particles, probably due to insufficient cross-linkage by the existence of ST-1 powder. As for the weight loss in the low-temperature region (ca. 623-723 K), endothermic peaks of the BS-x(ST-1)-PSM hybrid particles, as seen in Fig. 3-31, were larger in the minus direction value (ca. -200 μV) than that of the BS-PSM particles (ca. –75 μV), due to overlapping of endothermic decomposition of the Mg(OH)₂ powder. In the case of the weight loss

![TGA curves of BS-PSM particles and BS-x(ST-1)-PSM hybrid particles.](image)
in the high temperature region (ca. 773-823 K), exothermic peaks were confirmed in all the particles due to the combustion of the residual components, i.e., unburned hydrocarbons.

As mentioned above, the BS-PSM particles and the BS-x(ST-1)-PSM hybrid particles has unique properties and structure. Detailed properties of the BS-PSM particles and the BS-x(ST-1)-PSM hybrid particles were further investigated as follows. Figure 3-32 shows the results of DSC analyses for the BS-PSM particles and the BS-x(ST-1)-PSM hybrid particles. The glass transition temperatures ($T_g$) were determined with these DSC curves. The glass transition temperatures of all the particles were higher than that of general PS (ca. 371 K after preheating), because both the BS-PSM particle and the BS-x(ST-1)-PSM hybrid particles were bridged sectionally by a crosslinking agent. Moreover, $T_g$ values of the BS-x(ST-1)-PSM hybrid particles were slightly higher than that of the BS-PSM particles. This may be explained by the existence of ST-1 powder, although the $T_g$ values were not correlated with the additive amount of ST-1 powder.
Fig. 3-32  DSC curves of BS-PSM particles and BS-x(ST-1)-PSM hybrid particles.  
(a) BS-PSM particles and (b) x = 10, (c) x = 30 and (d) x = 50 of BS-x(ST-1)-PSM hybrid particles.

3. 3. 2. 3. Mechanical properties

These hybrid particles can be formed or molded to ideal shapes by employing some techniques, 
such as extrusion, electrothermal rolling and pressing, and molding.  When these hybrid particles 
are formed or molded, the operating conditions of the forming machines should be decided by the 
mechanical properties of these hybrid particles.  Therefore, it is important to investigate the 
mechanical properties, e.g. compressive strength, of these hybrid particles.  Fig. 3-33 shows 
variations in compressive strength of BS-x(ST-1)-PS and BS-x(ST-1)-PSM hybrid particles with the
content of ST-1 powder. The compressive strengths of BS-PS particles were higher than that of BS-PSM particles. This may be attributed to a decrease in degree of polymerization induced by the incorporation of MA into the PS chains. In the case of the BS-x(ST-1)-PS family, the compressive strength decreased linearly from 31.6 MPa for the BS-PS particles to 11.4 MPa for the BS-50(ST-1)-PS hybrid particles with increasing the ST-1 powder content. The decrease in compressive strength may arise from an increase in the frequency of crack generation from the interface between the PS-MA matrix and the agglomerated ST-1 powder.

On the other hand, the compressive strength of BS-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, i.e., 16.6, 15.5 and 18.6 MPa were measured for BS-10(ST-1)-PSM, BS-30(ST-1)-PSM and BS-50(ST-1)-PSM hybrids, respectively. In addition, The compressive strength values of BS-PSM particles and

![Graph showing variations in compressive strength](image)

**Fig. 3-33 Variations in compressive strength of BS-PS particles and BS-x(ST-1)-PS hybrid particles and BS-PSM particles and BS-x(ST-1)-PSM hybrid particles with x values.**
BS-x(ST-1)-PSM (x = 10 and 30) hybrid particles were lower than those of BS-PS particles and BS-x(ST-1)-PS (x = 10 and 30) hybrid particles. These results imply that the compressive strength of the hybrid particles is governed mainly by the property of the PS-based matrix itself in these regions. Almost the same compressive strength of BS-x(ST-1)-PSM hybrid particles may arise from low agglomeration of ST-1 powder, less formation of voids inside the hybrid particles, and a good affinity between hydrophobic ST-1 powder and PS matrix. As a result, the compressive strength value of BS-50(ST-1)-PSM hybrid particles was higher than that of BS-50(ST-1)-PS hybrid particles. Thus, the addition of MA was very effective for preventing a further decrease in compressive strength in the case of the 50 phr addition of ST-1 powder. Namely, in the case of the 50 phr addition of ST-1 powder, the addition of MA improved the potential of the resultant hybrid particles fabricated by the BS method.

Figure 3-34 shows SEM images of the fracture surfaces of BS-50(ST-1)-PS and BS-50(ST-1)-PSM hybrid particles. It is clear that the boundary separation between the PS-based matrix and ST-1 powder observed for BS-50(ST-1)-PSM hybrid particles is smaller than that of BS-50(ST-1)-PS hybrid particles. This result indicates excellent affinity between ST-1 powder and the PS matrix in the case of BS-50(ST-1)-PSM hybrid particles. Namely, the addition of MA was changed the microstructure inside the hybrid particles.

The reason for the higher compressive strength of BS-50(ST-1)-PSM hybrid particles than BS-50(ST-1)-PS hybrid particles may be explained by possible chemical reactions among PS-MA copolymer, MHS and Mg(OH)₂ powder (see a schematic illustration shown in Fig. 3-35). In general, the surface of untreated Mg(OH)₂ powder is covered with hydroxyl groups and therefore shows a hydrophilic nature. This results in a poor affinity with the PS matrix. However, ST-1 powder,
which is the Mg(OH)$_2$ powder treated with MHS, shows a hydrophobic nature as a result of chemical reaction between hydroxyl groups and MHS, and therefore guaranteed a good affinity to the PS matrix. In addition, MA is considered to be incorporated in the PS chains by the dehydration and condensation reaction during the bulk and suspension polymerization. Remaining surface hydroxyl groups on the Mg(OH)$_2$ powder are able to react with MA in PS-MA matrix, leading to a stronger affinity with the PS-MA matrix. Consequently, the boundary separation between ST-1 powder and the PS-MA matrix is considered to be small in BS-x(ST-1)-PSM hybrid particles. Therefore, no formation of huge voids, which act as starting points of fracture, is considered to be involved inside the BS-x(ST-1)-PSM hybrid particles, even if the hybrid particles contain a large amount of ST-1 powder.

Fig. 3-35 A schematic illustration of chemical reactions among PS-MA copolymer, MHS and Mg(OH)$_2$ in BS-x(ST-1)-PSM hybrid particles.
3.3.3. Tensile strength and flame retardancy of composites

Table 3-2 compares properties of three kinds of PS-based 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 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 20.10 observed for PSC-3 was higher than those of PSC-1 and PSC-2. This result indicates a potential advantage of the hybrid particles. Figures 3-36(a) and 3-36(b) show SEM images of the fracture surfaces of PSC-2 and PSC-3, respectively. It is obvious that homogenous distribution of ST-1 powder was achieved in PSC-3. The number of voids between ST-1 powder and the PS matrix in PSC-3 is smaller than that in PSC-2 shown in Fig. 3-36(a). Furthermore, a density of PSC-3 was higher than that of PSC-2. Therefore, it is considered that the dense structure, namely structure with small amount of voids, of PSC-3 may be one of the reasons for the higher oxygen index.

Table 3-2   Properties of a PS sheet (PSC-1), a composite sheet of a mixture of PS pellets and ST-1 powder (PSC-2) and a composite sheet of a mixture of PS pellets and BS-50(ST-1)-PSM hybrid particles (PSC-3)

<table>
<thead>
<tr>
<th>Sample</th>
<th>PS (component)</th>
<th>ST-1 (component)</th>
<th>BS-50(ST-1)-PSM Hybrid Particle Distribution ST-1 Content (wt%)</th>
<th>Total ST-1 Content (wt%)</th>
<th>Apparent Density (g/cm³)</th>
<th>Elongation (%)</th>
<th>Oxygen Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSC-1</td>
<td>120.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.131 (1.030-1.032)</td>
<td>11.8 (10.0-16.8)</td>
<td>18.0</td>
</tr>
<tr>
<td>PSC-2</td>
<td>148.3</td>
<td>38.6</td>
<td>0.0</td>
<td>20.7</td>
<td>1.144 (1.132-1.153)</td>
<td>8.2 (6.4-8.9)</td>
<td>19.0</td>
</tr>
<tr>
<td>PSC-3</td>
<td>50.0</td>
<td>0.0</td>
<td>98.3</td>
<td>20.7</td>
<td>1.182 (1.173-1.194)</td>
<td>7.9 (6.0-8.9)</td>
<td>20.1</td>
</tr>
</tbody>
</table>
Fig. 3-36  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 BS-50(ST-1)-PSM hybrid particles (PSC-3).
3.4. Conclusions

The present chapter reports the preparation process and characterization of PS-based flame retardant hybrid particles with different additive amount of ST-1 powder. PS-based hybrid particles containing ST-1 powder were fabricated by a bulk and suspension two-step polymerization method. The surface modification of Mg(OH)\textsubscript{2} powder with MHS was done to enhance the affinity to the PS matrix, and in some cases, MA was added to ensure a further increase in the affinity. The effects of the fabrication process and the additive amount of ST-1 powder on the microstructure and the mechanical properties of the hybrid particles have been investigated.

All the particles fabricated showed spherical shape and their particle sizes were about 500 µm, irrespective of the additive amount of ST-1 powder. The actual contents of ST-1 powder incorporated inside the BS-\textit{x}(ST-1)-PSM (\textit{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 BS-\textit{x}(ST-1)-PSM hybrid particles remained almost unchanged, irrespective of the increase in ST-1 powder content. Furthermore, the composite fabricated by employing PS pellets and the BS-50(ST-1)-PSM hybrid particles realized 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 significant degradation of mechanical properties.
References

4. Polystyrene-based Hybrid Particles Containing Mg(OH)$_2$ Powder or Multiple Fillers

4. 1. Introduction

4. 1. 1. Background

Chapter 3 reported the details of characteristics of the PS-based hybrid particles fabricated by the bulk and suspension two-step polymerization. The PS-MA/ST-1 hybrid particles fabricated was spherical in shape, and the actual contents of ST-1 powder incorporated inside the hybrid particles were almost the same as those in the raw mixtures. Furthermore, agglomeration of ST-1 powder was hardly observed inside these hybrid particles.

