

## Dispersion Stability of Particles Coated with Plasma Polymerized Hexamethyldisiloxane

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In order to improve the dispersion stability of the particles designed for electrorheological fluids, the particle surface was modified with plasma-polymerized hexamethyldisiloxane (HMDSO).

The particles used were inorganic-shell / organic-core composite particles with a diameter of ca. 14  $\mu\text{m}$ . The inorganic-shell was composed of titanium oxide and tin oxide, and the core was poly(butyl acrylate) sphere. The particles were placed in a round-bottom flask and exposed to the plasma of HMDSO gas. The plasma was generated with 13.56 MHz RF glow discharge under a continuous evacuation. The flask was rotated between the concave electrodes during polymerization.

The polymerization proceeded most efficiently under a system pressure of 25 Pa and a plasma power of 30 W. The Si concentration on particle surface increased during polymerization but the deposition was decelerated in the meantime. The composition of formed surface layer changed consequently. The particles covered by deposition layer with the surface Si content of 19-24 atom % showed an improved dispersion stability in dimethylsilicone oil.

**Key words:** plasma polymerization, surface modification, coated particles, dispersion stability, hexamethyldisiloxane

### 1. INTRODUCTION

Suspensions of particles are important fluids applied in a variety of fields. The poor dispersion stability of particles often brings practical limitation to the fluids usefulness.

Fluids in which the flow properties are drastically changed by the application of an electric field are known as electrorheological (ER) fluids. The fluids generally consist of micron or submicron solid particles suspended in an insulating liquid [1,2]. Since the coagulation of particles influences the ER effects and depresses the reliability of the system, good dispersion stability of the particles is desirable.

Various stabilizing agents are known for realizing a suspension or emulsion having a useful and persistent concentration of disperse phase. However, the use of ionic substances increasing the electrostatic repulsion is to be excluded for the present system because the surface charge on the particles leads the electrophoretic migration of dispersoid under an electric field. The most promising approach is surface modification of the particles with macromolecules. The steric stabilization interaction is expected from the modified particles. And more, if the surface macromolecular layer lowers the interfacial tension between the particle and the disperse medium, the flocculation becomes undesirable owing to the reduced thermodynamic gain through the process.

In this paper, we report that the modification of particles by plasma-polymerization is effective to improve their dispersion stability. Hexamethyldisiloxane (HMDSO) is used as the monomer so that the polymerized layer possesses a good affinity to the suspension medium, dimethylsilicone oil.

### 2. EXPERIMENTS

The particles used in the experiments were inorganic-shell / organic-core composite particles designed for ER fluids provided by Fujikura-kasei Co.,

Ltd. [3]. The inorganic-shell was composed of titanium oxide and tin oxide. The core sphere was the crosslinked copolymer of butyl acrylate and 1,3-butanediol dimethacrylate.

The particles of 4-5 g were placed in a 300 mL round-bottom flask with 12-15 g glass beads ( $\phi$  5 mm), and exposed to the plasma of HMDSO gas. The plasma was generated with 13.56 MHz RF glow discharge under a continuous evacuation using a plasma generator of Samco International Co., Ltd. The flask was rotated between the concave electrodes during polymerization. The schematic diagram of the apparatus is shown in Fig.1.

Firstly, polymerization was carried out under several system pressures. After the pressure of the vessel was reduced to 5 Pa, HMDSO was introduced into it until the inner pressure became a set value. The monomer feed ratio and the polymerization rate were measured with varying the plasma power from 5 to 30 W. The rates were evaluated by weighing the HMDSO in the supply flask and that in the cold trap soaked in liquid nitrogen before and after the polymerization. It was found that the

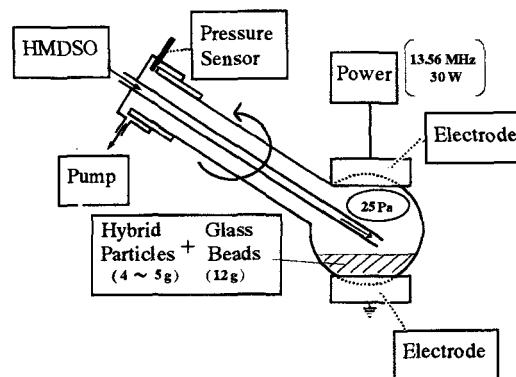


Fig.1 Plasma-polymerization apparatus.

polymerization proceeded most efficiently under the system pressure of 25 Pa and the plasma power of 30 W (See Fig.2).

