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The Effect of Humidity on the Compaction Behavior and the Adhesion Force for Surface-modified Quartz Powders[1]

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The compaction behavior and adhesive properties of original and surface-modified quartz powders were examined under various conditions of relative humidity.

Adhesive force at a contact point (H) decreased with the progress of surface modification in the whole region of the relative humidity. H falls at small water contents and shows a minimum when the amount of adsorbed water is close to that required to monolayer complection (V_m).

The patterns of the porosity of powder bed (ε) in a centrifugal field as a function of adsorbed water showed a striking resemblance to those for the adhesion force at a contact point.

Finally, the relationship among H, ε and the average force acting on a particle (F) was examined. A fairly good correlation was observed between log ($\varepsilon-0.26$) and log (H/F), regardless of the degree of surface modification.

Keywords——quartz powder; compaction; porosity; centrifugal acceleration; relative humidity; adhesion force; surface modification

The packing properties and the compaction behavior of powder particles play an important role in the manufacture of drugs, such as filling dies of tableting machine and filling capsules. The authors[3] have been doing researches on the compaction behavior of powders in centrifugal fields. It was found that the apparent adhesive force, which was defined as the ratio of the adhesive force between particles at a contact point (H) to the external force acting on a particle (F), greatly affected the packing structure of particles. It is well known that H is largely dependent on surface properties. Recently Arakawa and others,[4] Nishino and Arakawa[5] showed the effect of surface modification of alumina and glass on the adhesive force between particles. The tensile strength of lactose powder coated with fatty acids was investigated by Pilpel and Hepher.[6]

The purpose of this work is to examine the effect of surface characteristics of particles on the adhesive force between particles and on the compaction behavior of the powder. Original and surface-modified quartz powders were used as the samples. Measurements were carried out at various conditions of humidity and the results were explained on the basis of the moisture adsorption.

Experimental

Materials——Quartz powder was obtained as a commercial samples, having a mean particle diameter of 23 μm. 150 g of dried powder was added into 400 ml of 0.01 or 0.1% benzene solution of trimethylchlorosilane (TMCS). After stirring for 24 hr at room temperature, the powder was filtrated with a glass filter and washed several times with benzene and acetone, and then dried *in vacuo* at 110° for 4 days.

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[1] This paper constitutes the 9th report in a series of "Studies on Packing of Powder."

[2] Location: *Tempaku-cho, Tempaku-ku, Nagoya.*

[3] A. Otsuka, H. Sunada, and K. Danjo, *Yakugaku Zasshi*, **89**, 1013 (1969); A. Otsuka and K. Danjo, *Yakugaku Zasshi*, **96**, 1189 (1976).

[4] M. Arakawa, J. Okada, and E. Suito, *J. Soc. Materials Sci., Japan*, **15**, 151 (1966).

[5] M. Nishino and M. Arakawa, *J. Soc. Materials Sci., Japan*, **20**, 781 (1971).

[6] N. Pilpel and N.M. Hepher, *Materials Sci. Engr.*, **27**, 89 (1977).

Surface Area Measurements and Water Vapor Adsorption——The specific surface area was determined by BET method from the adsorption of Kr gas at the boiling point of liquid N_2 using Orr Surface Area Pore Volume Analyzer (Model 2100D). The water vapor adsorption was measured at 25°±0.5° under various conditions of relative humidity using the same apparatus as in surface area determination.

Tensile Strength Measurements——Tensile strength measurements were made using a split cell type apparatus[7] which was placed in a constant temperature and humidity cabinet.

Compaction Procedure in a Centrifugal Field——A given amount of powder was dried in a container at 110° for 30 hr under 10^{-4} mmHg prior to the moisture adsorption. A proper amount of water vapor was then introduced into container. After equilibrium was reached, the compaction experiments were carried out in the same manner as reported previously.[7]

Results and Discussion

Specific Surface Area Determined by Adsorption of Krypton and of Water

Fig. 1 shows the water vapor adsorption isotherms of the original quartz powder and the surface-methylated ones, in which Q represents the amount of adsorbed water (g/g), and S_k is the specific surface area determined by Kr adsorption. The values of S_k for all the powders were given in Table I together with the values from water vapor adsorption. As is seen, the value for Kr adsorption is not altered by changing the degree of surface modification, whereas the value for water adsorption decreases with the progress of the hydrophobic property of the surface.

