

# Preparation of Composite Particles Made from Solid Powders and Wasted Plastics by Semichemical Recycle Method

Yoshinari Taguchi, Masto Tanaka

Department of Chemistry and Chemical Engineering, Niigata University, 8050, Ikarashi 2-no-cho, Niigata 950-2181, Japan

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**ABSTRACT:** Composite particles composed of solid powders and polymer were prepared by semichemical recycle of wasted plastics. Waste expanded polystyrene was used as raw materials of polymer matrix of composite particles. Both magnetite and silicon carbide powders were used as solid powders to give thermal and electric conductivity and magnetization, respectively. In the experiment, the oil-phase dissolving expanded polystyrene was dispersed in fine droplets into the continuous water phase. Two kinds of powders were added at the same time or separately in the O/W dispersion. Composite particles were found to have the

structure that polymer particle was covered with two kinds of solid powders. The mean diameter of composite particles and the content of each solid powder were strongly affected by the addition time when silicon carbide powder was added into the dispersion. Furthermore, it was found that the gradient adhesion layer due to two solid powders was able to be formed on the surface of polymer particle. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 483–488, 2003

**Key words:** composites; recycling; waste; functional particles; solid powder

## INTRODUCTION

Preparation of composite particles composed of polymer and solid powder, we can give composite particles various characteristics according to the solid powders used. Composite particles prepared thus are applied in such diverse fields as information and recording materials, cosmetics, painting, medical materials, etc. Furthermore, these composite materials have the latent possibility, the various studies have been performed actively. We have also investigated a preparation of composite particles by various polymerization methods (suspension polymerization, soap-free polymerization, miniemulsion polymerization).<sup>1–9</sup> The morphology of composite particles was found to be affected considerably by an affinity for the liquid–liquid interface between the dispersed and the continuous phase.<sup>7,8</sup>

In this study, we tried, on the basis of previous studies, to prepare composite particles covered gradiently with two kinds of solid powders on the surface by the drying-in-liquid method. Since the drying-in-liquid method is able to prepare particles from wasted plastics, it is possible to develop useful recycle process of wasted polymer by this study. Moreover, by cover-

ing the surface of plastic particle gradiently with two kinds of solid powders, it was thought that composite particles might be given different characteristics.

In this study, expanded polystyrene was used as material of polymer matrix and magnetite and silicon carbide as solid powders. The study will discuss how the addition time and amount of solid powder affected such characteristics of composite particles as sizes, morphology, and electric conductivity.

## EXPERIMENTAL

### Materials

Materials used in this experiment were as follows. Waste expanded polystyrene (EPS; degree of polymerization, ca. 2,700) such as packing materials was used as matrix material of composite particles and dichloromethane (boiling temperature, 313 K, Wako Pure Chemical Industries) was used as the solvent. In order to give some characteristics to polymer particles and to stabilize O/W dispersion, two kinds of solid powders were added. For this, magnetite (Fe<sub>3</sub>O<sub>4</sub>; Dowa Mining) and silicon carbide (SiC; Fujimi) were adopted as the model solid powders to give thermal and electric conductivity and magnetization, respectively. The mean diameters of magnetite and silicon carbide were 0.3 and 0.63 μm, respectively. In order to support the stabilization of the O/W dispersion, polyvinyl alcohol (PVA; degree of polymerization, 500; Wako Pure chemical Industries) was added as a co-stabilizer.

Correspondence to: Masto Tanaka (tanaka@eng.niigata-u.ac.jp).

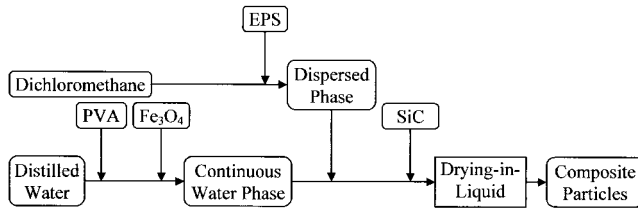


Figure 1 Flow chart of composite particle preparation.