In the following, all the polymerization were operated with keeping the total pressure in the reactor at 25 Pa, and the plasma power of 30 W was maintained.

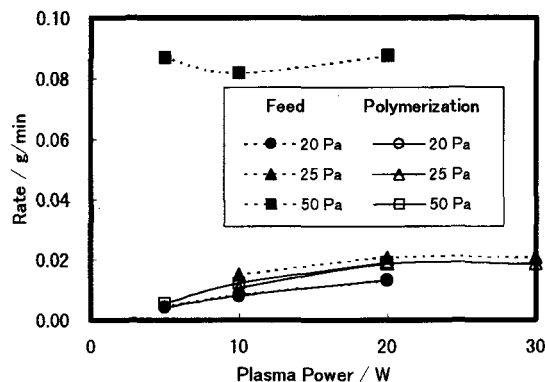


Fig.2 Plasma power dependency of rates of monomer feed and polymerization under various system pressures.

The number-average diameters ( $\Phi_n$ ) of particles were determined by measuring 50-70 particles on micrographs observed by using a JEOL JSM-T20 scanning electron microscopy (SEM).

The surface compositions of the particles were analyzed by X-ray photoelectron spectroscopy (XPS) using a Perkin-Elmer PHI 5600 ESCA instrument. XPS spectra were obtained with a conventional Mg K $\alpha$  X-ray source operated at 300 W.

Dispersion stability of particles were measured by optical method. According to van den Tempel [4], change in concentration of particles due to flocculation follows the equation,

$$\frac{1}{N} - \frac{1}{N_0} = Kt \quad (1)$$

where  $N$  is the number of particle at time  $t$ ,  $N_0$  is that at  $t = 0$ , and  $K$  is the coagulation constant.

If there is no light-absorption, the change of optical density arises by Rayleigh scattering. Then equation (1) can be transformed to equation (2):

$$\frac{1}{D} - \frac{1}{D_0} = K't \quad (2)$$

where  $D$  is optical density.

Strictly saying, the scattering is influenced by the particle size distribution, but it is known that the initial slope of the plot of equation (2) can be used as a measure of the relative rate of coagulation [5].

Therefore, we measured the change in optical density of the suspension. A suspension containing 0.1 wt% particles was prepared with using dimethylsilicone oil (GE Toshiba Silicone TSF451-10,  $d = 0.940$ ,  $\nu = 10$  cSt) as medium. 3 ml of the suspension was placed in a 1 cm-quartz cell, and was shook and treated with ultrasonic wave so as to realize complete dispersion. Immediately after the treatment, the cell was set in a JASCO V-560 photospectrometer, and the optical density at 600 nm was monitored. The incident light beam was aligned to irradiate a W 1 mm  $\times$  H 6 mm area at 8 mm above the cell bottom.

### 3. RESULTS AND DISCUSSION

#### 3.1 Changes in surface composition during plasma-polymerization

Typical XPS survey spectra of particles are shown in Fig.3. Very strong Sn3d peak is remarkable for the particle before plasma-polymerization treatment. After the treatment, Sn3d peak loses the intensity and Ti2p signal is scarcely distinguished. On the other hand, Si2s and Si2p peaks can be recognized remarkably around 150 and 100 eV, respectively, which clarifies that silicon-containing product is deposited on the surface of the hybrid particles.

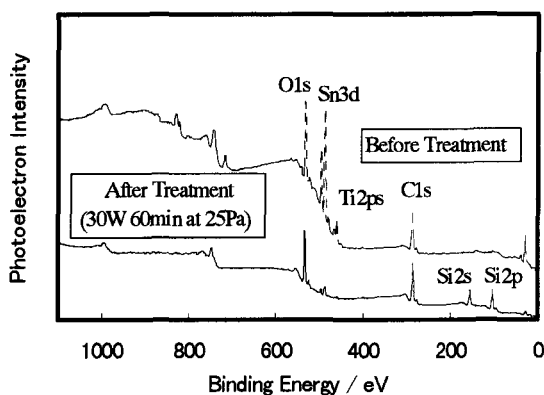


Fig.3 Changes in XPS survey spectrum of particle by plasma-polymerization treatment.