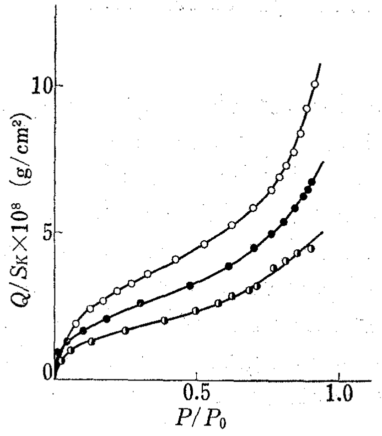

Fig. 1. Adsorption Isotherms of Water Vapor at 25° on Quartz Powders

○: C-0, ●: C-I, ◑: C-II.

Table I. Specific Surface Area of Samples used

Sample	Conc. of TMCS (%) in benzene	Specific surface area determined by H_2O adsorption (m^2/g)	Specific surface area determined by Kr adsorption (m^2/g)
C-0	0 (Original)	0.202	0.216
C-I	0.01	0.146	0.216
C-II	0.10	0.097	0.216

Effect of Humidity and Adsorbed Water on Adhesive Force between Particles

The tensile strengths of powder beds were measured under various humidities. The Rumpf equation[8] was used for obtaining the adhesive force at a contact point (H):

$$\sigma_z = \frac{9}{8} \cdot \frac{1-\varepsilon}{\pi d^2} \cdot kH \qquad (1)$$

where σ_z is the tensile strength per unit cross sectional area in g/cm^2, d is the particle diameter in cm, ε is the porosity of the bed, and k is the coordination number, which can be calculated by Ridgway and Turback equation.[9]

$$\varepsilon = 1.072 - 0.1193\,k + 0.00431\,k^2 \qquad (2)$$

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[7] A. Otsuka and K. Danjo, The 97th Annual Meeting of Pharmaceutical Society of Japan, Tokyo, Apr. 1977, p. 204.

[8] W. Pietsch and H. Rumpf, *Chem-Ing-Techn.*, 30, 885 (1967).

[9] K. Ridgway and K.J. Turback, *Brit. Chem. Eng.*, **12**, 384 (1967).