However, the bulk and suspension two-step polymerization was a time-consuming and skilled process. In the present chapter, therefore, PS-based hybrid particles containing ST-1 powder are fabricated by a convenient technique without utilization of polymerization, i.e. a solvent evaporation (SE) method [95-98]. The SE method consists of two steps. An organic solvent is employed to dissolve PS pellets at the first step and then the organic solvent dissolving PS pellets is put into a continuous phase, i.e. distilled water containing polyvinyl alcohol, to form a O/W emulsion. Thereafter, the organic solvent is evaporated from the droplets, leading to resolidification of PS. The details of the SE method will be explained in Section 4. 2. 2. The effects of the amount of the ST-1 powder to be added to the PS matrix on the thermal and mechanical properties of the resulting PS-based hybrid particles were investigated. Furthermore, we tried to fabricate PS-based hybrid particles containing multiple fillers, i.e. tetrakis-(methylene-3-(3', 5'-di-tert-butyl-4-hydroxylphenyl)propionate)methane powder (IRGANOX 1010, Chiba Speciality Chemicals Co., Ltd.) as an antioxidant, N, N'-bis(3-(3, 5-di-tert-butyl-4-hydroxyphenyl)propionyl)hydrazine powder (IRGANOX MD1024, Chiba Speciality Chemicals Co., Ltd.) as a copper inhibitor, 1, 2-hydroxy calcium stearate powder (EMS-6P, katsuta kako co., ltd.) as a lubricant, calcium carbonate powder (Eskaron #1500, Sankyo Seihun Co., Ltd.) treated with stearic acid (Wako Pure Chemical Industries, Ltd.) as a loading material and ST-1 powder, and the dispersion state of the fillers inside the PS-based hybrid particles containing the multiple fillers was observed.

4. 1. 2. Aim
The aim of this chapter is to investigate fabrication processes and to characterize two different hybrid particles; one is PS-based hybrid particles containing different additive amounts of ST-1 powder and another is PS-based hybrid particles containing Irganox 1010, Irganox MD1024, EMS-6P, Eskaron #1500 treated with stearic acid and ST-1 powders.
4. 2. Experimental

4. 2. 1. Materials

PS-based hybrid particles were fabricated from PS pellets (Wako Pure Chemical Industries, Ltd., degree of polymerization; 1600-1800) shown in Fig. 4-1, dichloromethane (DCM, Wako Pure Chemical Industries, Ltd.), PVA mentioned in Chapter 3 and ST-1 powder mentioned in Chapter 3. The detail of the surface modification process for preparation of ST-1 (1 wt% MHS surface treated Mg(OH)₂) powder was explained in Section 3. 3. 1. in Chapter 3. IRGANOX 1010 as an antioxidant, IRGANOX MD1024 as a copper inhibitor, EMS-6P as a lubricant, Eskaron #1500 as a loading material were also used as fillers.

Prior to fabricating hybrid particles, the surface of CaCO₃ powder was treated with stearic acid by the procedure shown in Fig. 4-2, in order to change the surface property 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 stearic acid was mixed with ethanol (1 : 99 in weight), and the mixture and CaCO₃ powder were mixed in a ball mill at 200 rpm for 1.8 ks. The amount of stearic acid used for the surface modification was controlled to be 1 wt% of CaCO₃ powder. Then, the resultant powder was dried at room temperature for 43.2 ks. This hydrophobic stearic acid-treated CaCO₃ powder will be referred to as ET-1 powder.

Figure 4-3 shows SEM images of IRGANOX1010, IRGANOX-MD1024, EMS-6P and ET-1 powders employed as raw fillers (see Fig. 3-22 for ST-1 powder). From Fig. 4-3(b), it is obvious that IRGANOX-MD1024 has a rod-like shape with about 100 µm of a long axis size. Other fillers were irregular in shape.
4.2.2. Fabrication of hybrid particles by a solvent evaporation method

PS-based hybrid particles were fabricated by the SE method of the procedure shown in Fig. 4-4. The SE method is a popular method for microencapsulation of a water-insoluble core material such as solid powder by a water-insoluble shell material such as polymers. In this method, the core material is dispersed in a mixture of a polymer and a volatile organic solvent. Then, the mixture of the core material, a polymer and an organic solvent (dispersed phase) is dropped into an aqueous phase (continuous phase) containing a dispersion stabilizer, an emulsifier or a surfactant. The organic solvent is removed by heating, solvent extraction, freeze-drying or vacuum, leading to resolidification of polymer with the core material.

4.2.2. Fabrication of hybrid particles by a solvent evaporation method

PS-based hybrid particles were fabricated by the SE method of the procedure shown in Fig. 4-4. The SE method is a popular method for microencapsulation of a water-insoluble core material such as solid powder by a water-insoluble shell material such as polymers. In this method, the core material is dispersed in a mixture of a polymer and a volatile organic solvent. Then, the mixture of the core material, a polymer and an organic solvent (dispersed phase) is dropped into an aqueous phase (continuous phase) containing a dispersion stabilizer, an emulsifier or a surfactant. The organic solvent is removed by heating, solvent extraction, freeze-drying or vacuum, leading to resolidification of polymer with the core material.

Fig. 4-3 SEM images of (a) IRGONOX 1010, (b) IRGANOX MD 1024, (c) EMS-6P and (d) ET-1 powders employed as fillers.

Fig. 4-4 A procedure for fabrication of polystyrene/ST-1 hybrid particles by a solvent evaporation method.
The collection of resultant polymer/core material hybrid particles is then performed by filtration, centrifugation and decantation, and then dried. Fig. 4-5 shows a schematic illustration of the SE method for the fabrication of polymer-based hybrid particles. There are several process variables in the SE process. These process variables may influence the characteristics of the resultant hybrid particles. Their process variables are listed below.

- Kind and concentration of an organic solvent
- Phase conditions of the emulsion (e.g. an O/W emulsion and a W/O emulsion))
- Mixed content of a core material
- Temperature of a dispersed phase or a continuous phase
- Kind and concentration of a dispersion stabilizer, an emulsifier or a surfactant

Generally, the actual content of the core material inside the hybrid particles fabricated by the SE method is lower than the content in the mixture, due to separation of the core material from the dispersed phase to the continuous phase.

**Solution evaporation method for polymer-based hybrid particles**

Fig. 4-5 A schematic illustration of fabrication process of a solvent evaporation method for PS-based hybrid particles.
In this chapter, PS-based hybrid particles containing ST-1 powder or five kinds of fillers were fabricated by the solvent evaporation method. As for the PS-based hybrid particles containing ST-1 powder, the detailed composition of the raw chemicals was 600 part of dichloromethane, \( x \) (\( x = 0, 10, 30, 50 \)) parts of ST-1 powder, and 100 parts of PS pellets on a basis of weight of chemicals. The PS pellets were dissolved in dichloromethane at room temperature, and thereafter, the mixture of the resultant PS solution and ST-1 powder was gradually dropped into the water dissolving 1.3 wt% PVA kept at 323 K and then was subjected to evaporation of dichloromethane for 10.8 ks while stirring. After the evaporation process, 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 SE-PS particles for no ST-1 powder and SE-\( x \)-(ST-1)-PS hybrid particles for \( x \) (\( x = 10, 30, 50 \)) parts of ST-1 powder, respectively. e.g. the SE-10(ST-1)-PS hybrid particle stands for the particle containing 10 parts of ST-1 powder.

On the other hand, as for the PS-based hybrid particles containing multiple fillers, the detailed composition of the raw chemicals was 600 part of DCM, 10 parts of ST-1 powder, 10 parts of IRGANOX1010, 10 parts of IRGANOX-MD1024, 10 parts of EMS-6P, 10 parts of ET-1 and 100 parts of PS pellets on a basis of weight of chemicals. Figure 4-6 shows the procedure for the fabrication of PS-based hybrid particles containing five kinds of fillers. The PS pellets were dissolved in DCM at room temperature, and thereafter, the mixture of the resultant PS solution and all the fillers was gradually dropped into the water dissolving 1.3 wt% PVA kept at 323 K and then was subjected to evaporation of DCM for 10.8 ks while stirring. After the evaporation process, 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 SE-50(5-fillers)-PS hybrid particles.

4. 2. 3. Characterization of hybrid particles

The shapes of all the PS-based particles were observed by a zoom stereo microscope (SMZ800, Nikon corp.) shown in Fig. 4-7 and SEM, and the outer surfaces and fracture surfaces of SE-50(ST-1)-PS and SE-50(5-fillers)-PS hybrid particles were also observed by SEM. Cross

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**Fig. 4-6** A procedure for fabrication of PS/multiple fillers hybrid particles by a SE method.
sections of these hybrid particles were polished by a buffing machine and EDX analysis of the cross sections were performed to observe the dispersion state of the fillers inside the hybrid particles.

SE-PS particles and SE-50(ST-1)-PS hybrid particles were characterized with a FT-IR (refer to Section 3.2.4. in Chapter 3) at room temperature using a KBr method at a 4 cm⁻¹ resolution.

SE-PS particles and SE-x(ST-1)-PS hybrid particles were fired to 1273 K at a heating rate of 6.7 deg/min under flowing air (flow rate: 100 ml/min), and then cooled. The amounts of MgO left behind were measured to confirm the actual contents of ST-1 powder in the hybrid particles.

Thermal properties of SE-PS particles and SE-50(ST-1)-PS hybrid particles were studied by TGA and DTA analyses (refer to Section 3.2.4. in Chapter 3), at a heating and cooling rate of 20 deg/min under flowing air (flow rate: 100 ml/min).

