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Measurement of the Adhesive Force between Particles of Powdered Materials and a Glass Substrate by Means of the Impact Separation Method. III.[1] Effect of Particle Shape and Surface Asperity

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The effect of particle shape and surface asperity on the adhesive force between particles of powdered materials and a glass plate was investigated by the impact separation method. It was found that the adhesive force between particles and the glass plate generally increased as the particle shape approaches a sphere and there is a linear relationship between the logarithm of adhesive force and shape index, regardless of the material. This result may be related to the effective area of contact and the contacting state between particles and the substrate. The presence of protuberances or fine particles on the surface reduced the adhesive force between particles and the plate. The mechanism is discussed on the assumption that the adhesive force is solely due to the van der Waals force.

Keywords——adhesive force; particle shape; surface asperity; shape index; impact separation method; pendulum-type shock testing machine

It is considered that the mechanical properties of powdered pharmaceuticals such as adhesive properties and flowability are largely dependent upon their geometrical properties such as particle size, shape and surface asperity. However, there are few reports on the influence of particle shape and surface asperity on the adhesive force between particles and a plane. Asakawa and Jimbo[2] and Sano *et al.* [3] have investigated the effect of particle shape of glass beads and crushed glass particles on the adhesive force on a glass plate. Using oxidized and reduced iron particles, Krupp[4] studied the effect of surface asperity on particle adhesion on an iron plate. Massimilla and Donsi[5] examined the influence of particle surface asperity on the adhesive properties of spherical silica particles. All the authors mentioned above used a single material or surface-modified materials as the test sample. In the present study, 26 different organic and inorganic powdered materials of different shapes were evaluated for adhesive properties on a glass plate using the impact separation method.[6] Characterization of particle shape and the presence of protuberances and or very fine particles on the particle surface was done by scanning electron microscopy (SEM) and image analysis. The general relationship between these geometrical properties and the adhesive force to a smooth glass surface is quantitatively discussed.

Experimental

Materials——Powders used are listed in Table I with their physical properties. The average particle diameter is expressed as the Heywood diameter, d. Particle density, ρ, was obtained with a Shimadzu-Micromeritics helium–air pycnometer.

Shape index, ψ, for each sample was determined by examining at least 1000 particles with an image analyzer (LUZEX 500, Nireco Ltd.). The shape index, ψ, is obtained by dividing the actual projected area of a particle, A, by

TABLE I. Physical Properties of Sample Powders Used

No.	Sample	Average particle diameter d (μm)	Particle density ρ (g/cm^3)	Shape index ψ	Mark
1	Glass beads	40.2	2.40	0.734	⊙
2	Crushed glass	35.4	2.40	0.552	◐
3	Calcium carbonate P-70	43.9	2.67	0.561	⬡*
4	Calcium carbonate P-70	26.6	2.67	0.588	⬡
5	White alundum 360	47.3	3.90	0.532	◨
6	Silica sand	32.6	2.61	0.530	■*
7	Silica sand	44.8	2.61	0.542	■
8	Dibasic calcium phosphate	51.6	2.09	0.431	⧋
9	Potato starch	41.8	1.48	0.653	⦶
10	Wheat starch	37.6	1.54	0.578	⊕
11	Corn starch	28.7	1.52	0.624	○
12	Sweet potato starch	25.8	1.53	0.611	●
13	α-Lactose	49.6	1.53	0.517	◇
14	β-Lactose	42.3	1.57	0.577	◈
15	Sulfadimethoxine	41.0	1.48	0.532	◑*
16	Sulfadimethoxine	57.6	1.48	0.568	◑
17	Caffeine	41.0	1.37	0.477	▽
18	Crystalline cellulose	32.1	1.57	0.411	△
19	Croscarmellose sodium	56.9	1.57	0.255	▲
20	Aspirin B-101	38.6	1.38	0.514	⊸
21	Aspirin B-102	42.6	1.35	0.470	◓
22	Aspirin B-103	51.2	1.37	0.437	◒
23	Aspirin M-105	46.7	1.38	0.312	○–
24	Aspirin M-107	58.4	1.35	0.398	◓–
25	Aspirin M-108	53.7	1.38	0.424	◒–
26	Aspirin M-109	33.2	1.34	0.420	●–

the area of a circle having a diameter equivalent to the maximum projected length, ML, as shown in the following equation:

$$\psi = \frac{A}{ML^2} \times \frac{4}{\pi} \tag{1}$$

Therefore, the value of shape index, ψ, ranges from zero to 1 and as ψ approaches unity, there is increased particle sphericity.