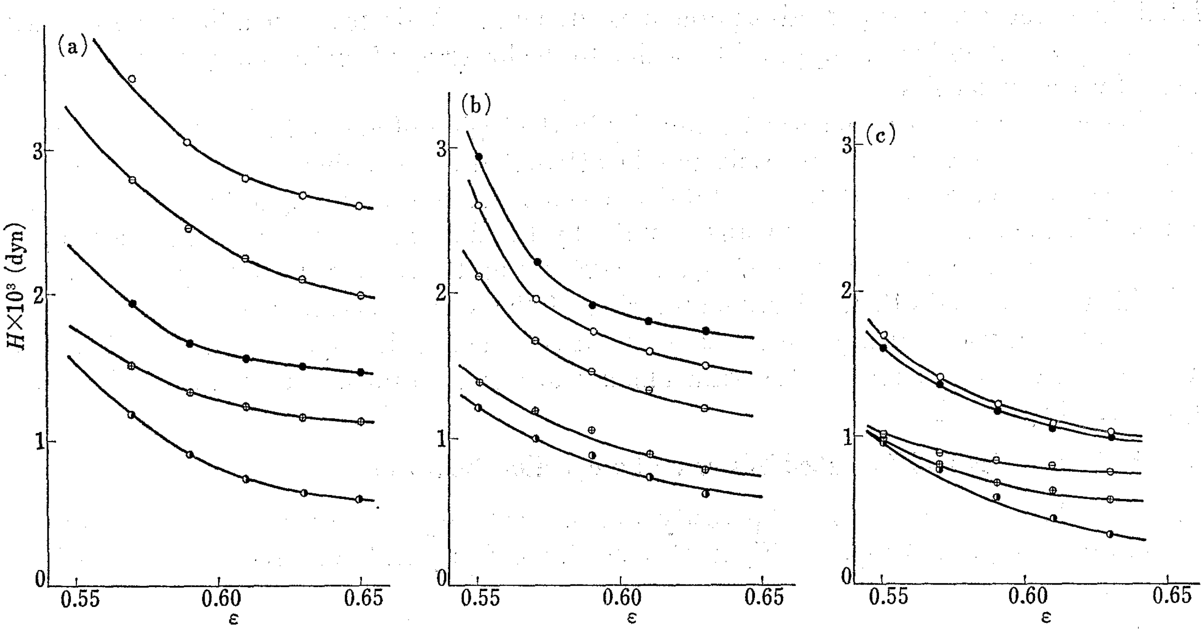

Fig. 2. Relationship between Adhesion Force at a Contact Point between Particles (H) and Porosity (ε) at Various Relative Humidities

(a) Original quartz powder
○: $P/P_0=0$, ◑: $P/P_0=0.257$,
⊕: $P/P_0=0.524$, ⊖: $P/P_0=0.725$,
●: $P/P_0=0.922$.

(b) Quartz powder modified with 0.01% benzene solution of TMCS
○: $P/P_0=0$, ◑: $P/P_0=0.269$,
⊕: $P/P_0=0.505$, ⊖: $P/P_0=0.741$,
●: $P/P_0=0.917$.

(c) Quartz powder modified with 0.1% benzene solution of TMCS
○: $P/P_0=0$, ◑: $P/P_0=0.303$,
⊕: $P/P_0=0.538$, ⊖: $P/P_0=0.724$,
●: $P/P_0=0.904$.

Figures 2(a)—2(c) show the dependence of ε on H. According to the Rumpf's theory, H should not be affected by ε. However, H virtually tends to increase with decreasing ε.

Figure 3 represents the plots of H against the relative humidity at the porosity of 0.55. It was found that the value of H decreased with the progress of surface methylation in the whole region of the air humidity, *i.e.*, hydrophobization of the surface reduced the adhesion between particles, as was stated by Zimon.[10]

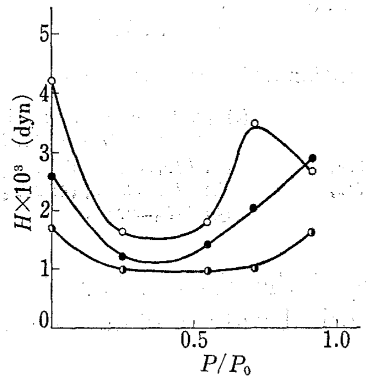

Fig. 3. Adhesion Force at a Contact Point between Particles (H) as a Function of Relative Humidity

○: C-0, ●: C-I, ◑: C-II.

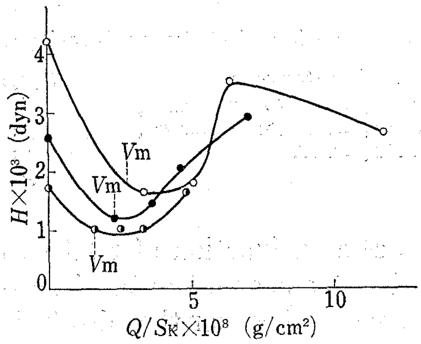

Fig. 4. Adhesion Force at a Contact Point between Particles (H) as a Function of Adsorbed Water

○: C-0, ●: C-I, ◑: C-II.

Using the data in Fig. 1 and Fig. 3, H can be plotted as a function of the amount of adsorbed water per unit area. As is seen in Fig. 4, H falls markedly at small water content and shows a minimum when adsorbed water is close to the monolayer capacity (V_m) calcu-

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[10] A.D. Zimon, "Adhesion of Dust and Powder," Plenum Press, New York–London, 1969, p. 63.

lated from the water vapor adsorption measurement. A decrease in adhesion force with increasing water content is supposed to be due to the lowering of surface energy by the adsorption of water molecules.