Compressive strengths of the SE-PS particles and the SE-50(ST-1)-PS hybrid particles were measured with a micro-compression testing machine (refer to Section 3.2.4. in Chapter 3), under the conditions of a maximum load of 4500 mN, a loading rate of 69 mN/sec and a diameter of 500 µm of an indenter with a flat surface. Particle sizes of the hybrid particles used for the measurements were under 500 µm in diameter. Compressive strength was calculated by the equation (6) shown in Section 3.2.4. in Chapter 3.
4. 3. Results and discussion

4. 3. 1. Hybrid particles containing Mg(OH)₂ powder

4. 3. 1. 1. Microstructure

Figures 4-8 and 4-9 show external views and SEM images of SE-PS particles and SE-x(ST-1)-PS hybrid particles fabricated by the SE method. It is obvious that all these particles are spherical in shape and have a smooth surface with a particle size of about 500 µm. Figure 4-10 shows SEM and EDX results of the cross sections of SE-x(ST-1)-PS hybrid particles. From the cross sectional views, it was confirmed that the ST-1 powder was involved in the particles, irrespective of the differences in the ST-1 powder content. SEM-EDX analyses of the cross section of the

![Fig. 4-8](image)

Fig. 4-8  (a) An external view, (b) an optical microscopic image, and (c) a SEM image of SE-PS particles fabricated by a solvent evaporation method.
SE-x(ST-1)-PS hybrid particles shown in Figs. 4-9(b), 4-9(d) and 4-9(f) confirm uniform and homogeneous distribution of ST-1 powder in the PS matrix due to monodispersion of ST-1 powder in the mixture of the PS solution and ST-1 powder. Furthermore, SEM images of the outer surfaces and fracture surfaces of SE-50(ST-1)-PS hybrid particles shown in Figs. 4-11(a) and 4-11(b) also reveal no formation of huge pores, although small pores in the boundary region between the PS matrix and ST-1 powder are still observed.

Figures 4-12(a) and 4-12(b) show the FT-IR spectra of the SE-PS particles and the
SE-50(ST-1)-PS hybrid particles, respectively. The IR spectra in Figs. 4-12(a) and 4-12(b) revealed C-H stretching around 3000 cm\(^{-1}\), aromatic C-C stretching around 1470 cm\(^{-1}\) and aromatic overtones between 1700 to 2000 cm\(^{-1}\). These peaks are attributed to PS. Moreover, the O-H stretching centered at 3696 cm\(^{-1}\) is observed in Fig. 4-12(b), indicating the existence of ST-1 powder.

A relationship between the mixed and the observed ST-1 powder contents in the SE-x(ST-1)-PS hybrid particles is shown in Fig. 4-13. The observed ST-1 powder contents in the hybrid particles were almost equivalent to the mixed ones, e.g. the observed contents were 10.2, 30.8 and 48.2 phr
for SE-10(ST-1)-PS, SE-30(ST-1)-PS and SE-50(ST-1)-PS hybrid particles, respectively. The high viscosity of the DCM solution dissolving PS pellets and hydrophobic ST-1 powder is anticipated to be the reason for the good agreement between the mixed and the observed ST-1 powder contents. The separation ratio of the ST-1 powder from the PS matrix is kept at a very low level during the solvent evaporation process.

Fig. 4-11 SEM images of (a) the outer surface and (b) the fracture surface of a SE-50(ST-1)-PS hybrid particle.
Fig. 4-12  FT-IR spectra of (a) SE-PS particles and (b) SE-50(ST-3)-PS hybrid particles.
Fig. 4-13  A variation in the observed content of ST-1 powder in SE-PS particles and SE-x(ST-1)-PS hybrid particles with the mixed content.
4.3.1.2. Thermal properties

To investigate relationships between thermal properties of hybrid particles and the additive amount of ST-1 powder, TGA and DTA curves of the SE-PS particles and SE-x(ST-1)-PS hybrid particles were measured (see Figs. 4-14 and 4-15). As shown in Fig. 4-14, all the particles exhibited a weight loss at almost the same temperature (ca. 573 K). The starting point of the weight loss was not affected by the additive amount of ST-1 powder. Maximum values of the endothermic peaks of SE-PS particles and SE-x(ST-1)-PS hybrid particles were also almost the same (ca. between -9 and -12 μV/mg in the temperature range between 673 to 773 K) for all the particles, as shown in Fig. 4-15. However, the addition of ST-1 powder into the PS matrix seems to increase the temperature of starting point of thermal decomposition, as shown in Fig. 4-14. This is due to the endothermic effect caused by decomposition of Mg(OH)$_2$ powder.

![TGA curves of SE-PS particles and SE-x(ST-1)-PS hybrid particles.](image)

Fig. 4-14  TGA curves of SE-PS particles and SE-x(ST-1)-PS hybrid particles.
Fig. 4-15  DTA curves of SE-PS particles and SE-x(ST-1)-PS hybrid particles.
4. 3. 1. 3. Mechanical properties

Figure 4-16 shows a variation in compressive strength of SE-PS particles and SE-x(ST-1)-PS hybrid particles with the content of ST-1 powder. The compressive strength of the SE-PS particles and SE-x(ST-1)-PS hybrid particles showed almost the same value of ca. 23.5 MPa, irrespective of the content of ST-1 powder. This is considered to arise from the homogeneous distribution of ST-1 powder and no formation of huge voids, which act as the starting points of fracture, inside the hybrid particles fabricated by the SE method.

4. 3. 2. Microstructure of hybrid particles containing multiple fillers

Figure 4-17 shows SEM images of the outer surfaces and cross sections of SE-50(5-fillers)-PS hybrid particles and EDX analyses of the cross section of these particles. Spherical
SE-50(5-fillers)-PS hybrid particles with relatively smooth surface and a particle size of ca. 350 µm could be fabricated by the SE method. From the cross sectional view, it was confirmed that uniform and homogeneous distribution of rod-like shaped IRGANOX-MD1024 particles and irregular shaped other fillers with micrometer size in diameter could be achieved inside the SE-50(5-fillers)-PS hybrid particles. In addition, SEM-EDX analyses of the cross section of the SE-50(5-fillers)-PS hybrid particle shown in Figs. 4-17(c) and 4-17(d) also indicated uniform and homogeneous distribution of Mg and Ca components, i.e. EMP-6P, ET-1 and ST-1 powder, in the PS matrix. This is due to monodispersion of each powder in the mixture of the PS solution and fillers, irrespective of the differences in shape and the size of fillers. These results indicated that PS-based hybrid particles containing multiple fillers with spherical shape and homogeneous distribution of the fillers could be fabricated by employing the SE method.

Fig. 4-17  SEM images of (a) the outer surface and (b) cross section of a SE-50(5-fillers)-PS hybrid particle. EDX analyses of the cross section of the SE-50(5-fillers)-PS hybrid particle;  (c) Mg-Kα and (d) Ca-Kα images.
4.4 Conclusions

The present chapter reported the fabrication process and the characterization of two different PS-based hybrid particles; one is PS-based hybrid particles containing different additive amounts of ST-1 powder and another is PS-based hybrid particles containing multiple fillers, i.e. IRGANOX 1010, IRGANOX MD1024, EMS-6P, ET-1 and ST-1 powders.

SE-PS particles and SE-x(ST-1)-PS (x = 10, 30, 50) hybrid particles with spherical shape could be fabricated by the SE method, which was a more convenient technique compared with the bulk and suspension two-step polymerization method demonstrated in Chapter 3. The observed contents of ST-1 powder were almost the same as those in the raw mixtures, and uniform and homogeneous distribution of ST-1 powder was observed inside these hybrid particles. The compressive strength of SE-x(ST-1)-PS hybrid particles remained almost unchanged, irrespective of the increase in the ST-1 powder content. These features are very attractive as a flame retardant PS material, since we can expect the enhancement of flame retardancy without any degradation of mechanical properties.

On the other hand, relatively spherically shaped PS-based hybrid particles containing IRGANOX 1010, IRGANOX MD1024, EMS-6P, ET-1 and ST-1 powders could be fabricated by the SE method. The fillers were confirmed to be dispersed uniformly and homogeneously in the hybrid particles. These PS-based hybrid particles may have a potential to be used in a wide variety of application fields.
References

5. Polyethylene/Mg(OH)₂ Hybrid Particles and Composites Fabricated from the Hybrid Particles

5.1. Introduction

Chapter 4 reported details of fabrication processes and characteristics of PS-based hybrid particles fabricated by the SE method. The SE method was a convenient technique to fabricate the PS-based hybrid particles containing the fillers. In present chapter, polyethylene (PE) is employed instead of PS as the shell material and PE-based hybrid particles containing different additive amounts of Mg(OH)₂ powder treated with different amounts of MHS fabricated are fabricated by the SE method. The detail of the SE method was explained in Section 4.2.2 in Chapter 4.

5.1.1. Potential advantages of polyethylene-based hybrid particles

Since PE is better than other polymer materials such as PS in some properties such as workability, impact resistance and chemical resistance and cost, it is one of important thermoplastic polymer materials used in various fields, especially electrical and agricultural fields, for the fabrication of household, packing and insulating products. Furthermore, PE has been also used inside various kinds of pollution-free products because PE is a halogen-free material. Depending upon their application fields, a flame retardant, Mg(OH)₂ powder is added to PE matrix to improve its poor flame retardancy [99, 100]. Therefore, in this chapter, special attentions have been focused on the fabrication of PE-based hybrid particles containing Mg(OH)₂ powder.

Among several techniques so far reported for the fabrication of the PE-based hybrid particles, the SE method is interest from the viewpoint of simplicity of the preparation process [101-104]. To our knowledge, however, the SE method was not a relevant method for certain polymers such as PE and polypropylene, because of limitation of environmentally-friendly solvents capable of dissolving these polymers completely. Therefore, the fabrication process of the PE-based hybrid particles by the SE method, microstructure and properties of both the PE-based hybrid particles and the composites fabricated by employing the resultant PE-based hybrid particles have not been investigated satisfactorily yet.