The SEM photographs of several sample powders are shown in Fig. 1.

Surface Treatment of Powders——Removal of Fine Particles or Protuberances from Particle Surface: Calcium carbonate P-70, sulfadimethoxine and silica sand were treated with dilute hydrochloric acid (0.03 M), dilute ethanol (0.5%) and hydrofluoric acid (46.5%), respectively, to dissolve the fine particles or protuberances on the surface. About 0.5 g of sample particles was added to 200 ml of the appropriate solvent in a beaker and the mixture was stirred for a specified time, then filtered; the residue was washed with fresh solvent and dried at 70°C for calcium carbonate P-70 and silica sand, and at room temperature for sulfadimethoxine.

Addition of Fine Particles to the Surface-Treated Particles: Calcium carbonate, which had been surface-treated as described above, was mixed with finely pulverized calcium carbonate[7] in a test tube using a vibrator (Vortex-Genie model K-550-G, Scientific Industries Inc.).

Measurement of Adhesive Force——The adhesive force between particles on a glass plate was determined by the impact separation method.[6] Sample particles were placed on the glass plate in a measuring cell which was fixed to the impact hammer of a pendulum shock testing machine (PST-300, Yoshida Seiki Co., Ltd.). The hammer was motor-driven to a desired height and then allowed to fall to impact a shock-absorbing mat. The impact acceleration generated was measured with an accelerometer. The percentage of particles adhering to the substrate was determined by counting the numbers of particles before and after impact. A plot of separation force *vs.* percentage of particles remaining on a logarithmic probability paper yields the average adhesive force, f_{50}, at which 50% of particles still

