

Preparation of composite particles coated with two kinds of solid powders by semi-chemical recycle method

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Polymer microspheres coated with two kinds of solid powders were prepared by the semi-chemical recycle method of waste plastics. Magnetite (Fe_3O_4) and silicon carbide (SiC) were added as solid powders so as to give thermal and electric conductivity and magnetization. Waste expanded polystyrene was used as raw materials of polymer matrix of composite particles. In the experiment, the oil phase dissolving expanded polystyrene was dispersed to form the O/W dispersion in the continuous water phase in which polyvinyl alcohol and magnetite powders were added. And then, silicon carbide powder was added into the O/W dispersion. Composite particles prepared had the structure that a polymer particle was covered with two kinds of solid powders. The amount of each solid powder adhered on the surface of polymer microsphere was strongly affected by an addition time of silicon carbide powder. Furthermore, the gradient adhesion layer due to two solid powders was found to be formed on the surface of polymer microsphere. © 2006 Springer Science + Business Media, Inc.

1. Introduction

Composite particles composed of polymers and solid powders will be given various characteristics by solid powders used. Composite particles are applied in such various fields as information and recording materials, cosmetics, paintings, medical materials, etc. according to their characteristics. Furthermore, as these composite particles have latent possibility according to combination of polymer and powder species, many studies have been actively performed [1–3]. We have also prepared many kinds of composite particles by such various polymerization methods as suspension polymerization, soap-free polymerization, mini emulsion polymerization [4–13]. In the case of composite particles with the structure which a polymer microsphere was coated with solid powder, it was found that the morphology of composite particles was

considerably affected by size of solid powder and an affinity of solid powder for interface between the dispersed and the continuous phase [9, 11].

In this study, on the basis of previous studies, we tried to prepare composite particles with the structure which polymer microsphere was covered with two kinds of solid powders by the Semi-Chemical Recycle method [14]. Since the semi-chemical recycle method is able to prepare polymer microsphere from waste plastics by applying an appropriate solvent, it is possible to prepare composite particles composed of various solid powders and waste plastics.

In this study, we prepared composite particles by using expanded polystyrene as a material of polymer matrix and magnetite and silicon carbide as solid powders. It was discussed how the addition time and amount of solid

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powder affected such characteristics of composite particles as mean size, morphology, structure of adhesion layer and electric conductivity.

2. Experimental

2.1. Experimental apparatus and procedure

Fig. 1 shows the reactor of a separable flask with three inlets. The inner diameter of this reactor was 8.5×10^{-4} m and the capacity was 5.0×10^{-4} m³. Four baffles made of aluminum were fixed on the inner wall in order to prevent air entrainment from the free surface of the dispersion with stirring [10]. The impeller was a six-bladed disk turbine with the blade diameter of 5.0×10^{-2} m and a blade height of 1.0×10^{-2} m. This impeller was installed at one third of the liquid depth from the bottom. Fig. 2 shows the flow chart of preparing composite particles in this experiment.

The experimental procedure was as follows. At first, the continuous water phase was prepared by dissolving polyvinyl alcohol (PVA : degree of polymerization 500) of a given concentration into distilled water of 3.0×10^{-4} m³. A given amount of magnetite powder (Fe₃O₄ : mean diameter 0.3 μm) was added into the continuous water phase. Then, the continuous water phase was heated up to 313 K with a thermostatic water bath under stirring by the given impeller speed. On the other hand, the dispersed oil phase was prepared by dissolving a given amount of expanded polystyrene (EPS : degree of polymerization 2700) into dichloromethane as solvent. The dispersed phase was poured and dispersed into