### Experimental apparatus and procedure

The flow chart of preparing composite particles in this experiment is shown in Figure 1. A reactor was a separable flask with three inlets. The inner diameter of this reactor was  $8.5 \times 10^{-4}$  m and the capacity was  $5.0 \times 10^{-4}$  m<sup>3</sup>. In order to prevent air from entraining into the free surface of the dispersion, four baffles made of aluminum were fixed onto an inner wall.<sup>9</sup> The impeller was a six-bladed-disk turbine type. The blade diameter was  $5.0 \times 10^{-2}$  m and the blade height was  $1.0 \times 10^{-2}$  m. It was installed at one-third of the liquid height from the bottom.

Experimental procedure was as follows. At first, the continuous water phase was prepared by dissolving polyvinyl alcohol of a given concentration into distilled water of  $3.0 \times 10^{-4}$  m<sup>3</sup>. Then a given amount of magnetite powder was added into the continuous water phase. After that, the continuous water phase was heated up to 313 K with a thermostatic water bath under stirring by given impeller speed. The dispersed phase was prepared by dissolving a given amount of expanded polystyrene into dichloromethane. The dispersed phase was poured into the continuous water phase to form the O/W dispersion. From this time on, the process of semichemical 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. In the fundamental operation stated above, the addition time of SiC and the addition ratio of SiC and Fe<sub>3</sub>O<sub>4</sub> were changed stepwise.

### Characterization

Characterizations of solid powders and composite particles were as follows. Shapes and surface morphologies were examined with a scanning electric microscopy (SEM; JEOL model JSM-5800). Adhesion layers were examined by an energy-dispersive X-ray spectroscopy (EDX; NORAN Instruments).

Mean diameters were determined as follows. At first, diameters of about 500 solid powder or composite particles were measured directly from secondary electron images (SEI) and optical micrographs (OM), and mean diameters were calculated as Sauter mean diameter ( $d_{32}$ ; in mm) using eq. (1):

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

where  $d_i$  was a diameter of a microcapsule. Zeta potentials of solid powders in the continuous water phase were determined by a streaming potential analyzer (Shimadzu model ZP-10B).

Wetting characteristics of solid powders were determined by the penetrating rate method, namely, one end of tubular cell filled with each powder was contacted vertically with EPS solution, then the weight of solution penetrating through powder bed was measured continuously. Contact angle was calculated from the relationship between penetration weight and time using Washburn's equation. Viscosity and surface tension in the equation were determined by a vibrating viscometer (Yamaichi Electronics model VM-1A) and by a Wilhelmy surface tensiometer (Kyowa Kaimenkagaku model CBVP-A3), respectively.

Adhesion ratios ( $F_A$ ; in mN/m) were determined as follows. At first, a given amount of composite particles ( $W_{CP}$ ; in g) was added into tetrahydrofuran to dissolve polystyrene of themselves and then filtrated. The residual, SiC and Fe<sub>3</sub>O<sub>4</sub> powders, was dried and weighed ( $W_{F+S}$ ; in g). Moreover, Fe<sub>3</sub>O<sub>4</sub> powder of the residual was dissolved by hydrochloric acid, dried, and weighed (weight of silicon carbide,  $W_S$ ; in g). Then the adhesion amount of Fe<sub>3</sub>O<sub>4</sub> ( $W_F$ ; in g) was calculated by subtracting  $W_S$  from  $W_{F+S}$ :

$$W_F = W_{F+S} - W_S \quad (2)$$

Thus, adhesion ratios of Fe<sub>3</sub>O<sub>4</sub> and SiC powders on composite particles were calculated with eq. (3):

$$F_A = \frac{W_F}{W_{CP}} \text{ or } \frac{W_S}{W_{CP}} \quad (3)$$

The stuck number ( $N_S$ ; in number) was determined as follows. Total project area of all solid powder particles adhered on the surface of one composite particle was defined as effective area ( $A_E$ ; in m<sup>2</sup>). If an effective area is equal to a surface area of a composite particle ( $A_{CP}$ ; in m<sup>2</sup>), the adhesion layer is formed from a single layer. Moreover, if an effective area is larger than that of a composite particle, then the adhesion layer is formed from multiple layers. Therefore, the stuck numbers of adhesion layers were calculated with eq. (4):