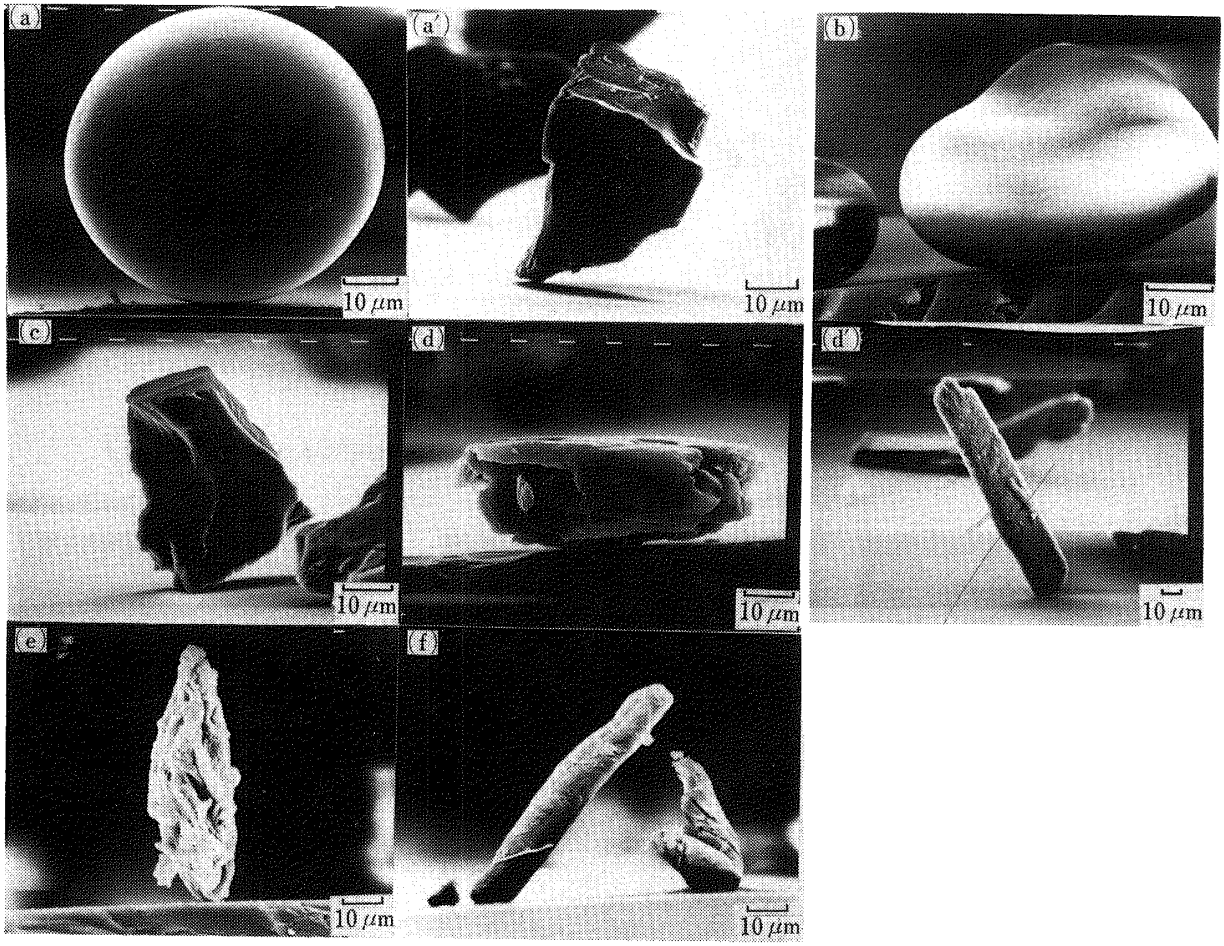

Fig. 1. Scanning Electron Micrographs of Several Sample Powders

a, glass beads; a′, crushed glass; b, potato starch; c, white alundum 360; d, aspirin B-101; d′, aspirin M-105; e, crystalline cellulose; f, croscarmellose sodium.

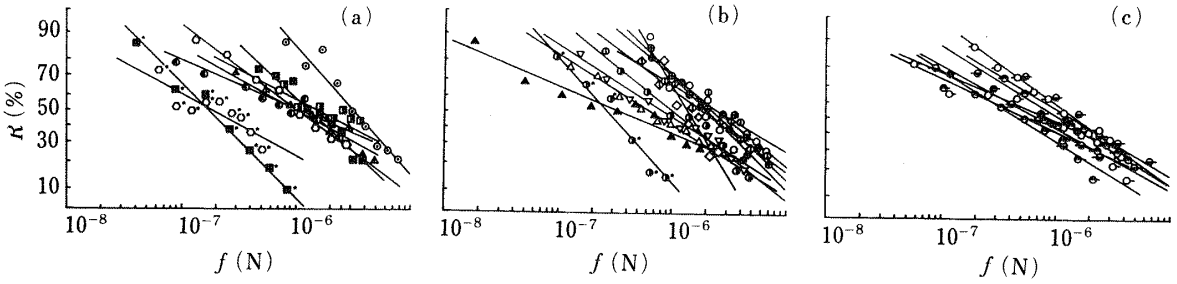

Fig. 2. Plots of Percentage of Remaining Particles against Separation Force on log-Probability Paper

a, inorganic powders; b, organic powders; c, aspirin powders.

remain on the substrate after separation. The impact tests were carried out at 20 ± 5 °C and a relative humidity of $50\pm10\%$.

Results

The percentage of particles remaining on a glass plate was plotted against the separation force on logarithmic probability paper (Fig. 2a—c). Linear relationships were obtained for all