The spectral regions of Sn3d, Ti2p, C1s, O1s and Si2p were measured in a high-resolution mode. The peak area of each region was analyzed and subsequently interpreted into surface atomic percentage by the data reduction software supplied with the instrument.

The changes in surface Si concentration are plotted in Fig.4. It is obvious that deposited amount of Si increases continuously with polymerization time. The deposition rate, however, is decelerated gradually to reach a constant value observed after 30 min. It is possible that the plasma-etching of deposit layer occurs simultaneously along with plasma-polymerization. Since plasma-polymerization rate is usually constant under a constant plasma condition, the etching rate is supposed to be increased in the meantime. The area of particles covered by plasma-polymerized deposit was probably increased until the deposit coated entire surface of

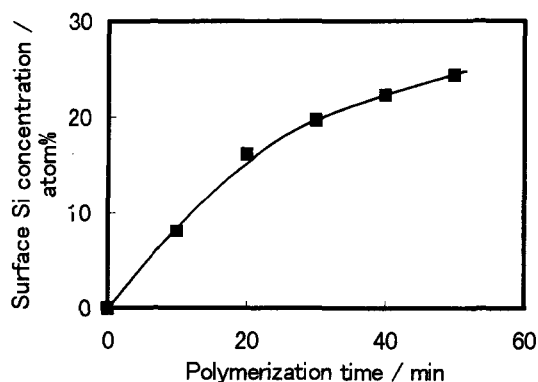


Fig.4 Changes in surface composition during plasma-polymerization at 30 W, 25 Pa.

particles resulting in the change of etching rate.

Changes in surface atomic percentage of particles during plasma-polymerization are summarized in Table 1 along with their number-average diameters. The average diameter can be regarded as constant within the error. There was not any anomalous particles observed on SEM micrographs. The composition of the deposited layer was estimated with using these data.

Table 1 Surface atomic compositions of particles.

Time / min	Surface Concentration / atom%					$\Phi n$ / $\mu\text{m}$
0	12.0	3.8	42.6	41.6	0.0	$14.0 \pm 5.8$
10	9.5	3.4	38.6	40.5	8.0	$14.0 \pm 5.8$
30	2.5	0.8	40.3	36.7	19.7	$13.0 \pm 5.6$
50	0.6	0.2	40.8	34.1	24.3	$12.5 \pm 5.3$

The detected intensity of photoelectron of the inner portion through overlaid layer of  $t$  nm thickness ( $I_i$ ) is deduced from the original intensity ( $I_0$ ) by  $\exp(-t/\sin\theta/\lambda_i)$ , where subscript  $i$  corresponds to the element considered,  $\theta$  is a take-off-angle and  $\lambda_i$  is the inelastic mean free path of electron in the layer. That is

$$I_i = I_0 \exp(-t/\lambda_i)$$

where  $\tau = t/\sin\theta$ .

Considering that Sn and Ti exist only in the core sphere and assuming that the core is coated thoroughly by uniform deposit layer produced by plasma-polymerization, the relative photoelectron intensity of Ti from the core is expressed as equation (3) with using the intensity of Sn as an internal standard.

$$\begin{aligned} a' &= \frac{I_{\text{Ti}}}{I_{\text{Sn}}} = \frac{I_{0\text{Ti}} \exp(-\tau/\lambda_{\text{Ti}})}{I_{0\text{Sn}} \exp(-\tau/\lambda_{\text{Sn}})} \\ &= a \exp\left(-\tau\left(\frac{1}{\lambda_{\text{Ti}}} - \frac{1}{\lambda_{\text{Sn}}}\right)\right) \\ \therefore \tau &= \left(\ln \frac{a'}{a}\right) / \left(\frac{1}{\lambda_{\text{Sn}}} - \frac{1}{\lambda_{\text{Ti}}}\right) \end{aligned} \quad (3)$$