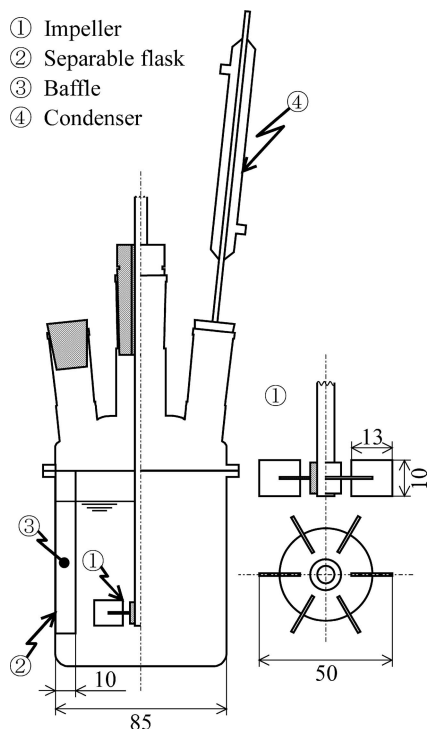


Figure 1 Experimental apparatus for preparing composite particles.

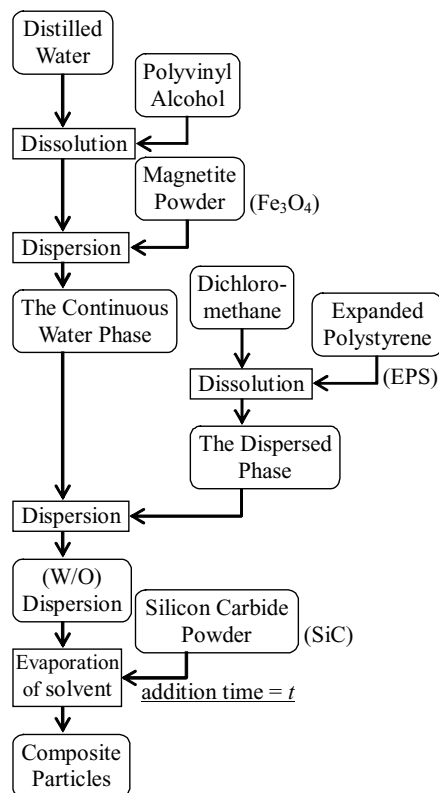


Figure 2 Flow chart for preparing composite particles by the semi-chemical-recycle method.

the continuous water phase to form the O/W dispersion. Then, a given amount of silicon carbide powder (SiO₂ : mean diameter 0.63 μm) was added into this dispersion. From this time, the process of semi-chemical recycle was carried out. Namely, dichloromethane was removed from the dispersed droplets by evaporation under low vacuum. The gassed solvent was trapped by the cold-trap equipment (IWAKI Glass Co., Ltd, model: CLT-050).

In the fundamental operation stated above, an addition time of SiC and an amount ratio of SiC and Fe₃O₄ were mainly changed stepwise.

2.2. Characterization

2.2.1. Characterizations of composite particles

The shape and surface morphologies of composite particles were examined with scanning electric microscopy (SEM, JEOL Ltd., model: JSM-5800) by using samples prepared by the same method as the previous works [10, 11, 13]. The adhesion layer on the surface of polymer microsphere was examined by energy dispersive X-ray spectroscopy (EDX, NORAN Instruments Inc.).

2.2.2. Mean diameter of composite particles

The diameters of about 50 composite particles were measured directly from the optical micrographs (OM; Olympus Ltd.). From these images, the mean diameter was calculated as the Sauter mean diameter (d_{32}) with

Equation 1.

$$d_{32} = \frac{\sum_{i=1}^n n \cdot d_i^3}{\sum_{i=1}^n n \cdot d_i^2} \quad (1)$$

where n was the number of composite particles in each diameter and d_i was a diameter of composite particles with each diamate.

2.2.3. Zeta potentials of solid powders and oil droplets

Zeta potentials of the solid powder in the continuous water phase were determined by the streaming potential analyzer (Shimadzu Corporation, model: ZP-10B). Zeta potential of the dispersed oil droplets in the continuous water phase was measured by the zeta potential analyzer (OTSUKA Electronics Ltd., ELS-800).