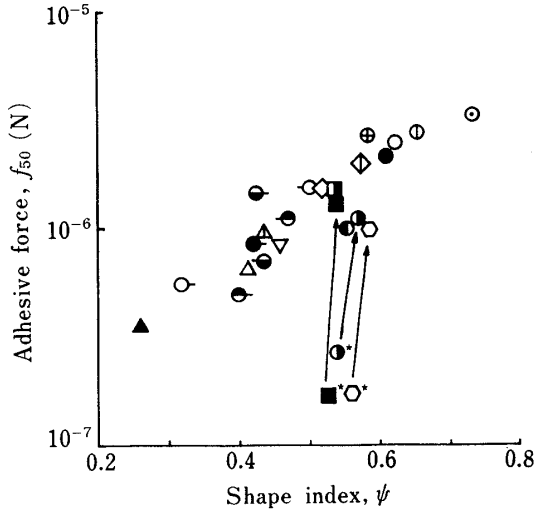

Fig. 3. Relationship between f_{50} and ψ

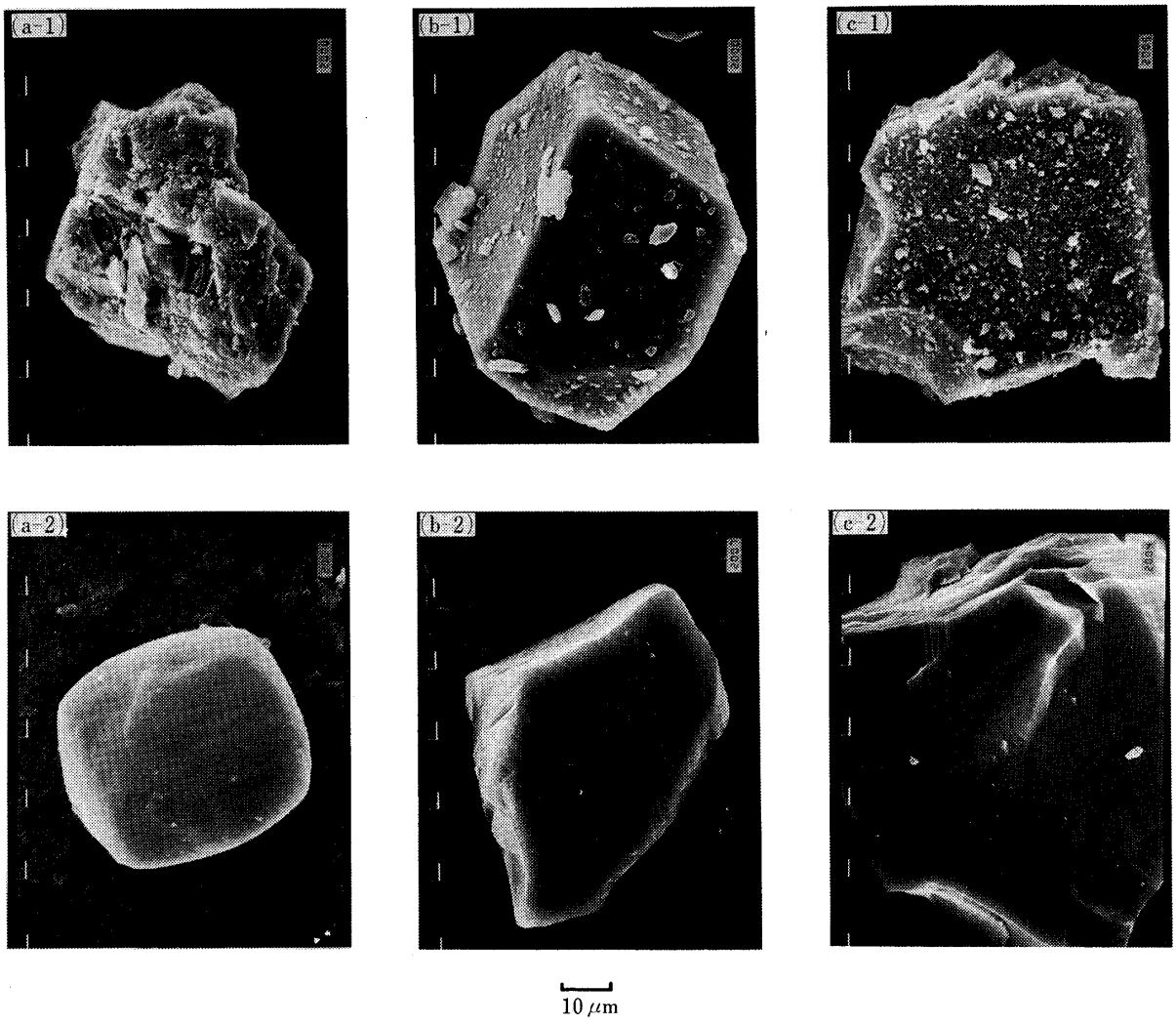

Fig. 4. Scanning Electron Micrographs of Some Powders before and after Surface Treatment

a, calcium carbonate P-70; b, sulfadimethoxine; c, silica sand. 1, untreated; 2, treated.

samples and the average adhesive force, f_{50}, of each sample was obtained graphically.

The relationship between f_{50} and the shape index, ψ, can be seen in Fig. 3. Regardless of the type of sample, $\log f_{50}$ and ψ were well correlated as a linear relationship, and as the