Therefore,

$$\begin{aligned} \beta &= \frac{I_0}{I_{\text{Sn}}} = \frac{I_{0\text{O}} \exp(-\tau/\lambda_0)}{I_{0\text{Sn}} \exp(-\tau/\lambda_{\text{Sn}})} \\ &= b \exp\left(-\tau\left(\frac{1}{\lambda_0} - \frac{1}{\lambda_{\text{Sn}}}\right)\right) \\ &= b \exp\left(\left(\ln \frac{a'}{a}\right) \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_{\text{Sn}}}\right) / \left(\frac{1}{\lambda_{\text{Ti}}} - \frac{1}{\lambda_{\text{Sn}}}\right)\right) \\ &= b \exp\left(\left(\ln \frac{a'}{a}\right) \frac{\lambda_{\text{Sn}} - \lambda_0}{\lambda_{\text{Sn}} - \lambda_{\text{Ti}}}\right) \end{aligned} \quad (4)$$

For the most organic material,  $\lambda_i$  is estimated by Ashley's equation (5) where  $M$ ,  $\rho$  and  $n$  are respectively the molecular weight, density and number of the valence electron of the repeating unit of the layer.  $E_i$  is the kinetic energy of considered photoelectron [6]:

$$\begin{aligned} \lambda_i(\text{nm}) &= \frac{M}{\rho n} E_i / (136 \ln E_i - 176 - \frac{14000}{E_i}) \\ &= \frac{M}{\rho n} f(E_i) \end{aligned} \quad (5)$$

Inserting eq.(5) to eq.(4)

$$\beta = b \exp\left(\left(\ln \frac{a'}{a}\right) \frac{f(E_{\text{Sn}}) - f(E_0)}{f(E_{\text{Sn}}) - f(E_{\text{Ti}})} \frac{f(E_{\text{Ti}})}{f(E_0)}\right)$$

Similarly,

$$\begin{aligned} \chi &= \frac{I_{\text{C}}}{I_{\text{Sn}}} = \frac{I_{0\text{C}} \exp(-\tau/\lambda_{\text{C}})}{I_{0\text{Sn}} \exp(-\tau/\lambda_{\text{Sn}})} \\ &= c \exp\left(-\tau\left(\frac{1}{\lambda_{\text{C}}} - \frac{1}{\lambda_{\text{Sn}}}\right)\right) \\ &= c \exp\left(\left(\ln \frac{a'}{a}\right) \frac{f(E_{\text{Sn}}) - f(E_{\text{C}})}{f(E_{\text{Sn}}) - f(E_{\text{Ti}})} \frac{f(E_{\text{Ti}})}{f(E_{\text{C}})}\right) \end{aligned}$$

By expressing the photoelectron intensity from the deposited layer as  $I'_i$ , the relative photoelectron intensity observed for the plasma-polymerization treated particles are described as follows:

$$\begin{aligned} b' &= \frac{I_0 + I'_0}{I_{\text{Sn}}}, \quad c' = \frac{I_{\text{C}} + I'_{\text{C}}}{I_{\text{Sn}}}, \quad d' = \frac{I'_{\text{Si}}}{I_{\text{Sn}}} \\ \frac{I'_0}{I_{\text{Sn}}} &= b' - \beta, \quad \frac{I'_{\text{C}}}{I_{\text{Sn}}} = c' - \chi \\ \therefore \frac{I'_0}{I'_{\text{Si}}} &= \frac{b' - \beta}{d'}, \quad \frac{I'_{\text{C}}}{I'_{\text{Si}}} = \frac{c' - \chi}{d'} \end{aligned}$$

It should be noted here that  $a$  ( $=I_{0\text{Ti}}/I_{0\text{Sn}}$ ),  $a'$ ,  $b$  ( $=I_{0\text{O}}/I_{0\text{Sn}}$ ),  $b'$ ,  $c$  ( $=I_{0\text{C}}/I_{0\text{Sn}}$ ),  $c'$  and  $d'$  are all obtained experimentally. That means  $\beta$  and  $\chi$ , and hence,  $I'_0/I'_{\text{Si}}$  and  $I'_{\text{C}}/I'_{\text{Si}}$  can be estimated without knowing  $\tau$ ,  $M$ ,  $\rho$  nor  $n$ . Finally  $I'_0/I'_{\text{Si}}$  and  $I'_{\text{C}}/I'_{\text{Si}}$  are interpreted to the ratios of atomic concentration (O/Si and C/Si) by using the sensitivity factor of each element. This method mentioned above enables the estimation of the composition of deposit layer quite empirically though the plasma polymerization of HMDSO is known to form silicon-containing substances which varies from dimethylsilicone-like compound to silica-like material depending on the operating conditions [7-10].