2.2.4. Adhesion amount and adhesion ratio in the adhesion layer

Amount of the solid powder adhered on the surface of polymer microsphere was measured as follows. At first, free solid powders which did not adhere were removed by the sieve operation. Then, a given amount of composite particles (M_{CP}) was added into tetrahydrofuran (THF) to dissolve polystyrene, and this solution was removed by a pipet. After this, residual powders were washed twice by THF, dried at the room temperature and then, weighed (M_{F+S}). Moreover, the Fe_3O_4 powder in the residual was dissolved by the aqueous solution of hydrochloric acid (IN). The residual powder (SiC) was washed twice by water, dried in the drier at 30°C and then, the weight of silicon carbide powder (M_S) was measured. Then, the adhesion amount of Fe_3O_4 (M_F) was calculated by subtracting M_S from M_{F+S} according to Equation 2.

$$M_F = M_{F+S} - M_S \quad (2)$$

Thus, the adhesion ratios of Fe_3O_4 and SiC powders in the adhesion layer were calculated according to Equation 3, respectively.

$$F_A = \frac{M_F}{M_{CP}} \quad \text{or} \quad \frac{M_S}{M_{CP}} \quad (3)$$

The stuck number (n_S) was determined as follows. The total project area of all solid powder particles adhered on the surface of a composite particle was defined as the effective area (S_E). If the effective area is equal to the surface area of a composite particle (S_{CP}), the adhesion layer is formed from the single layer of solid powder. Moreover, if the effective area is larger than the surface area of a composite particle, then the adhesion layer is formed from the multiple layers. Namely, the stuck number of the

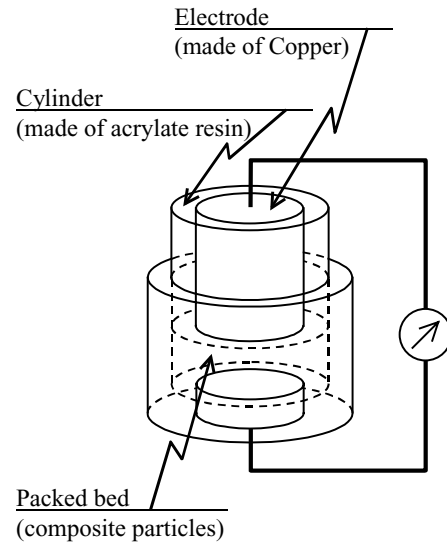


Figure 3 Cell for measuring specific resistances of composite particles.

adhesion layer was calculated according to Equation 4.

$$n_S = \frac{S_E}{S_{CP}} \quad (4)$$

2.2.5. Specific resistance of composite particles

In order to discuss the amount of solid powders adhered on the surface of polymer microsphere, specific resistance of composite particles prepared was measured with a cell as shown in Fig. 3. At first, composite particles were packed in the cell giving a shock three times by hand. Then, an upper electrode was let on the cell to measure resistance (R) of the packed layer of composite particles. Specific resistance (ρ_a) of the packed layer of composite particles was calculated by the following equation.

$$\rho_a = \frac{S_{ER} \cdot R}{h} \quad (5)$$

where S_{ER} and h were the area of electrode and the height of the packed layer in the cell, respectively.

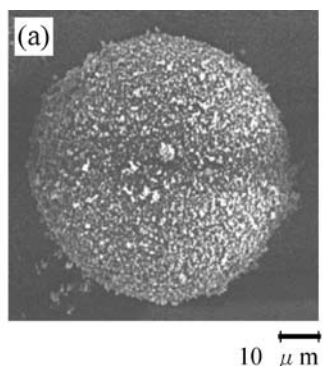
3. Results and discussion

3.1. Shapes and surface morphologies

Fig. 4 shows the SEM photograph of the surface of composite particle. It is found that the shape of composite particle is spherical, and solid powders adhere closely on the surface of composite particle. Fig. 5 shows the XRI images of composite particle. From the XRI images, these solid powders are found to be Fe_3O_4 and SiC.