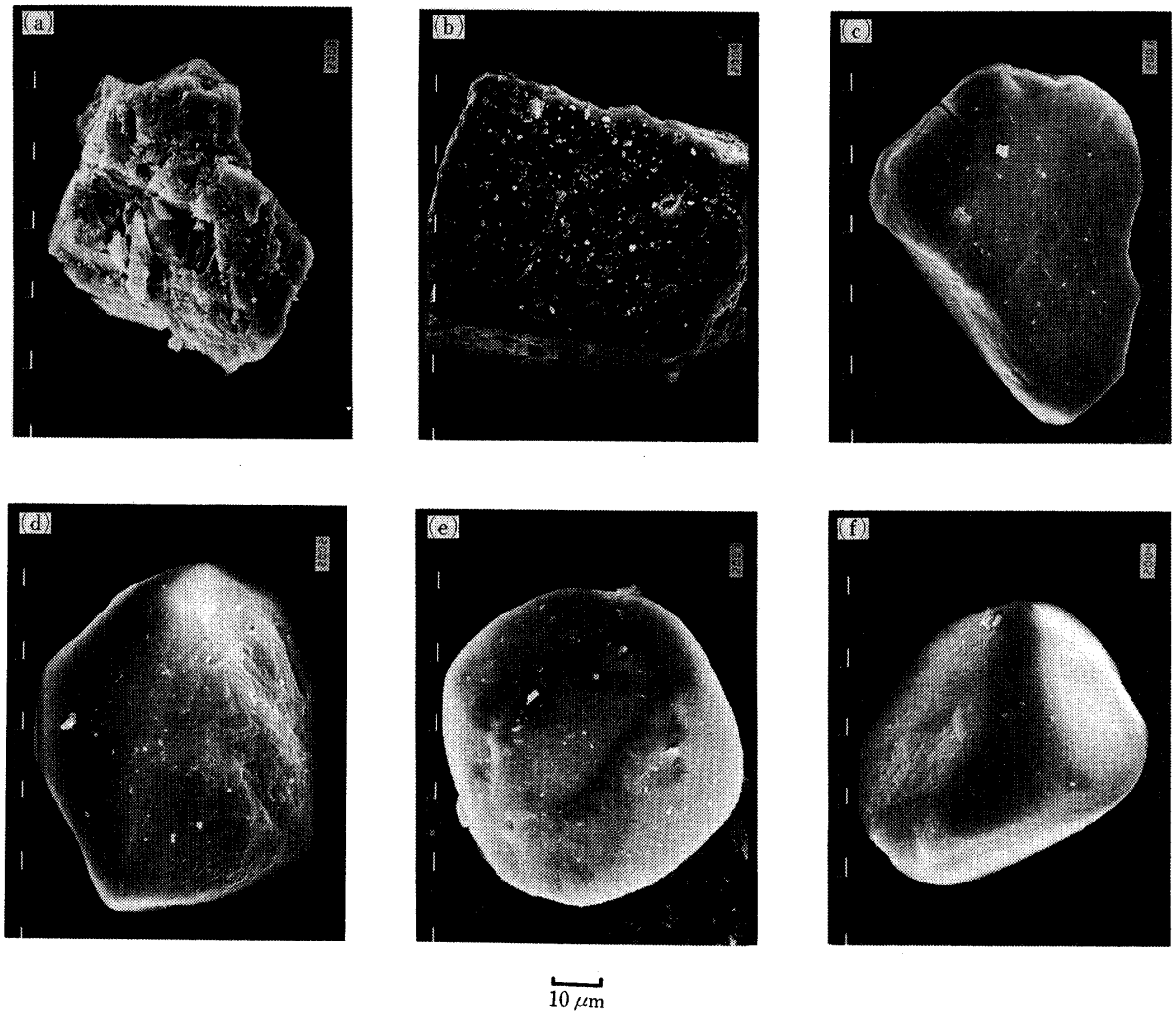

Fig. 5. Scanning Electron Micrographs of Calcium Carbonate P-70 Treated with Hydrochloric Acid

Concentration of hydrochloric acid: a, 0 M; b, 0.001 M; c, 0.01 M; d, 0.02 M; e, 0.03 M; f, 0.04 M.

particles became more spherical, f_{50} increased linearly. Exceptions to this relationship were seen for untreated particles of calcium carbonate P-70, sulfadimethoxine and silica sand. For these materials the f_{50} values were much lower than expected. SEM photographs (Fig. 4 a-1, b-1, c-1) revealed that these particles have a coat of fine particles or protuberances on their surfaces. Treatment of these particles with the appropriate solvents produced particles with smooth surfaces (Fig. 4 a-2, b-2, c-2). After treatment, the f_{50} values of the particles were found to increase about ten-fold. The change is shown in Fig. 3 (indicated by the arrows). As a result of this revision, the correlation between the logarithm of the adhesive force, f_{50}, and the shape index, ψ, improved dramatically, and the coefficient of correlation obtained was 0.886. It is clear from these findings that the adhesive force between particles and a glass plate can be influenced by the presence of fine particles and protuberances on the particle surface. Therefore, further work was carried out to evaluate the effect of surface asperity of particles on the adhesive force on a glass plate. Calcium carbonate P-70 was chosen as a model particle system and was treated with various concentrations of hydrochloric acid. With increasing concentration of hydrochloric acid, more fine particles present on the surface of the large particles were dissolved (Fig. 5) and the adhesive force, f_{50}, increased as shown in Fig. 6

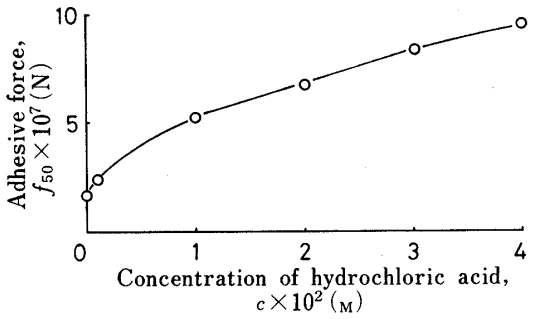

Fig. 6. Relationship between f_{50} and Concentration of Hydrochloric Acid

Treatment time: 15 s.