$$N_S = \frac{A_E}{A_{CP}} \quad (4)$$

**TABLE I**  
**Zeta Potentials of Polystyrene and Solid Powders**

Material	Zeta potential (mV)
Polystyrene	-43
Magnetite	-12
Silicon carbide	-53

**RESULTS AND DISCUSSION**

**Zeta potential**

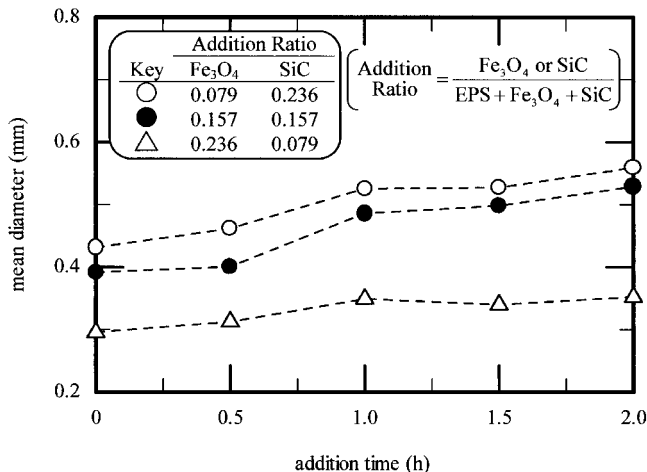
Table I shows zeta potentials of polystyrene and solid powders in the continuous water phase. Zeta potential was thought to be one important factor that affects adhesion of solid powder onto polymer droplet, but the any zeta potentials were negative signs. Thus, in this experiment, zeta potential was supposed not to affect the adhesion so much. In other words, the adhesion of solid powder onto the polymer droplet is thought to be due to collision by stirring and then adhesion force.

**Shapes and surface morphologies**

Figure 2 shows SEI and XRI of a surface of a composite particle. The shape of a composite particle was spherical, and solid powder adhered closely on the surface of a composite particle. From XRI, these solid powders were found to be Fe<sub>3</sub>O<sub>4</sub> and SiC. It is also revealed that composite particles with a similar morphology were formed in the other conditions.

**Mean diameter**

Figure 3 shows the dependence of the mean diameters of composite particles on the addition time of SiC using addition ratios of SiC and Fe<sub>3</sub>O<sub>4</sub> as parameters. Figure 3 shows that in any addition ratios, according



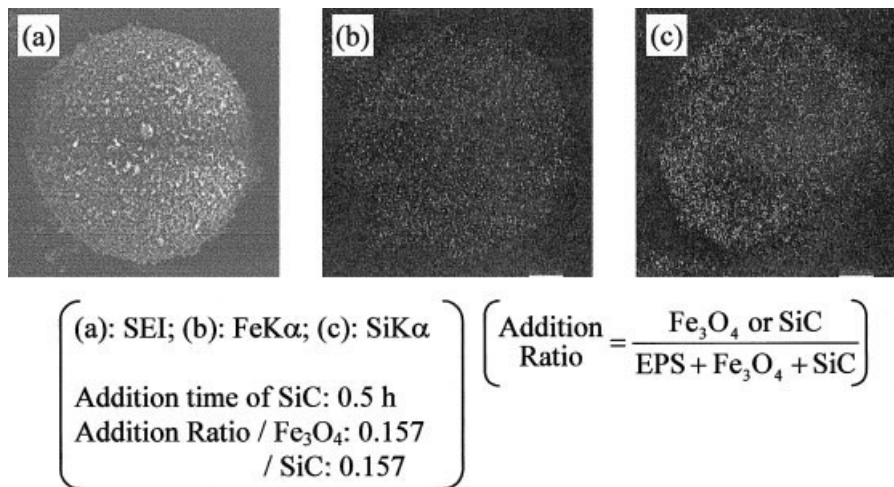
**Figure 3** Dependence of mean diameters on the addition time of SiC.

to addition time, the mean diameters increased. This suggests that the addition of only Fe<sub>3</sub>O<sub>4</sub> could not stabilize polymer droplets. Because polymer droplets also coalesce with each other after the addition of only Fe<sub>3</sub>O<sub>4</sub>, the mean diameters of polymer droplets increased with elapsing time when SiC was added.

Moreover, in any addition time, the mean diameters decreased with an increase of the addition ratio of Fe<sub>3</sub>O<sub>4</sub>. Although the reason is not clear at the present time, it is thought that this was because coalescence of the initial polymer droplets was prevented more strongly by the addition of more amounts of Fe<sub>3</sub>O<sub>4</sub>.