3.2. Zeta potentials of solid powder and oil droplet

In order to know how the composite particle with the structure stated above was prepared, zeta potentials of solid powders and oil dispersed droplets in the continuous water phase were measured. Table I shows the values of the zeta potentials. It is found that these values have negative sign. Although zeta potential is thought to be one important factor that may affect adhesion of solid powders on polymer droplet [15, 16], the zeta potential in this dispersion is supposed not to affect so much. Accordingly, adhesion of the solid powder on the surface of the oil dispersed droplet is thought to be due to the hydrophobic-hydrophilic interaction between the solid powders and the oil dispersed, as shown in the previous work [10].



SEM photograph

- Addition time of SiC: 0.5 h
- Fractional amount of powder
 $\text{Fe}_2\text{O}_3 = 0.157$; $\text{SiC} = 0.157$

Figure 4 SEM photograph of composite particle.

3.3. Mean diameter

Fig. 6 shows the dependence of the mean diameters of composite particles on the addition time of SiC, where the addition ratio of SiC and Fe_3O_4 was used as a parameter. It is found from this figure that, in any addition ratios, the mean diameters increased with the addition time. This may suggest that the addition of only Fe_3O_4 could not stabilize the oil dispersed droplets. Namely, as the oil dispersed droplets coalesced each other after the addition of only Fe_3O_4 , the mean diameters of the oil dispersed droplets increased with the addition time of SiC. Behavior of the oil dispersed droplet was shown above in Fig. 6. Accordingly, it is suggested that coalescence between the oil dispersed droplets was prevented by the SiC powder.

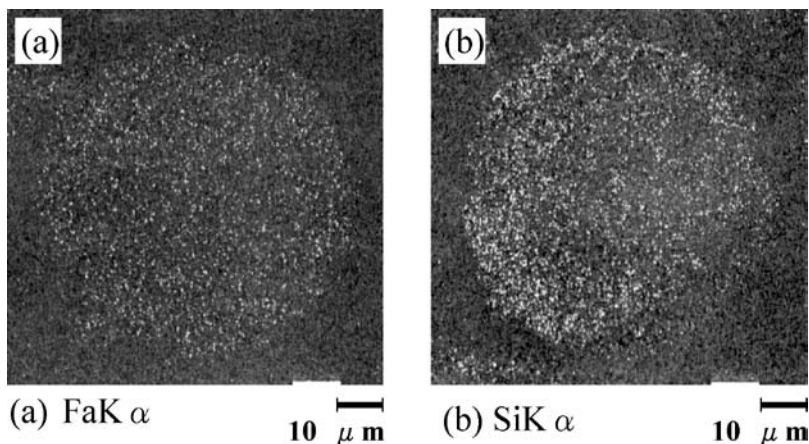
However, in any addition times, the degree of increase in the mean diameter decreased with an increase in the addition ratio of Fe_3O_4 . It is thought that this was because coalescence between the oil dispersed droplets was prevented more strongly by the addition of the Fe_3O_4 powder of more amount.

3.4. Specific resistance of composite particles

Fig. 7 shows the dependence of specific resistances of the packed layer of composite particles on the addition time of SiC. From this figure, it is found that specific resistances decreased considerably with the addition time of SiC and

TABLE I Zeta potential of polystyrene particles and solid powders

Object	Zeta potential (mV)
Polystyrene particles	-43
Magnetite powder	-12
Silicon carbide powder	-53



Conditions

- Addition time of SiC: 0.5 h
- Fractional amount of powder
 $\text{Fe}_2\text{O}_3 = 0.157$; $\text{SiC} = 0.157$

Figure 5 XRI images of composite particles.