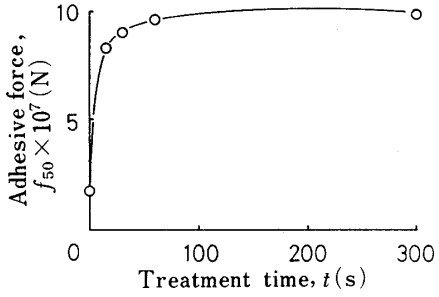

Fig. 7. Relationship between f_{50} and Treatment Time

Concentration of hydrochloric acid: 0.03 M.

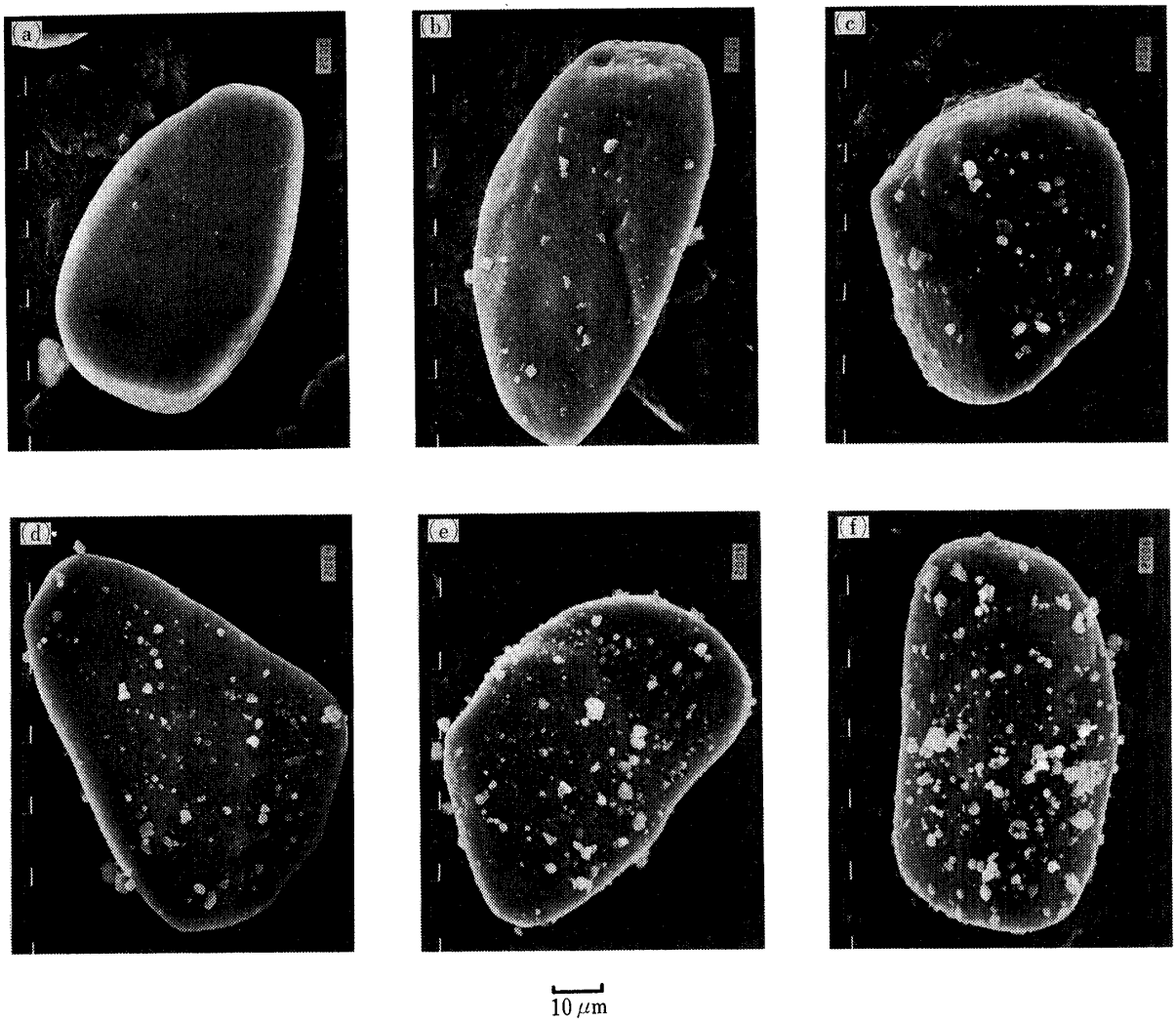

Fig. 8. Scanning Electron Micrographs of Samples to which Fine Particles of Calcium Carbonate had been Added