**Adhesion amount and stuck number of solid powder**

Figure 4 shows the dependence of adhesion ratios of solid powder on the addition time of SiC using addition ratio as parameters. In Figure 4, according to the



**Figure 2** SEI and XRI of composite particle surfaces.

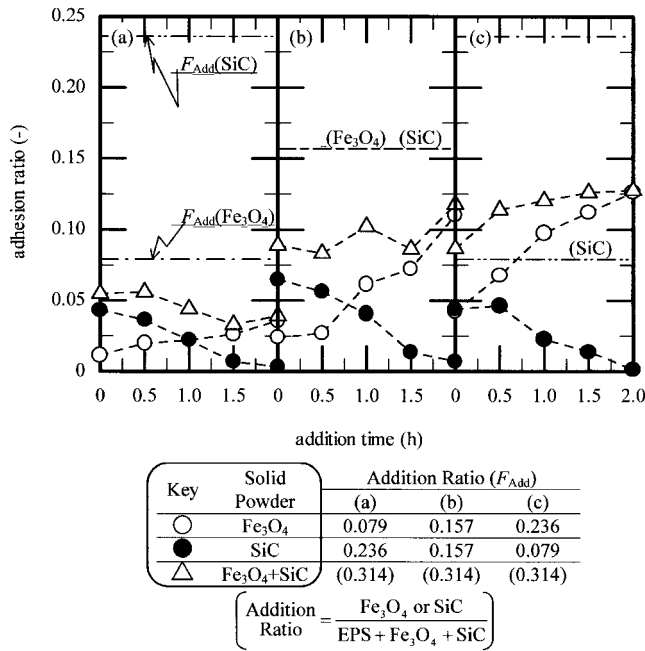


Figure 4 Dependence of adhesion ratios of solid powder on the addition time of SiC.

addition time and ratios, the adhesion ratios of SiC and  $Fe_3O_4$  were changing considerably. In the earlier region, in any addition ratio,  $Fe_3O_4$  increased with the addition time. Unlike  $Fe_3O_4$ , SiC decreased with time. Moreover,  $Fe_3O_4$  increased with the addition ratio of  $Fe_3O_4$ , though SiC almost did not change. These are due to more wetting of solid powder to polymer solution.

Figure 5 shows the dependence of the stuck number on the addition time of SiC. According to the addition time, the stuck number of  $Fe_3O_4$  and SiC was changed contrarily. The stuck number of  $Fe_3O_4$  increased considerably with the addition time. Unlike  $Fe_3O_4$ , the

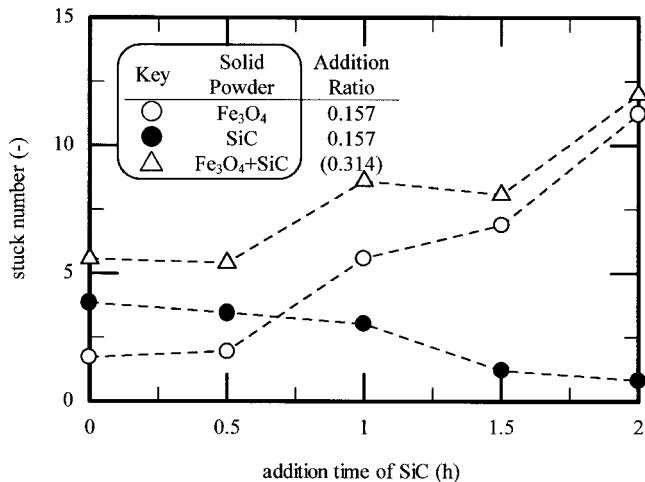


Figure 5 Dependence of the stuck number on the addition time of SiC.

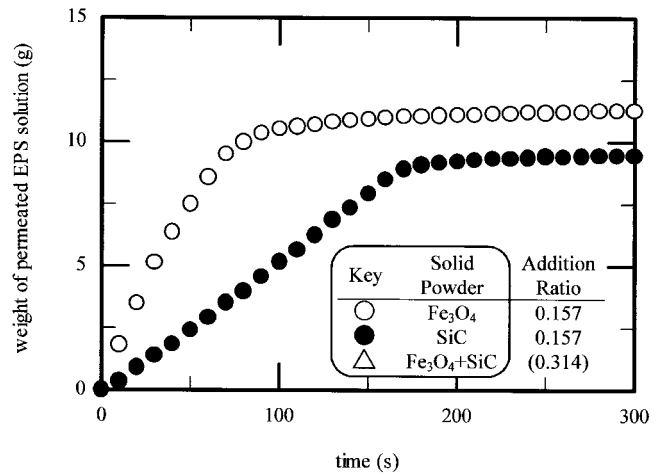


Figure 6 Relationship between time and weight of permeated polymer solution.

stuck number of SiC decreased gradually. From these results, it was clear that earlier addition of SiC made adhesion layer of composite particles SiC-richer. In other words, later addition made adhesion layer of composite particles  $Fe_3O_4$ -richer.