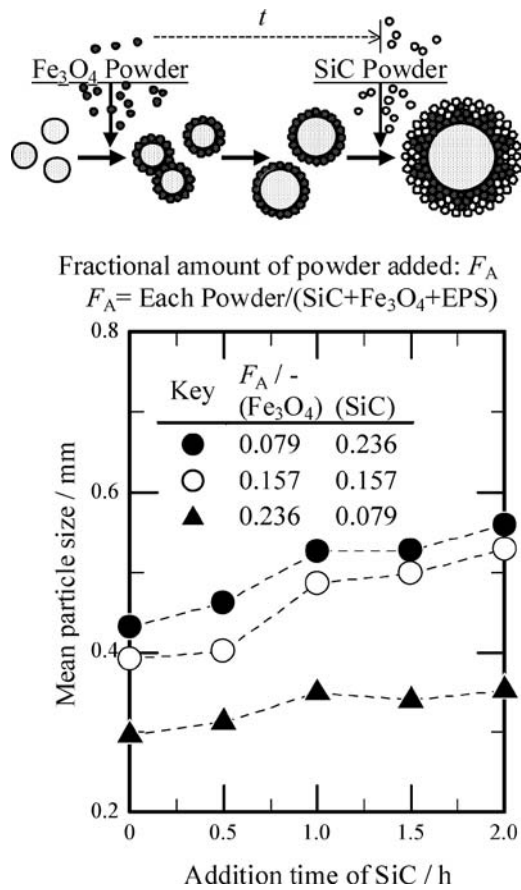


Figure 6 Dependence of mean particle size on addition time of SiC

the addition ratio of Fe_2O_3 . This suggests that the later addition of SiC and the larger addition of Fe_3O_4 formed the more Fe_3O_4 -rich adhesion layer as shown above in Fig. 7. Accordingly, specific resistance must decrease, because the Fe_3O_4 powder is more conductive than the SiC powder.

3.5. Stuck number of solid powder

Fig. 8 shows the dependence of the stuck number on the addition time of SiC. The stuck numbers of Fe_3O_4 and SiC changed contrarily with the addition time. The stuck number of Fe_3O_4 increased considerably from 2 to 11 with the addition time. Contrary to this, the stuck number of SiC decreased gradually from 4 to 1. From these results, it is found that the earlier addition of SiC made the adhesion layer SiC-richer, in other words, the later addition of SiC made the adhesion layer Fe_3O_4 -richer.

3.6. Adhesion mechanism

Fig. 9 shows the mechanism of adhesion of solid powders onto the surface of the oil dispersed droplet during the process of solvent evaporation. First, in the case of the earlier addition of SiC, the SiC powder begins to adhere on the surface of the oil dispersed droplet together with Fe_2O_3 before the formation of the thick Fe_3O_4 layer. The