Percentage of fine particles of calcium carbonate (w/w%): a, 0; b, 0.1; c, 0.3; d, 0.5; e, 1.0; f, 2.0.

(treatment time: 15 s). Figure 7 shows the relationship of the adhesive force, f_{50}, with the treatment time of calcium carbonate P-70 with 0.03 M hydrochloric acid. The f_{50} value increased with treatment time and tends to a constant value with longer treatment times.

The effect of mixing of fine particles into the large particles with a smooth surface was

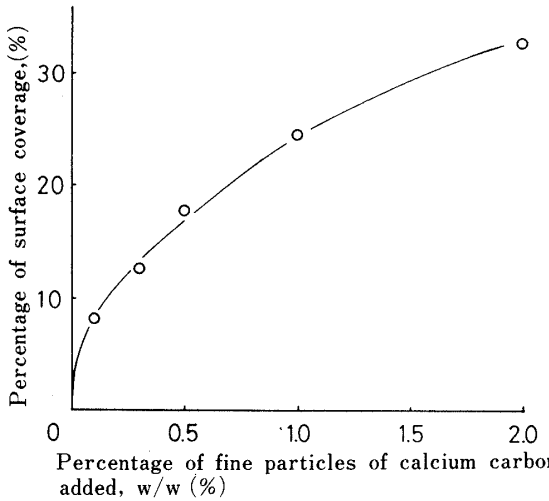

Fig. 9. Relationship between Percentage of Surface Coverage and Percentage of Fine Particles of Calcium Carbonate Added

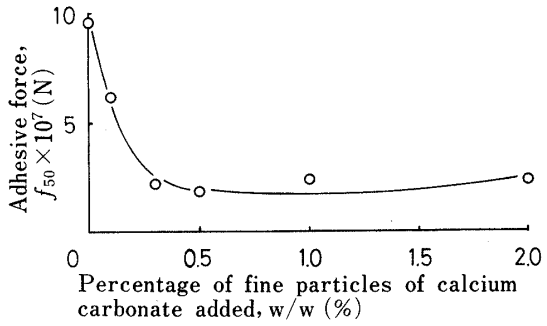

Fig. 10. Relationship between f_{50} and Percentage of Fine Particles of Calcium Carbonate Added

examined. Figure 8 indicates that the fine particles of calcium carbonate are distributed on the surface of the large calcium carbonate particle.

Figure 9 shows the percentage of area of surface coverage by the added fine particles on the large particle surface, as obtained by image analysis of SEM photographs. As the amount of the fine particles of calcium carbonate increased, the ratio of surface coverage become larger. Figure 10 shows the relationship between the adhesive force, f_{50}, and the percentage of fine particles of calcium carbonate mixed. It was noted that the adhesive force was reduced to approximately 1/10 by the addition of fine particles of calcium carbonate at concentrations greater than 0.3%.

Discussion

It has been reported that, as particles become more spherical, f_{50} values become larger when the same materials with different particle shapes are used to evaluate the effect of particle shape on the adhesive force between the particles and a glass plate.[2,3] In the present study, similar results were obtained. In addition, it was found that for smooth-surfaced particles there is a linear relationship between log f_{50} and ψ within the range of $25\mu m < d < 60\mu m$, and $0.255 < \psi < 0.734$, regardless of material. Although the reason for this is not clear, it is obvious that the smaller the value of ψ is, the more angular the shape of the particles is, as seen in Fig. 1b, d. The angular particles (crushed glass, white alundum, *etc.*) contact the substrate with the tip or short edge of the particle and the effective area of contact may be decreased as compared with that of spherical particles. For fibriform particles such as crystalline cellulose and croscarmellose sodium, the contacting state is extremely unstable, and it seems to be easy to separate the particles from the substrate. This tendency is also evident in the aspirin series.