### Adhesion mechanism

Figure 6 shows change of the weight of polymer solution permeated through a packed bed of solid powder with time. Both weights increased with time, but the rates of weight increase were different. Polymer solution penetrated earlier through  $Fe_3O_4$ -packed bed than SiC-packed bed. This indicates that  $Fe_3O_4$  is easier to wet than SiC. Thus, contact angle as the degree of wetting was calculated to discuss adhesion mechanism. Figure 7 shows the relationship between contact angle of solid powder to polymer solution, and the difference of adhesion ( $\Delta W_A$ ; in mN/m) and immer-

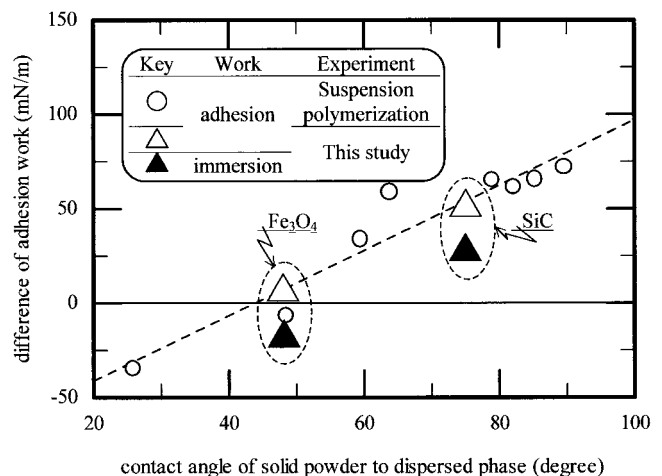


Figure 7 Relationship between contact angle and difference of adhesion work.

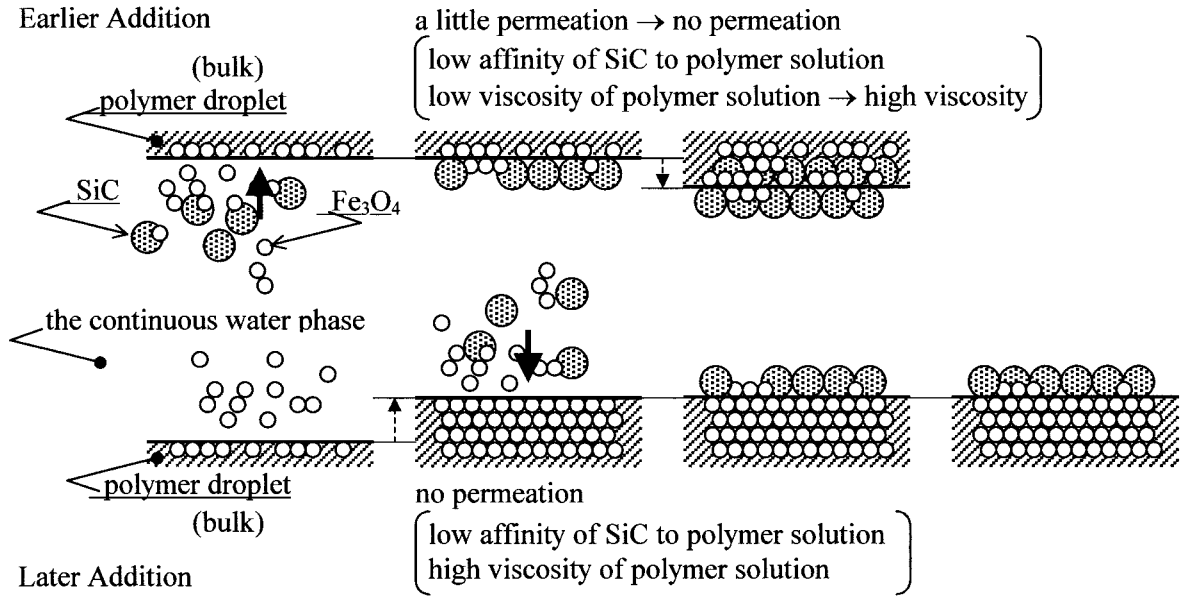


Figure 8 Adhesion mechanism of solid powder.