5.1.2. Aim

Our efforts have been directed to establishing the fabrication process of PE-based hybrid particles
containing different additive amounts of Mg(OH)₂ powder treated with different amounts of MHS by the environmentally-friendly SE method. The effects of the kinds of raw materials and the conditions of fabrication process on the microstructure, the thermal and the mechanical properties of resultant PE-based hybrid particles and the composites fabricated by employing the resultant PE-based hybrid particles have been investigated.
5. 2. Experimental

5. 2. 1. Materials

Mg(OH)$_2$ powder was used as a filler for the PE-based flame retardant hybrid particles and MHS (see Section 3. 2. 1. in Chapter 3) was used as a surface modification agent for Mg(OH)$_2$ powder, respectively.

Irregularly shaped PE powder (UF-80, Sumitomo Seika Chemicals, Co., Ltd.) with particle size of 10-30 µm shown in Fig. 5-1, cyclohexane (Wako Pure Chemical Industries, Ltd.), heptane (Wako Pure Chemical Industries, Ltd.), octane (Wako Pure Chemical Industries, Ltd.), nonane (Wako Pure Chemical Industries, Ltd.), decane (Wako Pure Chemical Industries, Ltd.), a mixture of cyclohexane and heptane (1 : 1 in volume), a mixture of cyclohexane and octane (1 : 1 in volume), a mixture of cyclohexane and nonane (1 : 1 in volume) or a mixture of cyclohexane and decane (1 : 1 in volume) as a solvent, and Triton X-100 (4-(C$_8$H$_{17}$)C$_6$H$_4$(OCH$_2$CH$_2$)$_{10}$OH, HLB value = 13.5, Wako Pure Chemical Industries, Ltd.) or Triton X-114 (4-(C$_8$H$_{17}$)C$_6$H$_4$(OCH$_2$CH$_2$)$_{8}$OH, hydrophile-lipophile balance (HLB) value = 12.4, Wako Pure Chemical Industries, Ltd.) as a surfactant (a chemical construction of Triton X-100 or Triton X-114 is shown in Fig. 5-2) are used as raw materials.

The surface of Mg(OH)$_2$ powder was treated with MHS so as to change to a hydrophobic nature and to guarantee a good affinity with the PE matrix.  Details of the surface modification process for

![Fig. 5-1 SEM images of PE powder employed as a raw material.](image1)

![Fig. 5-2 A chemical construction of Triton X-100 and X-114.](image2)
the preparation of ST-1 powder were already explained in Section 3.2.1 in Chapter 3.

5 wt% MHS surface-treated Mg(OH)\textsubscript{2} powder was prepared as follows. MHS was mixed with IPA in a weight ratio of 1 : 5, and the mixture was sprayed to the Mg(OH)\textsubscript{2} powder in a general mixer while stirring at 1740 rpm for 0.9 ks. The amounts of MHS used for the surface modification was controlled to be 5 wt% of Mg(OH)\textsubscript{2} powder by adjusting the amount of the mixture sprayed. 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 a chemical reaction between Mg(OH)\textsubscript{2} powder and MHS. These hydrophobic Mg(OH)\textsubscript{2} powders treated with 5 wt% MHS will be referred to as ST-5 powder. Because the FT-IR spectrum of ST-5 powder was almost the same as that for ST-1 powder, FT-IR spectrum data of ST-5 powder is not shown (refer to Section 3.3.1 in Chapter 3 for the FT-IR spectrum of ST-1 powder).

5.2.2. Fabrication of hybrid particles by a solvent evaporation method

The SE method was adopted to fabricate PE particles or PE-based hybrid particles containing ST-1 or ST-5 powder. Procedures for fabrications of the PE particles and the PE-based hybrid particles are shown in Figs. 5-3 or 5-4, respectively. First, to investigate the effect of a variety of solvents to dissolve PE powder on the shape of PE particles, PE particles were reshaped by the SE method by employing some different solvents, namely, chlorobenzene, cyclohexane, mixtures of cyclohexane and heptane (cyclohexane : heptane = 7 : 3, 6 : 4, 1 : 1, 4 : 6 and 3 : 7 in volume), a mixture of cyclohexane and octane (cyclohexane :
octane = 1 : 1 in volume), a mixture of cyclohexane and nonane (cyclohexane : nonane = 1 : 1 in volume) and a mixture of cyclohexane and decane (cyclohexane : decane = 1 : 1 in volume). PE powder of 2 g was dissolved in 20 g of one of solvents described above at 353 K. Thereafter, the resulting mixture (a dispersed phase) was gradually dropped into 900 ml of a continuous phase, i.e. the deionized water including Triton X-100, kept around 348 K. The temperature of the continuous phase was higher than clouding points of Triton X-100. The composition of raw chemicals was controlled to be 45000 parts of deionized water, 450 parts of Triton X-100, 1000 parts of the solvent, and 100 parts of PE powder on a basis of weight of chemicals. The resulting O/W emulsion was suspended by using a homomixer (T. K. Auto Homo Mixer, Tokushu Kika Kogyo Co., Ltd.) shown in Fig. 5-5 at a rotation speed of 4000 rpm for 0.6 ks and then was subjected to evaporation of the solvent at 353 K for 14.4 ks while stirring at a speed of 2.5 rps. After the evaporation process, the resulting PE particles were collected by filtrations under reduced pressure, washed sufficiently with deionized water and dried at 353 K for 7.2 ks.

Then, PE-based hybrid particles were fabricated as follows. PE powder of 2 g was dissolved in 20 g of a mixture of cyclohexane-heptane (cyclohexane : heptane = 1 : 1 in volume) at 353 K. Then, a given amount of ST-1 or ST-5 powder was added to the mixed solvent. Thereafter, the resulting mixture containing ST-1 or ST-5 powder (a dispersed phase) was gradually dropped into 900 ml of a continuous phase, i.e. the deionized water dissolving Triton X-114 or Triton X-100, kept around 348 K. The temperature of the continuous phase was higher than the clouding points of these two surfactants. The detailed composition of raw chemicals was controlled to be 45000 parts of deionized water, 225 or 450 parts of Triton X-114 or Triton X-100, 1000 parts of a cyclohexane-heptane mixed solvent, x (x = 0, 10, 30, 50 and 70) parts of ST-1 or ST-5 powder, and 100 parts of PE powder on a basis of weight of chemicals.

Small droplets of the raw mixture in the continuous phase will be referred to as green PE-based droplets at x = 0, or green PE-based hybrid droplets at x ≥ 10, respectively. The detailed composition of each sample is summarized in Table 5-1 along with the sample number: the first numeral expresses the kind of filler (zero: no addition), the second the amount of the filler added, the third the kind of surfactant (A: Triton X-114 and B: Triton X-100) and the forth the amount of surfactant used for fabricating the sample. Resulting PE-based hybrid particles were collected by filtration under reduced pressure, washed sufficiently with deionized water and dried at 353 K for 7.2 ks.
uniaxial pressing, and heated at 423 K for 7.2 ks. For comparative purpose, a mixture of PE and

5.2.3 Fabrication of composites from hybrid particles

In order to confirm the dispersion behavior of ST-1 powder in the PE-based composites, 1-7-B-4.5
and 1-7-B-9 samples were formed into a cylinder shape (10 mm in diameter and 2 mm in height) by
uniaxial pressing, and heated at 423 K for 7.2 ks. For comparative purpose, a mixture of PE and
ST-1 powders (2 : 1 in weight) was also formed into a cylinder shape under the same conditions.

Furthermore, the effects of the dispersion level of ST-1 powder inside PE-based composite sheets fabricated by employing ST-1 powder or 1-7-B-9.0 hybrid particles on apparent density, mechanical strength and oxygen index are estimated. The procedure for fabrication of the composite sheets is shown in Fig.5-6. ST-1 powder or 1-7-B-9.0 hybrid particles were incorporated into PE polymer, by using a two-roll mill, at 403±5 K for about 900 s. The composites obtained were then compression molded into a form of sheet at 453 K for 240 s under an applied pressure of 0.83 MPa, and subsequently at 453 K for 120 s at 2.4 MPa. Thereafter, the compressed sheets were cooled down to room temperature within 300 s under the same pressure, and those resultant composite sheets were cut into a predefined shape suitable for tensile testing and oxygen index measurement. For reference, a PE sheet without any ST-1 powders was also prepared by a similar procedure.

5. 2. 4. Characterization of hybrid particles

Affinities of untreated Mg(OH)$_2$, ST-1 and ST-5 powders to deionized water and the continuous phase, i.e. the deionized water dissolving Triton X-114 or Triton X-100 at different concentrations were evaluated by measuring the contact angles of droplets of these aqueous phases kept around 348 K, which was higher than the clouding points of both surfactants, on the tablets of those powders with a θ/2 method. The concentrations of the surfactants in deionized water were controlled to be the same as that for the continuous phase used for the SE method (refer to Table 5-1).

Microstructure of the raw PE powder and all PE-based particles were observed by SEM.

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**Fig. 5-6** A procedure of fabrication of PE sheets and PE-based composite sheets.

**Fig. 5-7** An external view of a field-emission scanning electron microscope and an energy dispersion X-ray spectrometer.
Microstructure of 1-7-B-9.0 was observed by a field-emission scanning electron microscopy (FE-SEM, JSM-7500FA, JEOL Ltd.) shown in Fig. 5-7 and energy dispersion X-ray spectrometer (EDS, JSM-7500FA, JEOL Ltd.) analysis was performed to observe the dispersion state of ST-1 powder on surface of 1-7-B-9.0.

Raw PE powder and 1-x-B-9.0 series samples including 0-0-B-9.0 were examined with a FT-IR (refer to Section 3.2.4 in Chapter 3) at room temperature using a KBr method at a 4 cm⁻¹ resolution.