When the amount of adsorbed water lies in the region of about V_m to $2V_m$, H increases with the water contents. This result may be attributed to the reduction of the mean separation distance between particles.[11] Similar mechanism has been suggested by Eaves and Jones[12] in the studies on the moisture uptake by the fine fractions of sodium chloride. It is also of interest that the plots of H against Q/S_k for all the samples in this region are almost coincident with each other. The modification of the surface certainly reduces the adsorption amount of water at a given relative humidity as shown in Fig. 3. On the other hand, if each of the samples adsorbs the same amount of water on its surface, values of H become approximately equal.

Effect of Humidity and Adsorbed Water on Compaction Behavior

The relationship between the porosity and the centrifugal acceleration at various relative humidities was given in Fig. 5. Figure 6 shows the porosity at the centrifugal acceleration of 10^5 cm/sec² as a function of relative humidity. In Fig. 7 the abscissa is replaced by the adsorbed water per unit area. The patterns of the adsorbed water-ε plots show a striking resemblance to those for the adsorbed water-H plots.

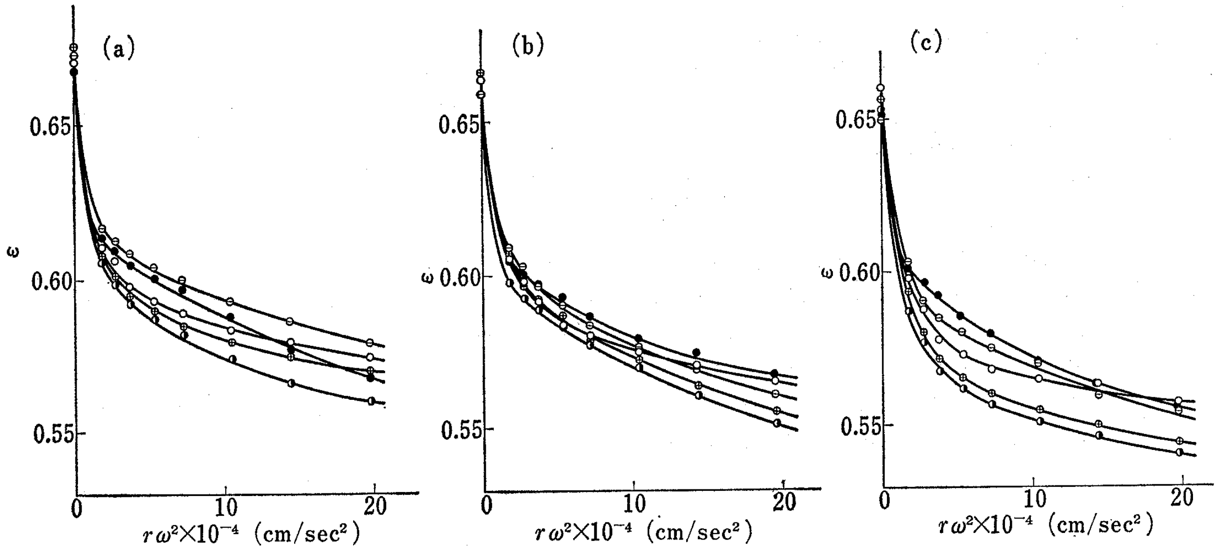

Fig. 5. Relationship between Porosity and Centrifugal Acceleration at Various Relative Humidities

(a) Original quartz powder
○: $P/P_0=0$, ◑: $P/P_0=0.257$,
⊕: $P/P_0=0.524$, ⊖: $P/P_0=0.725$,
●: $P/P_0=0.922$.

(b) Quartz powder modified with 0.01% benzene solution of TMCS
○: $P/P_0=0$, ◐: $P/P_0=0.269$,
⊕: $P/P_0=0.505$, ⊖: $P/P_0=0.741$,
●: $P/P_0=0.913$.

(c) Quartz powder modified with 0.1% benzene solution of TMCS
○: $P/P_0=0$, ◑: $P/P_0=0.303$,
⊕: $P/P_0=0.538$, ⊖: $P/P_0=0.724$,
●: $P/P_0=0.905$.