Results are listed in Table 2. The abnormal minus C/Si value estimated for 10 min-polymerization suggests that the particle surface is not covered uniformly by the deposit at this stage. After 20 min-polymerization, O/Si decreases gradually from 1.5 to 1.3 while C/Si increases from 1.2 to 1.6. The composition seems to become a steady value close to that of polydimethylsiloxane (O/Si=1, C/Si=2) after 40 min. These tendencies correspond to the simultaneous deposition-etching mechanism proposed previously in the consideration about the change in surface Si concentration.

Assuming that the inelastic mean free path of electron in the surface layer is the same as that in polydimethylsiloxane, the thickness of deposit layer was estimated roughly as 6 nm and 9 nm for the treatment of 30 min and 50 min, respectively.

Table 2 Compositions of plasma-deposit layer

Deposition Time / min	Composition	
	O/Si	C/Si
10	1.5	-3.1
20	1.5	1.2
30	1.5	1.3
40	1.4	1.6
50	1.3	1.6

### 3.2 Effect of plasma-polymerization coating on dispersion stability

The time-depending changes in optical density ( $D$ ) at 600 nm are illustrated in Fig.5. It is obvious that  $D$  decreases more slowly in the suspensions of modified particles than in the original one. It is also noticeable that each decay curve consists of two lines. One is of small inclination observed at early stage, and the other shows more rapid decay. As the detected region is located in low part of the optical cell, the decrease in  $D$  at early stage is considered to occur by the slow coagulation of particles.

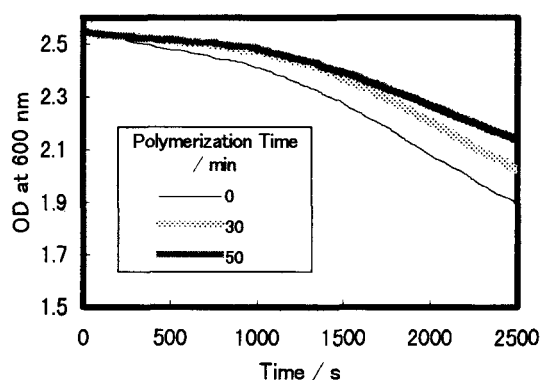


Fig. 5 Decrease in OD at 600 nm due to coagulation and sedimentation.

Though the overall kinetics of slow coagulation are not simple even for dilute system because of size dispersion of particles and multiple coalescence, it is well accepted that only the doublets are formed in the earliest stages. On the other hand, the phenomena in the later stages should be very complicated including multiplets formation and sedimentation. Indeed, the decay curves observed after 1000 s had very poor reproducibility. However, the slope of the curve before 900 s was thought to be reliable.

The plot of  $1/D$  vs. time is given in Fig.6 according to eq. (2). Comparison of the gradients of regression lines leads the conclusion that the coagulation rates of particles modified by plasma-polymerization are about

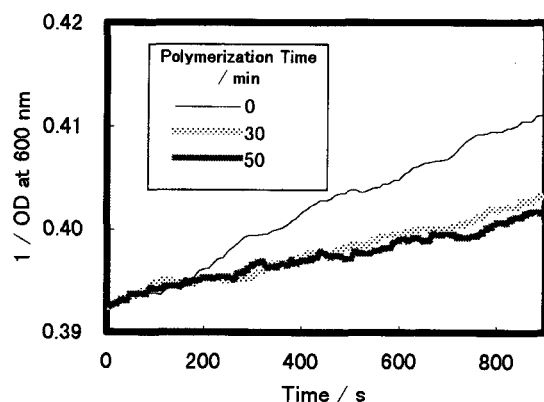


Fig.6 Changes in coagulation rate by plasma-polymerization treatment.

half of the original value. On the contrary, the difference between the particles prepared by the two different polymerization time is quite small though the particles obtained by 50 min-polymerization seem to coagulate slightly slower than those prepared by 30 min-treatment. It is reasonable since the composition of the deposit layers of those two kinds of particles were very similar to each other as shown in Table 2.

### 4. CONCLUSIONS

ER particles consisting of polymer core and inorganic shell were successfully coated with silicone-like layer by plasma polymerization of HMDSO. Plasma power of 30 W under total pressure of 25 Pa was found to be optimal polymerization condition. Plasma-polymerized HMDSO layer contributed to the improvement of dispersion stability.

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