All PE-based hybrid particles were fired to 1273 K at a heating rate of 6.7 deg/min under flowing air (flow rate: 100 ml/min), and then cooled. The amounts of MgO left behind were measured to confirm actual contents of ST-1 or ST-5 powder in the hybrid particles.

Mean degrees of circularity (MC), their standard deviation (MC-SD), mean aspect ratios (MAr) and their standard deviation (MAr-SD) of all PE particles and 1-x-B-9.0 series samples including 0-0-B-9.0 hybrid particles were measured from SEM images by employing a particle size distribution analysis software (Mac-View version 4.0, Mountech Co., Ltd.). One hundred particles for each sample were used for the measurements. MC values were calculated by the following equation.

\[
MC = 4\pi \cdot \frac{D}{C^2}
\]

(8)

where D is the dimension of a particle and C is the length of the circumference of a particle.

The particle size distributions of 1-x-B-4.5 series samples including 0-0-B-4.5 and 1-x-A-9.0 series samples including 0-0-A-9.0 were measured with a laser particle size analyzer (SALD-3000s, Shimadzu Corp.) shown in Fig. 5-8. The measurement was done under the conditions where they were dispersed into deionized water with an alcohol ethoxy sulfate.

Thermal properties of 1-x-A-9.0 series samples including 0-0-A-9.0 were studied by TGA and DTA analyses (see Section 3.2.4 in Chapter 3) at a heating and cooling rate of 20 deg/min under flowing air (flow rate: 100 ml/min).

Relative ratios of restorable strain of 1-x-A-9.0 series samples including 0-0-A-9.0 was measured with a micro-compression testing machine (refer to Section 3.2.4 in Chapter 3), under the conditions of a maximum load of 4500 mN, a minimum load of 50 mN, an loading rate of 69 mN/sec, a unloading ratio of 69 mN/sec and a diameter of 500 µm of an indenter with a flat surface. Particle sizes of the particles used for the measurements were 5.0 – 8.0 µm. The definition and calculation method of a relative ratio of restorable strain were illustrated in Fig. 5-9.
5.2.5. Characterization of composites

Fracture surfaces of the PE-based composites were observed by field-emission scanning electron microscopy (FE-SEM, JSM-7500FA, JEOL Ltd.). In addition, energy dispersion X-ray spectrometer (EDS, JSM-7500FA, JEOL Ltd.) analysis was performed to observe the dispersion state of ST-1 powder inside the composites.

Flame retardancy of the composite sheets was evaluated with the oxygen index, and the composite sheets were then subjected to tensile tests by using the tensile test machine. Details of these measurements have already been explained in Section 3.2.5 in Chapter 3. During these tensile tests, the following strain values were measured:

- Compression ratio: \( Cr = \frac{L_1}{d} \times 100 \% \)
- Ratio of restorable strain: \( R_r = \frac{L_1 - L_2}{d} \times 100 \% \)
- Relative ratio of restorable strain: \( R_{r2} = \frac{R_r}{Cr} \times 100 \% \)

\( L_1 \): strain in maximum stress (B) – strain in minimum stress (A) (µm)
\( L_2 \): strain in minimum stress after unload process (C) – strain in minimum stress (A) (µm)

Load

![Diagram](image)

Fig. 5-9  A schematic illustration of the calculation method of the relative ratio of restorable strain of 0-0-B-9.0 and 1-x-B-9.0 series samples.
tests, elongations of the composite sheets were also measured. The experimental results were evaluated with the average value of five measurements for each specimen. Furthermore, apparent densities of the composite sheets were measured with the densimetry assembly shown in Section 3.2.5. in Chapter 3. Apparent density was decided by equation (7) in Chapter 3.

5.3. Results and discussion
5.3.1. Characterization of hybrid particles

5.3.1.1. Microstructure

PE particles were prepared from raw PE powder without addition of any fillers by the SE method by employing chlorobenzene or cyclohexane as a solvent to investigate the shape of resultant PE particles. Spherical PE particles with smooth surface and a particle size of ca. 60 µm could be fabricated, as shown in Fig. 5-10(a). However, the use of chlorobenzene leads to serious environmental problems, and therefore, our efforts were first directed to finding an alternative environmentally-friendly organic solvent, which can be used for the SE method.

The use of saturated hydrocarbon solvents such as hexane, cyclohexane, heptane, octane, nonane and decane may reduce the environmental damages. Especially, cyclohexane was found to be useful for dissolving PE. However, the boiling point of cyclohexane, 81.0 ℃, is low for stable fabrications of PE particles or PE-based hybrid particles by the SE method (temperature of the solvent evaporation process is 80.0 ℃). Therefore, viscosity of green PE-based droplets increased drastically at an early stage of the solvent evaporation process. The high viscosity leads to formation of agglomerations of PE as shown in Fig. 5-10(b), although it was possible to fabricate a small amount of spherical PE particles, as shown in Fig. 5-10(c).

Fig. 5-10 SEM images of the PE particles obtained with the SE method by employing (a) chlorobenzene and (b) and (c) cyclohexane as a solvent.
To prevent the drastic increase in viscosity of green PE-based droplets, several kinds of saturated hydrocarbon solvents, which have a higher boiling point than cyclohexane, were mixed to
cyclohexane. Figure 5-11 shows SEM images of the PE particle fabricated by employing a mixture of cyclohexane and heptane, octane, nonane or decane (1 : 1 in volume, respectively) as a solvent. Variations in MC and MC-SD and MAr and MAr-SD of the resulting PE particles with the carbon number of the saturated hydrocarbons mixed to cyclohexane are shown in Figs. 5-12(a) and 5-12(b), respectively. The surface condition of the PE particles varied with the kind of the saturated hydrocarbon mixed to cyclohexane. In Fig. 5-12, the MC value decreased gradually from 0.83 to 0.70 and the MAr value increased gradually from 1.09 to 1.27 with an increase in carbon number of saturated hydrocarbons mixed to cyclohexane. These results are explained as follows. Because the boiling point increases with an increase in carbon number, green PE-based droplets in the continuous phase are hard to form solid PE particles in a short period of time. Therefore, the green PE-based droplets have enough time to combine with neighboring green PE-based droplets. As a result, the particle sizes of the green PE-based droplets increase through agglomeration among the green PE-based droplets, even though the continuous phase includes the surfactant. Then, the agglomeration of the green PE-based droplets with the high viscosity resulted in an irregular shape because of a difficulty of rapid mass diffusion of the material. Therefore, a number of irregularly and elliptically shaped PE particles formed obviously with an increase in carbon number of saturated hydrocarbons mixed to cyclohexane.

Furthermore, the effects of the heptane content in a mixture of cyclohexane and heptane on MC, MC-SD, MAr and MAr-SD values of the resulting PE particles was investigated. SEM images of PE particles fabricated by employing a mixture of cyclohexane and heptane (7 : 3, 6 : 4, 1 : 1, 4 : 6 or 3 : 7 in volume) are shown in Fig. 5-13. Variations in MC and MC-SD and MAr and MAr-SD values of the resulting PE particles with heptane content in a mixture of cyclohexane and heptane are shown in Figs. 5-14(a) and 5-14(b), respectively. When the volume ratio of cyclohexane and heptane was 7 : 3, the PE agglomerated to large particles with undesirable shapes, as shown in Fig. 5-13(a), and showed a low MC and a high MAr values, as shown in Fig. 5-14. This is anticipated to arise from the drastic increase in viscosity of green PE-based droplets in the continuous phase in comparison with the other volume ratios. On the other hand, when the volume ratio of a mixture of cyclohexane and heptane is 4 : 6 or 3 : 7, irregularly and elliptically shaped PE particles increased because of an increase in boiling point of the mixed solvent with increasing the heptane content. From these results, a mixture of cyclohexane-heptane (1 : 1 in volume) was selected as a suitable solvent for the fabrication of PE-based hybrid particles.

Figure 5-15 shows variations in MC, MC-SD, MAr and MAr-SD values of PE particles with the rotation speed of a homomixer, and Fig. 5-16 shows variations in MC, MC-SD, MAr and MAr-SD values of PE particles with the operating time of the homomixer. At the rotation speed of 1000 rpm, a mixture of the dispersed phase and the continuous phase divided into only 2 layers could not form an O/W emulsion, and formed one large PE agglomerate. Thus, no data is available at 1000 rpm in
Fig. 5-12. Variations in (a) mean degree of circularity and standard deviation and (b) mean aspect ratio and standard deviation of PE particles with the carbon number of saturated hydrocarbons mixed to cyclohexane.

Fig. 5-15. In addition, although the PE particles fabricated under the conditions of the rotation speeds of 2000 and 3000 rpm, MC values were still low and MAr values were still high. However, at the rotation speed of 4000 rpm, it was possible to fabricate highly spherical PE particles (the MC value was 0.83 and the MAr value was 1.09). As seen in Fig. 5-16, on the other hand, MC values increased from 0.53 to 0.83 and MAr values decreased linearly from 1.58 to 1.09 with an increase of operating time of the homomixer. These results indicated that the operating conditions of the homomixer had a major effect on the shape of PE particles. Insufficient suspension of an O/W
Fig. 5-13  SEM images of PE particles obtained with the SE method by employing a mixture of cyclohexane and heptane of (a) 7 : 3, (b) 6 : 4, (c) 1 : 1, (d) 4 : 6 and (e) 3 : 7 in volume.

emulsion by the homomixer led to formation of agglomerates of PE particles. Spherical PE particles could be fabricated by the suspension at 4000 rpm for 10 min.