When fine particles and protuberances on the surface of the adhering particles are present, the f_{50} value is much less than expected, and thus, the following assumption can be made. An adhesion–separation model between the particles and the substrate was hypothetically constructed as shown in Fig. 11a—c. If the adhesive force is solely due to van der Waals force, F_{vdw}, then F_{vdw} may be expressed as[4]:

$$F_{vdw}=\frac{\hbar\omega}{8\pi z_0^2}R \qquad (2)$$

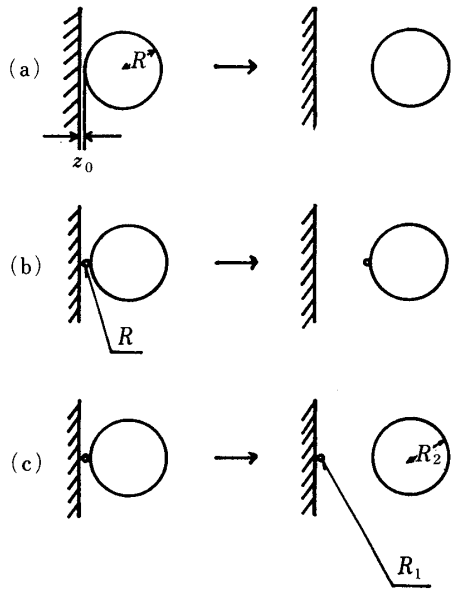

Fig. 11. Adhesion–Separation Models between a Particle and a Substrate

R, R_1 and R_2, particle radius; z_0, adhesional distance.

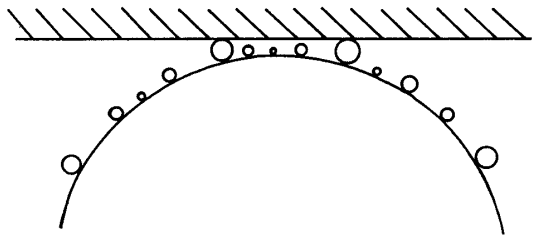

Fig. 12. Adhesion Model between a Substrate and a Particle with Fine Particles on the Surface

where $\hbar\omega$ is the Lifshitz–van der Waals constant, z_0 is the adhesional distance between a particle and the glass plate, and R is the radius of the particle. A model of the adhesion–separation of the surface-treated calcium carbonate particles on the substrate was constructed as shown in Fig. 11a. In this equation, R, the particle radius of the hydrochloric acid-treated calcium carbonate P-70 was 13 μm, z_0 can be taken as 0.5 nm,[5] and F_{vdw} was found to be 9.6×10^{-7} N, which is the measured value of the adhesive force of 0.04 M hydrochloric acid-treated calcium carbonate P-70. Thus, from Eq. 2 $\hbar\omega$ can be calculated to be 5×10^{-19} J. The value of $\hbar\omega$ is generally considered to be in the range of $1—15\times10^{-19}$ J,[4] so the obtained value appears reasonable.

In the next experiment, where surface-treated calcium carbonate particles were mixed with fine particles of calcium carbonate, adhesion of fine particles to the surface of a large particle can be modeled as shown in Fig. 11b, c. In the case of (b), where the fine particles of calcium carbonate are separated from the substrate, R, the radius of the fine particle, can be calculated to be 2.3 μm by substituting 1.8×10^{-7} N for F_{vdw}, the value of f_{50} measured at the concentration of fine particles of 0.5% in Fig. 10, and 5×10^{-19} J for $\hbar\omega$. In the case of Fig. 11c, that is, when surface-treated calcium carbonate and fine calcium carbonate particles are separated, the radius of the fine particle R_1 can be obtained from Eqs. 3 and 4[4]:

$$F_{vdw}=\frac{\hbar\omega}{16\pi z_0^2}R' \tag{3}$$

$$R'=\frac{2R_1R_2}{R_1+R_2} \tag{4}$$

where R_2 is the radius of the large particle and R' is the harmonic average radius. In Eq. 4, when R_2 is 13 μm and $\hbar\omega$ is assumed to be 5×10^{-19} J, R_1 was calculated as 3 μm. The mean particle radius of the fine particles obtained from the SEM photographic image was 0.5 μm (range 0.1 to 3 μm), and this value is less than those calculated from the model of Fig. 11b, c. The reason may be as follows. When the adhering particles have a large particle size distribution, the adhesion model of the particle to the glass plate is constructed to be as shown

in Fig. 12. In such a case, the major factor influencing to the adhesive force may be the relatively larger particles among the adhering particles.

References and Notes

1) This work was presented at the 107th Annual Meeting of the Pharmaceutical Society of Japan, Kyoto, April 1987.
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7) Pulverized using a Hosokawa Micron Angmill (particle diameter: 0.2—6 μm).