sion works ( $\Delta W_i$ ; in mN/m) is defined by eqs. (5) and (6):

$$\Delta W_A = W_{A(S/W)} - W_{A(S/O)} \quad (5)$$

$$\Delta W_I = W_{I(S/W)} - W_{I(S/O)} \quad (6)$$

where  $W_{A(S/W)}$  and  $W_{A(S/O)}$  are the adhesion work (in mN/m) between the continuous water phase and solid particle and between polymer solution and solid particle, and  $W_{I(S/W)}$  and  $W_{I(S/O)}$  are the immersion work (in mN/m) between the continuous water phase and solid particle and between the polymer solution and solid particle, respectively. Each work is given by eqs. (7)–(10) as follows:

$$W_{A(S/W)} = \gamma_{(A/W)} + F_S^{(A/S)} - F_S^{(W/S)} = \gamma_{(A/W)}(1 + \cos\theta_W) \quad (7)$$

$$W_{A(S/O)} = \gamma_{(A/O)} + F_S^{(A/S)} - F_S^{(O/S)} = \gamma_{(A/O)}(1 + \cos\theta_O) \quad (8)$$

$$W_{I(S/W)} = \gamma_{(A/W)}\cos\theta_W \quad (8)$$

$$W_{I(S/O)} = \gamma_{(A/O)}\cos\theta_O \quad (10)$$

where  $F_S^{(A/S)}$ ,  $F_S^{(O/S)}$ , and  $F_S^{(W/S)}$  are surface energy (in mN/m) of solid powder to air, polymer solution, and the continuous water phase, respectively,  $\gamma_{(A/O)}$  and  $\gamma_{(A/W)}$  are surface tension (in mN/m) of polymer solution and the continuous water phase, and  $\theta_O$  and  $\theta_W$  are contact angle (in degree) of solid powder to polymer solution and the continuous water phase,

respectively. From eqs. (5) and (6), larger  $\Delta W_A$  or  $\Delta W_I$  indicates that solid powder is easier to wet to water. On the other hand, smaller  $\Delta W_A$  or  $\Delta W_I$  indicates that solid powder is easier to wet to oil. From the results of suspension polymerization made in our group,<sup>10</sup> the contact angle of oil phase is found to be one index of controlling coalescence of droplets. In the case of larger contact angle,  $\Delta W_A$  is larger (Fig. 7). Thus, the solid powder adhered on droplet is easier to water than to oil. As a result, coalescence of droplets is prevented. If the contact angles of solid powder under the condition of this experiment were put in Figure 7, both  $\Delta W_A$  and  $\Delta W_I$  of  $Fe_3O_4$  would be found to be smaller than those of SiC.

Figure 8 shows the mechanism of adhesion of solid powders onto the surface of polymer droplets in the process of drying-in liquid (solvent evaporation). First, in the case of earlier addition of SiC, SiC powder begins to adhere on the surface of polymer droplets before the formation of thick  $Fe_3O_4$  layer. Polymer droplets are stabilized by SiC adhesion to be prevented from coalescing to one another. Moreover, permeation of polymer solution into the solid powder layer is prevented. But in the early time, because the viscosity of polymer droplets is low, a little permeation goes on until the viscosity becomes high. In the case of later addition, SiC powder begins to adhere after the formation of thick layer of  $Fe_3O_4$ . Then the polymer droplets are stabilized. Moreover, the permeation of polymer solution is prevented, and the next adhesion of solid powder is also prevented. As a result, later addition of SiC makes the adhesion layer  $Fe_3O_4$ -richer and the diameter larger.

### CONCLUSIONS

In this experiment, the addition time of silicon carbide and the addition ratio of magnetite and silicon carbide both affected the morphology of composite particles. The addition of only magnetite was not enough to prevent polymer droplets from coalescing together, so that later addition of silicon carbide made composite particle diameter larger. Moreover, the covering layer of the composite particles prepared by means of later addition was richer in magnetite. According to these results, the ability to control the morphology of composite particle was suggested.

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