In addition, to prevent agglomeration of green PE-based droplets in the O/W emulsion, the effect of surfactants in the continuous phase on the shape of resulting PE particles was evaluated. Figure 5-17 shows SEM images of the resulting four kinds of PE particles, i.e. 0-0-A-4.5, 0-0-A-9.0, 0-0-B-4.5 and 0-0-B-9.0 samples (see Table 5-1 for details). The 0-0-A-4.5 and 0-0-A-9.0 samples fabricated by employing Triton X-114 resulted in agglomerated large particles with an undesirable shape, irrespective of the additive amount of Triton X-114, as shown in Figs. 5-17(a) and 5-17(b). Therefore, when Triton X-114 was used, spherical PE particles with smooth surface could not be fabricated due to agglomerations of green PE-based droplets. In contrast, the use of Triton X-100, instead of Triton X-114, led to formation of small sized, spherically shaped and monodispersed PE particles with smooth surface, irrespective of the additive amount of Triton X-100, as shown in Figs. 5-17(c) and 5-17(d).
Fig. 5-14 Variations in (a) mean degree of circularity and standard deviation and (b) mean aspect ratio and standard deviation of PE particles with the heptane content in a mixture of cyclohexane and heptane.
Fig. 5-15  Variations in (a) mean degree of circularity and standard deviation and (b) mean aspect ratio and standard deviation of PE particles with the revolution rate of a homomixer.
Fig. 5-16 Variations in (a) mean degree of circularity and standard deviation and (b) mean aspect ratio and standard deviation of PE particles with the operating time of a homomixer at 4000 rpm.
Fig. 5-17 SEM images of the PE particles. (a) 0-0-A-4.5, (b) 0-0-A-9.0, (c) 0-0-B-4.5 and (d) 0-0-B-9.0.

By the way, when the green PE-based hybrid droplets with ST-1 or ST-5 powder were used as the dispersed phase, the resulting PE-based hybrid particles also agglomerated to large particles with rough surface, as far as Triton X-114 was used as a surfactant in the continuous phase, irrespective of the additive amount of Triton X-114. However, Triton X-100 was found to be effective for fabrication of spherically shaped and monodispersed PE-based hybrid particles.

Figure 5-18 shows variations in MC, MC-SD, MAr and MAr-SD values of 0-0-A-4.5, 0-0-A-9.0, 0-0-B-4.5 and 0-0-B-9.0 samples with the mixed content of Triton X-100 or Triton X-114 as a surfactant. MC values of 0-0-B-4.5 and 0-0-B-9.0 samples prepared with Triton X-100 were much higher than those of 0-0-A-4.5 and 0-0-A-9.0 samples prepared with Triton X-114, and MAr values of 0-0-B-4.5 and 0-0-B-9.0 samples were much lower than those of 0-0-A-4.5 and 0-0-A-9.0 samples, as seen from the SEM images in Fig. 5-17. When the deionized water including Triton X-114 was used as the continuous phase, the formation of a stable O/W emulsion is quite difficult due to high affinity between the green PE-based droplets and the continuous phase including Triton
X-114. Therefore, almost all the 0-0-A-4.5 and 0-0-A-9.0 samples resulted in agglomerated large particles with rough surface. In addition, a MC value increased slightly and a MAr value decreased slightly with an increase of the mixed content of Triton X-100 or Triton X-114. These results confirmed that the most suitable shaped PE particles could be fabricated under the condition of 9.0 g of Triton X-100 per 100 ml of deionized water.

Fig. 5-18 Variations in (a) and (b) mean degree of circularity and standard deviation and (c) and (d) mean aspect ratio and standard deviation of PE particles based on (a) and (c) Triton X-100 and (b) and (d) Triton X-114 as a surfactant with mixed surfactant content.
Figures 5-19 and 5-20 show SEM images of 1-x-B-4.5 and 1-x-B-9.0 series samples fabricated under the conditions shown in Table 5-1, respectively. It is obvious that these hybrid particles are spherical in shape with a smooth surface and a primary particle size of about 5 - 10 µm, especially when the mixed content of ST-1 powder is 10 phr. However, the surfaces of these hybrid particles became rough with increasing the additive amounts of ST-1 powder. Especially, under higher Triton X-100 concentration and higher ST-1 powder content conditions, surface roughness seems to originate from adhesion of small PE particles and ST-1 powder on large PE-based hybrid particles, as shown in Figs. 5-19(h) and 5-20(h), rather than the uneven surfaces of large PE-based hybrid particles themselves. EDS analysis has revealed that ST-1 powder is not distributed homogeneously inside the PE-based hybrid particles and tends to gather in the surface region of the PE-based hybrid particles, especially for higher ST-1 powder contents, as shown in Fig. 5-21. A similar tendency was also found more or less for all the series of samples. This phenomenon may be explained by either one of the following two factors or by both: an increase in surface to volume ratio by decreasing the size of the green PE-based hybrid droplets during the mixing in the SE method and better affinity of ST-1 powder to the continuous phase than the PE matrix. Besides the primary particles, both the secondary particles in the size of 4 - 10 µm and the agglomerated particles in the size of ca. 100 µm were observed by SEM and an optical microscope, respectively, for 1-x-B-4.5 and 1-x-B-9.0 series samples.

When ST-5 powder was employed, segregation of ST-5 powder in the surface region of PE-based hybrid particles was found. Although the primary particle size of PE-based hybrid particles was 4 - 10 µm, the formation of agglomerated PE-based hybrid particles was pronounced irrespective of the amounts of Triton X-100 in the continuous phase (the data is not shown here). Therefore, ST-1 powder was found to be superior to ST-5 powder as a filler for the PE-based hybrid particles.

Figure 5-22 shows the FT-IR spectra of raw PE powder and 1-x-B-9.0 series samples including O-0-B-9.0. All the IR spectra revealed the existence of C-H asymmetrical stretching at 2926 cm⁻¹, C-H symmetrical stretching at 2853 cm⁻¹, C-H asymmetrical bending at 1465 cm⁻¹ and C-H symmetrical bending at 1375 cm⁻¹ originating from PE. Besides these absorption peaks, an additional peak attributed to O-H stretching was observed at 3696 cm⁻¹ in the IR spectra of Figs. 5-22(c) - (f). This result also confirms the existence of ST-1 powder in the PE matrix, i.e. the formation of PE-based hybrid particles by the present method. The peak attributed to O-H stretching was also observed in 5-x-B-9.0 series samples, although the data is not shown here.

Relationships between the mixed and the observed MHS-treated Mg(OH)₂ powder contents in 1-x-A-4.5, 1-x-A-9.0, 5-x-A-4.5 and 5-x-A-9.0 series samples and 1-x-B-4.5, 1-x-B-9.0, 5-x-B-4.5 and 5-x-B-9.0 series samples are shown in Figs. 5-23 and 5-24, respectively. When Triton X-114 was employed, the actual contents of MHS-treated Mg(OH)₂ powder incorporated in all the PE-based hybrid particles were far less than the mixed values. Especially, the observed contents of
Fig. 5-19  SEM images of (a) and (b) 1-1-B-4.5, (c) and (d) 1-3-B-4.5, (e) and (f) 1-5-B-4.5, (g) and (h) 1-7-B-4.5 samples.
Fig. 5-20  SEM images of (a) and (b) 1-1-B-9.0, (c) and (d) 1-3-B-9.0, (e) and (f) 1-5-B-9.0, (g) and (h) 1-7-B-9.0 samples.
1-x-A-9.0 and 5-x-A-4.5 series samples were less than 4 phr even at the mixed content of 70 phr, while the observed contents of 1-7-A-4.5 and 5-7-A-9.0 samples increased to ca. 20 phr, as shown in Fig. 5-23. These results indicate that almost all ST-1 or ST-5 powder involved in green PE-based hybrid droplets was extracted into the continuous phase during the second stage of the present SE method, namely during the evaporation of organic solvents from the droplets in the continuous phase. In contrast, when Triton X-100 was used, i.e. in the cases of 1-x-B-4.5, 1-x-B-9.0, 5-x-B-4.5 and 5-x-B-9.0 series samples, the observed content of MHS-treated Mg(OH)$_2$ powder increased almost linearly with an increase in the mixed contents, although they showed a 30 - 40% loss from the mixed contents, with only one exception observed for the 5-7-B-4.5 sample, as shown in Fig. 5-24. These results indicate that Triton X-100 is useful for limiting the extraction of ST-1 or ST-5 powder from the droplets in the continuous phase and then for increasing the contents of ST-1 or ST-5 powder in the resulting PE-based hybrid particles. Such phenomena undoubtedly arise from differences in nature of the continuous phases dissolving the surfactants; namely, the affinity of ST-1 or ST-5 powder with the continuous phase dissolving Triton X-100 is anticipated to be smaller than that dissolving Triton X-114 which shows more oily nature than Triton X-100. Such a tendency is more pronounced in the case of ST-1 powder, in comparison with the case of the ST-5 powder.

Fig. 5-21 EDS data measured for 1-7-B-9.0 samples. (a) A SEM image, (b) a C-Kα image, (c) a Mg-Kα image and (d) a O-Kα image.
Variations in MC and MAr of resulting 1-x-B-9.0 series samples including 0-0-B-9.0 with increasing ST-1 powder content are shown in Figs. 4-25(a) and 4-25(b), respectively. The MC value decreased gradually from 0.83 to 0.67 and the MAr value increased gradually from 1.09 to 1.24 with an increase in ST-1 powder content. These results are ascribed to the increased in ST-1 content in the surface region of the hybrid particles with an increase of ST-1 powder content.

Figure 5-26 shows the particle size distributions of the 1-x-B-9.0 series samples including 0-0-B-9.0. It is found that the particle size of the series samples distributes over a wide range of ca. 1.0 - 127.0 µm. This result also confirms that these samples are a mixture of primary and secondary particles, as was observed by SEM and the optical microscope. In addition, no
remarkable change in particle size distribution was observed, irrespective of ST-1 powder contents.