Relationship between Apparent Adhesive Force and Porosity

It is well known that the stronger the adhesive force between particles, the looser is the packing structure. In the previous paper,[3] authors assumed that the porosity of the powder bed was affected by the ratio of the interparticle adhesion force (H) to the external force acting on a particle (F). In the present experiments F can be calculated from:

$$F = mr\omega^2 \tag{3}$$

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[11] C.A. Walton and N. Pilpel, *J. Pharm. Pharmacol.*, **24**, 10 p (1972).
[12] T. Eaves and T.M. Jones, *J. Pharm. Sci.*, **61**, 256, 342 (1972).

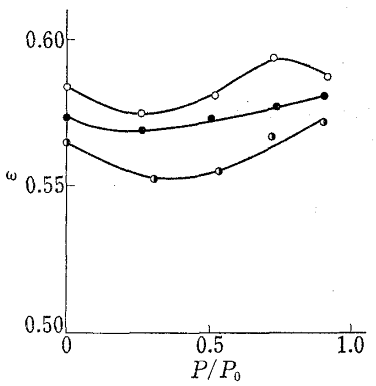

Fig. 6. Porosity at Centrifugal Acceleration of 10^5 cm/sec^2 as a Function of Relative Humidity

○: C-0, ●: C-I, ◑: C-II.

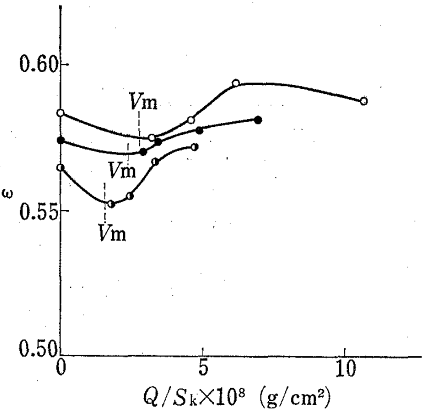

Fig. 7. Porosity at Centrifugal Acceleration of 10^5 cm/sec^2 as a Function of Adsorbed Water

○: C-0, ●: C-I, ◑: C-II.

where m is the mass of a particle, r is the distance of the center of the powder bed from the axis of rotation and ω is the angular velocity of the rotation. When the value of H is sufficiently large compared to the value of F, the particle may stay at the contact point with the neiboring particle even if vacant spaces exist in the lower layer of the powder bed. As the value of F increases, the falling probability of a particle into the vacant spaces will increase to make the bed more compact. Thus, the equation as to the relationship between the apparent adhesive force (H/F) and the porosity (ε) was presented as follows:

$$\varepsilon = K(H/F)^n + \gamma \qquad (4)$$

where K and n are constants. γ is the limiting porosity for $F \to \infty$ and the value of 0.26, which is the porosity of the closest packing of monosize spheres, is employed in the present work. In order to examine the fitness of the equation to the experimental results, a plot of log ($\varepsilon - 0.26$) against log (H/F) was made using the data at the centrifugal acceleration of 5, 10 and 20×10^4 cm/sec^2 and those at the gravitational field in various relative humidities. As shown in Fig. 8, a fairly good correlation was observed between log ($\varepsilon - 0.26$) and log (H/F) regardless of the degree of surface modification.

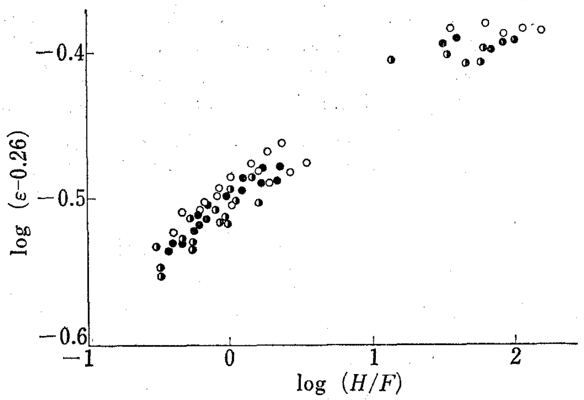

Fig. 8. Relationship between log(H/F) and log(ε −0.26)

○: C-0, ●: C-I, ◑: C-II.