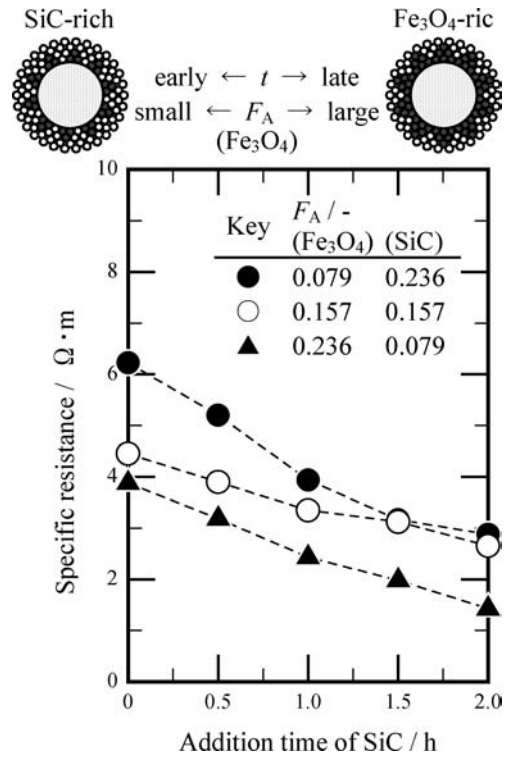


Figure 7 Dependence of specific resistance on addition time of SiC

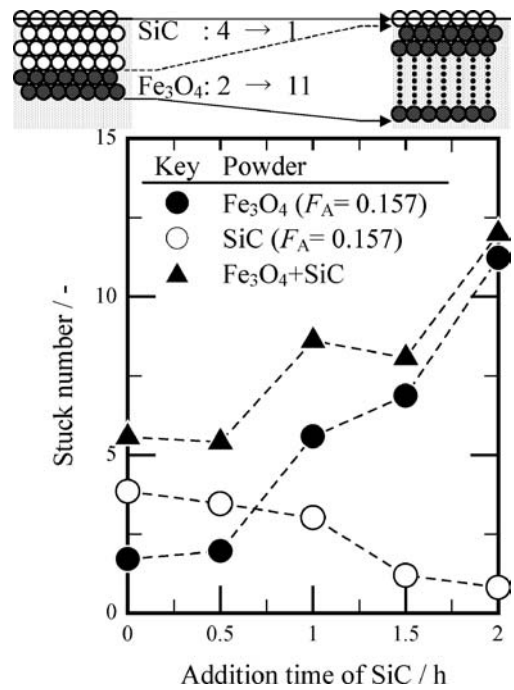


Figure 8 Dependence of stuck number of powder covering on composite particle on addition time of SiC

oil dispersed droplets are stabilized by the SiC adhesion to be prevented from coalescing each other. Moreover, permeation of polymer solution into the solid powder layer occurs. Successive adhesion of SiC and Fe_2O_3 may occur on the upper portion of the adhesion layer soaked with the polymer solution by hydrophobic-hydrophilic interaction.

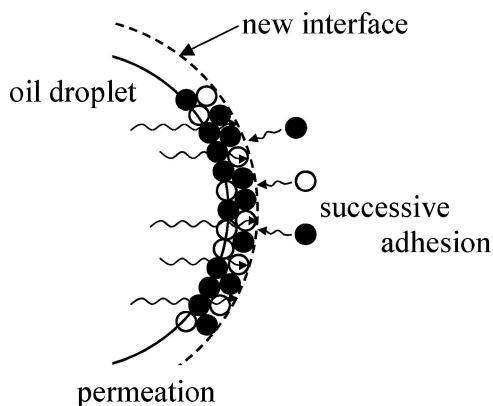


Figure 9 Formation mechanism of composite particles.

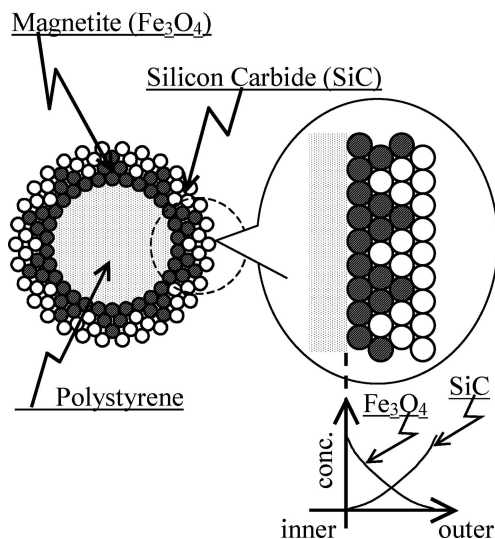


Figure 10 Detailed structure of adhesion layer.

From these results, it is supposed that composite particles with the gradient adhesion layer as shown in Fig. 10 could be able to be prepared.

The composite particles with the gradient adhesion layer will be expected as a filler or a ball bearing with thermal and electric conductivity.

4. Conclusions

Composite particles composed of two kinds of solid powders, magnetite and silicon carbide, and waste expanded polystyrene were prepared by the semi-chemical recycle method. In the experiment, it was investigated how the addition time of silicon carbide and the addition ratio of

magnetite and silicon carbide affected the morphology of the composite particle and the structure of adhesion layer. The following results were obtained.

(1) Addition of only magnetite was not enough to prevent polymer droplets from coalescing each other, so that the later addition of silicon carbide made composite particle diameter larger.

(2) By the later addition of the SiC powder, the adhesion layer was richer in the magnetite powder.

(3) Composite particles with the gradient adhesion layer were able to be prepared by changing the addition time of the SiC powder and the addition ratio of two kinds of solid powders.

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