Fig. 5-23  Relationships between the mixed and the observed MHS-treated Mg(OH)₂ powder contents in the 1-x-A-4.5, 1-x-A-9.0, 5-x-A-4.5 and 5-x-A-9.0 series samples.
Fig. 5-24  Relationships between the mixed and the observed MHS-treated Mg(OH)$_2$ powder contents in the 1-x-B-4.5, 1-x-B-9.0, 5-x-B-4.5 and 5-x-B-9.0 series samples.
Fig. 5-25  Variations in (a) mean degree of circularity and its standard deviation and (b) mean aspect ratio and its standard deviation of 1-x-B-9.0 series samples including 0-0-B-9.0 with the mixed ST-1 content.
Fig. 5-26  Particle size distributions of 1-x-B-9.0 series samples including 0-0-B-9.0.

5.3.1.2. Affinities to deionized water dissolving a surfactant

As mentioned above, microstructure of the resultant PE-based hybrid particles was markedly affected by the kind of the surfactant dissolved in the continuous phase and the amount of MHS used for the treatment of Mg(OH)$_2$ powder. In order to find possible reasons to explain such phenomena, the affinity of ST-1 and ST-5 powders to the continuous phase dissolving Triton X-114 or Triton X-100 was estimated from the contact angles of the droplets of the continuous phases on the tablets of ST-1 and ST-5 powders. This is because most of ST-1 and ST-5 powders are anticipated to gather in the surface region of green PE-based hybrid droplets and therefore such a segregation is considered to affect the behavior of green PE-based hybrid droplets in the continuous phase.
Figure 5-27 shows external views and contact angles of the droplets of the continuous phases on the tablets of ST-1 and ST-5 powders. For comparative purpose, the contact angles of the droplets of the continuous phases and deionized water on a tablet of untreated Mg(OH)$_2$ powder were also measured. As expected, the contact angle of zero, i.e. fairly good affinity to every continuous phase including deionized water, was confirmed with untreated Mg(OH)$_2$ powder. On the other hand, contact angle values between the droplets of deionized water and the tablets of ST-1 and ST-5 powders were 120.7° and 123.9°, respectively, confirming the change from the hydrophilic to hydrophobic nature by the MHS treatment. The contact angle values between the droplets of the continuous phase dissolving Triton X-114 and the tablets of ST-1 and ST-5 powders were lower than those of the continuous phase dissolving Triton X-100, when the comparison was made at the same concentration of surfactants. This indicates better affinity of the continuous phase dissolving Triton X-114 to MHS-treated Mg(OH)$_2$ powders than that dissolving Triton X-100. Such phenomena is suggested to arise from the higher lipophilic nature of Triton X-114 than Triton X-100, as is expected from its functional groups involved in its molecule. An increase in surfactant concentration resulted in a lower contact angle and then a further increase in affinity. The better affinity is considered to lead to extraction of ST-1 or ST-5 powder from the surface of green PE-based hybrid droplets into the continuous phase. Therefore, this may be the main reason for the lower Mg(OH)$_2$ contents observed for 1-x-A-4.5, 1-x-A-9.0, 5-x-A-4.5 and 5-x-A-9.0 series samples, than those observed for 1-x-B-4.5, 1-x-B-9.0, 5-x-B-4.5 and 5-x-B-9.0 series samples (see Figs. 5-23 and 5-24). When comparison was made between ST-1 and ST-5 powders, a larger contact angle was obtained with ST-5 powder for every continuous phase. This implies poor affinity of ST-5 powder to the continuous phase, in comparison with ST-1 powder, and predicts less extraction of ST-5 powder from the green PE-based hybrid droplets. However, the results shown in Figs. 5-23 and 5-24 cannot be explained by the changes in contact angle only. The details are not clear at present.

5.3.1.3 Thermal properties

TGA curves of 1-x-B-9.0 series samples including 0-0-B-9.0 are shown in Fig. 5-28. It is obvious that the amount of remaining MgO generated from ST-1 by calcination also increased gradually with an increase in ST-1 powder content. In addition, larger weight losses were observed with all the particles. Temperatures at 5 or 10 wt% weight loss of 1-x-B-9.0 series samples including 0-0-B-9.0 are plotted against the mixed ST-1 powder content in Fig. 5-29. The temperatures at 5 wt% and 10 wt% weight losses increased obviously from 637 K to 687 K and from 672 K to 700 K, respectively, with an increase of ST-1 powder content. This result indicates the endothermic effect caused by decomposition of Mg(OH)$_2$ powder.
Moreover, DTA curves of 1-x-B-9.0 series samples including 0-0-B-9.0 are shown in Fig. 5-30. The maximum endothermic peaks appeared at ca. 698 K. This may be also explained by the existence of ST-1 powder. In the case of the high-temperature region (ca. 773-823 K), exothermic peaks were confirmed in all the particles due to the combustion of the residual components, i.e. unburned hydrocarbons.

Figure 5-31 shows DTA curves in a temperature region between 323 to 423 K to evaluate the melting temperatures and the amount of heat of fusion of 1-x-B-9.0 series samples including 0-0-B-9.0. The melting temperature of all the particles was almost the same value (ca. 385 K). On the other hand, the amount of heat of fusion decreased gradually with increasing the additive amounts of ST-1 powder, due to the decrease in the amount of PE component.

5. 3. 1. 4. Mechanical properties

Figure 5-32 shows a variation in relative ratio of restorable strain of 1-x-A-9.0 series samples including 0-0-A-9.0 with ST-1 powder content. Almost the same value of the mean relative ratio of restorable strain was kept even if 70 phr of ST-1 powder was added, i.e. 85.06, 85.63, 79.56, 82.93 and 82.76 % were measured for 0-0-A-9.0, 1-1-A-9.0, 1-3-A-9.0, 1-5-A-9.0 and 1-7-A-9.0, respectively. It was found that the compressive performances of these hybrid particles remained almost unchanged, even though the additive amount of ST-1 powder increased.
Contact angle measurement ($\theta/2$ method)

A droplet of deionized water or a mixture of deionized water and surfactant
A tablet of untreated Mg(OH)$_2$ or MHS-treated Mg(OH)$_2$

<table>
<thead>
<tr>
<th></th>
<th>Deionized water</th>
<th>Continuous phase 1 TritonX-114 (0.5 g/100 ml)</th>
<th>Continuous phase 2 TritonX-114 (1.0 g/100 ml)</th>
<th>Continuous phase 3 TritonX-100 (0.5 g/100 ml)</th>
<th>Continuous phase 4 TritonX-100 (1.0 g/100 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Mg(OH)$_2$</td>
<td></td>
<td>0.0 (0.0 - 0.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ST-1 1 wt% MHS surface treated Mg(OH)$_2$</td>
<td>120.7 (118.0 - 123.0)</td>
<td>22.4 (20.4 - 25.0)</td>
<td>16.9 (15.4 - 17.8)</td>
<td>26.0 (23.8 - 29.8)</td>
<td>19.4 (16.8 – 21.6)</td>
</tr>
<tr>
<td>ST-5 5 wt% MHS surface treated Mg(OH)$_2$</td>
<td>123.9 (121.0 - 126.0)</td>
<td>39.2 (38.2 - 40.0)</td>
<td>35.0 (33.0 - 38.4)</td>
<td>46.9 (44.4 - 49.2)</td>
<td>42.3 (41.0 - 43.6)</td>
</tr>
</tbody>
</table>

Unit: degree of the angle, scale bar: 1 mm

Fig. 5-27 External views and contact angles of droplets of the continuous phases on tablets of ST-1 and ST-5 powders.
Fig. 5-28  TGA curves of 1-x-B-9.0 series samples including 0-0-B-9.0.

Fig. 5-29  Variations in temperature at the 5 or 10 wt% weight loss of 1-x-B-9.0 series samples including 0-0-B-9.0 with the mixed ST-1 content.
Fig. 5-30  DTA curves of 1-x-B-9.0 series samples including 0-0-B-9.0.

Fig. 5-31  DTA curves in the temperature range between 323 to 423 K of 1-x-B-9.0 series samples including 0-0-B-9.0.
5. 3. 2. Tensile strength and flame retardancy of composites

To confirm the usefulness of the PE-based hybrid particles, dispersion states of ST-1 powder in the composites fabricated from 1-7-B-4.5 and 1-7-B-9.0 samples or a mixture of raw PE powder and ST-1 powder were observed. The fabricated composites could maintain their cylindrical shape after the molding without the addition of other binders, and no cracks were observed after their heat treatment. Figures 5-33, 5-34 and 5-35 show external views, SEM images and EDS results (Mg-Kα) of the fracture surfaces of these composites. The EDS analyses shown in Figs. 4-33(d), 4-33(f) and 4-33(h) indicate insufficient distribution of ST-1 powder in the PE matrix, i.e. two different regions, high ST-1 powder content and no ST-1 powder region, were clearly observed. In contrast, more uniform and homogeneous distribution of ST-1 powder in the PE matrix was confirmed at the fracture surfaces of the composites fabricated from the PE-based hybrid particles.
Fig. 5-33  (a) and (b) External views, (c), (e) and (g) SEM images, and (d), (f) and (h) EDS analyses (Mg-Kα) of fracture surfaces of the composite fabricated from a mixture of PE and ST-1 powders.

This result revealed an advantage of the PE-based hybrid particles to achieve sufficient dispersion of Mg(OH)$_2$ powder in the final composites, even though Mg(OH)$_2$ powder was rather gathered in the surface region of the PE-based hybrid particles. The small particle size of the resulting PE-based hybrid particles was anticipated to be useful for achieving uniform and homogeneous distribution of ST-1 powder in the PE matrix in the final products with a short processing time.
Fig. 5-34  (a) and (b) External views, (c), (e) and (g) SEM images, and (d), (f) and (h) EDS analyses (Mg-Kα) of fracture surfaces of the composite fabricated from 1-7-B-4.5.
Fig. 5-35  (a) and (b) External views, (c), (e) and (g) SEM images, and (d), (f) and (h) EDS analyses (Mg-Kα) of fracture surfaces of the composite fabricated from 1-7-B-9.0.
Table 5-2. Properties of PE sheet (PECOM-3), a composite sheet fabricated from a mixture of PE pellets and ST-1 powder (PECOM-4) and a composite sheet fabricated from a mixture of PE pellets and 1-7-B-9.0 hybrid particles (PECOM-5)

<table>
<thead>
<tr>
<th>Sample</th>
<th>PE (observed)</th>
<th>ST-1 (observed)</th>
<th>1-7-B-9.0 hybrid particle PE (observed)</th>
<th>1-7-B-9.0 hybrid particle ST-1 (observed)</th>
<th>Total ST-1 content (wt%)</th>
<th>Apparent density (%)</th>
<th>Elongation (%)</th>
<th>Oxygen index</th>
</tr>
</thead>
<tbody>
<tr>
<td>PECOM-1</td>
<td>120.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.920 (9.919-0.922)</td>
<td>760 (750-775)</td>
<td>17.0</td>
</tr>
<tr>
<td>PECOM-2</td>
<td>98.2</td>
<td>24.6</td>
<td>0.0</td>
<td>0.0</td>
<td>20.0</td>
<td>1.039 (1.038-1.040)</td>
<td>696 (675-710)</td>
<td>18.9</td>
</tr>
<tr>
<td>PECOM-3</td>
<td>50.0</td>
<td>0.0</td>
<td>48.2</td>
<td>24.6</td>
<td>20.0</td>
<td>1.036 (1.035-1.037)</td>
<td>550 (475-585)</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Table 5-2 compares properties of three kinds of PE sheets: one without ST-1 powder (PECOM-1) and two containing ST-1 (PECOM-2) or 1-7-B-9.0 hybrid particles (PECOM-3). The oxygen index values observed for PECOM-2 and PECOM-3 were the same and higher than that of PECOM-1, because of the flame retardant effect of Mg(OH)₂ powder. This result indicates a potential advantage of the hybrid particles for practical use. However, the value of elongation of PECOM-3 was lower than those of PECOM-1 and PECOM-2. This may be due to the lower elongation property of raw PE powder, which is employed to fabricate the hybrid particles, than that of raw PE pellets. Figure 5-36 shows SEM images of the fracture surfaces of PECOM-1, PECOM-2 and PECOM-3. It is obvious that homogenous distribution of ST-1 powder is achieved in PECOM-3 and the number of voids between ST-1 powder and the PE matrix is smaller than that of PECOM-2. Therefore, it can be considered that the use of these hybrid particles increases the affinity between PE matrix and ST-1 powder because of good affinity of ST-1 powder with the PE inside the raw hybrid particles.
Fig. 5-36  SEM images of fracture surfaces of (a) and (b) PE sheet (PECOM-1), (c) and (d) PE/ST-1 composite sheet (PECOM-2), and (e) and (f) PE/ST-1 composite sheet (PECOM-3) fabricated by employing 1-7-B-9.0 hybrid particles.
5.4. Conclusions

Spherically shaped PE particles and PE-based hybrid particles with different additive amounts of ST-1 powder were obtained with an environmentally-friendly and convenient SE method, namely a cyclohexane and heptane mixed solvent (1:1 in volume) was employed to dissolve PE powder at the first step and then distilled water containing a surfactant was employed as a continuous phase when the mixed solvent was evaporated from green PE-based droplets or green PE-based hybrid droplets. The shape, microstructure and other properties of the resulting PE-based hybrid particles were dependent markedly on the amounts of Mg(OH)₂, the amounts of MHS used for the treatment of Mg(OH)₂ and the kind of surfactants. The PE-based hybrid particles by using ST-1 powder and Triton X-100 as a surfactant showed superior properties in terms of the actual content of MHS-treated Mg(OH)₂ powder incorporated inside the hybrid particles and particle shape, in comparison with other PE-based hybrid particles fabricated by using ST-5 powder and/or Triton X-114 as a surfactant. This is due to the relevant affinity (average contact angle was 19.4°) between ST-1 powder and the aqueous phase dissolving Triton X-100, i.e. the continuous phase. Temperatures at an early stage of weight loss of these hybrid particles increased obviously with an increase in additive amount of ST-1 powder. This is considered to arise from the endothermic effect caused by the decomposition of Mg(OH)₂ powder inside the PE-based hybrid particles. On the other hand, uniform and homogeneous distribution of ST-1 powder in the PE matrix was observed in the composite fabricated by employing these PE-based hybrid particles without a mixing process. These results also provide useful information on the fabrication of a PE-based product by employing hybrid particles and the fabrication of PE-based hybrid particles mixed with other functional fillers such as lubricants and antioxidants. These PE-based hybrid particles have a potential to be used in a wide variety of application fields such as household, packing and electrical insulating material.
References

6. Conclusions

The present study reported fabrication processes and characteristics of polymer-based hybrid particles containing fillers, i.e. organic-inorganic hybrid particles. These organic-inorganic hybrid particles were fabricated by the hybridization method, the bulk and suspension two-step polymerization method, or the solvent evaporation method.

In Chapter 2, PMMA/carbonyl iron hybrid particles and PMMA/carbonyl iron-ferrite hybrid particles were fabricated by the hybridization method, and then electromagnetic wave absorption properties of the composites fabricated by employing resultant hybrid powders have been investigated.

As for the PMMA/carbonyl iron hybrid composite, the reflection loss less than -20 dB could be achieved in a frequency range of 1.7 to 5.0 GHz when the composite thickness was below 5.00 mm. In the case of the PMMA/carbonyl iron-ferrite hybrid composite, a similar reflection loss was observed in a frequency range of 4.3 to 13.0 GHz. Thus, the addition of ferrite was found to be useful for achieving a large absorption in a wide frequency range, especially for higher frequency values. Both the good agreement between the simulated and the observed values for the minimum reflection loss and the good electromagnetic wave absorption properties confirmed advantages of utilizing hybrid particles fabricated by the hybridization method. Namely, it is considered that composites with uniform and homogeneous distribution of magnetic materials in a polymer matrix are suitable for electromagnetic wave absorbers. These results enable us to make a tailored design and/or control of absorption properties of electromagnetic wave absorbers by employing the hybrid composites.

In Chapter 3, PS-based hybrid particles containing ST-1 powder were fabricated by the bulk and suspension two-step polymerization method. The effects of the fabrication process and the additive amount of ST-1 powder on the microstructure, thermal and mechanical properties of the hybrid particles have been investigated.

All the particles fabricated showed spherical shape and their particle sizes were about 500 µm, irrespective of the additive amounts of ST-1 powder. The actual contents of ST-1 powder incorporated inside the BS-x(ST-1)-PSM (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 BS-x(ST-1)-PSM hybrid particles remained almost unchanged, irrespective of an increase in ST-1 powder content. Furthermore, the composite fabricated by employing PS pellets and the BS-50(ST-1)-PSM hybrid particles realized 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 significant degradation of mechanical properties.

Chapter 4 reported the fabrication process and the characterization of two different PS-based hybrid particles; one is PS-based hybrid particles containing different additive amounts of ST-1 powder and another is PS-based hybrid particles containing multiple fillers, i.e. IRGANOX 1010, IRGANOX MD1024, EMS-6P, ET-1 and ST-1 powders.

SE-PS particles and SE-x(ST-1)-PS (x = 10, 30, 50) hybrid particles with spherical shape could be obtained by the solvent evaporation method, which was a more convenient technique compared with the bulk and suspension two-step polymerization method demonstrated in Chapter 3. The observed contents of ST-1 powder were almost the same as those in the raw mixtures, and uniform and homogeneous distribution of ST-1 powder was observed inside these hybrid particles. The compressive strength of SE-x(ST-1)-PS hybrid particles remained almost unchanged, irrespective of an increase in ST-1 powder content. These features are very attractive as a flame retardant PS material, since we can expect the enhancement of flame retardancy without any degradation of mechanical properties.

On the other hand, relatively spherically shaped PS-based hybrid particles containing IRGANOX 1010, IRGANOX MD1024, EMS-6P, ET-1 and ST-1 powders could be fabricated by the solvent evaporation method. The fillers were confirmed to be dispersed uniformly and homogeneously in the hybrid particles. These PS-based hybrid particles may have a potential to be used in a wide variety of application fields.

In Chapter 5, spherically shaped PE particles and PE-based hybrid particles with different additive amounts of ST-1 powder were obtained with the environmentally-friendly solvent evaporation method by employing a cyclohexane and heptane mixed solvent (1:1 in volume).

The shape, microstructure and other properties of the resulting PE-based hybrid particles were dependent markedly on the amounts of Mg(OH)₂, the amount of MHS used for the treatment of Mg(OH)₂ and the kind of surfactants. The PE-based hybrid particles by using ST-1 powder and Triton X-100 as a surfactant showed superior properties in terms of the actual contents of MHS-treated Mg(OH)₂ powder incorporated inside the hybrid particles and the particle shape, in comparison with other PE-based hybrid particles fabricated by using ST-5 powder and/or Triton X-114 as a surfactant. This is due to the relevant affinity (average contact angle was 19.4°) between ST-1 powder and the aqueous phase dissolving Triton X-100, i.e. the continuous phase. Temperatures at an early stage of weight loss of these hybrid particles increased obviously with an increase in additive amount of ST-1 powder. This is considered to arise from the endothermic effect caused by the decomposition of Mg(OH)₂ powder inside the PE-based hybrid particles. On the other hand, uniform and homogeneous distribution of ST-1 powder in the PE matrix was
observed in the composite fabricated by employing these PE-based hybrid particles without a mixing process. These results also provide useful information on the fabrication of a PE-based product by employing hybrid particles and the fabrication of PE-based hybrid particles mixed with other functional fillers such as lubricants and antioxidants. These PE-based hybrid particles have a potential to be used in a wide variety of application fields such as household, packing and electrical insulating material.

The understanding of the fabrication processes and the characterizations of these organic-inorganic hybrid particles mentioned above may be useful for application and improvement of properties of polymer-based hybrid particles containing fillers. I strongly believe large contribution of the present study to the research area of organic-inorganic hybrid particles.
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