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Granulating Processes. II.[1] Apparent Specific Volume and Breaking Strength of Solid/Liquid Mixed System in Relation to the Filling Properties

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The apparent specific volume (ASV) and the breaking strength (BS) of mixed systems were investigated in relation to the filling properties of the systems. Two inflection points were given on the BS *vs.* water content curves and on the ASV *vs.* water content curves. The air permeability method was adopted to examine the relationship between two inflection points and two critical points C_1 and C_2. The two inflection points were supported to be two critical points, because they were nearly consistent with those on the mean capillary diameter *vs.* water content curves.

The changes of the extrusion weight and of the properties of mixed systems, with the lapse of time in the process of granulations, were discussed in relation to the changes of the particle compactness and of the breaking strength of mixed systems. In the extrusion type granulator, mixtures may first be compressed between basket wall and extruder, and then the powder bed may be deformed to be pushed out through holes in the basket wall by continued extrusive force.

In general, granulating processes are first carried out by mixing powders and binder solutions, and then those mixtures are granulated through various types of granulators, according to the purposes. In those processes, especially through extrusion type granulators, several kinds of troubles are experienced. Awada, *et al.*[3] reported that the extrusion amount through a rotary wet granulator and the pressure against wall varied with the properties of the mixed system and with the lapse of time through the granulating process. Moreover, the properties of granules obtained, such as apparent specific volumes, breaking strengths, *etc.*, are empirically known to differ with a mixed system and with the lapse of time. For the purpose of elucidating such phenomena, it is necessary to find out the properties of solid/liquid mixed system, such as apparent specific volumes and breaking strengths of the binary systems, especially in relation to the filling properties of the system.

On the filling properties of powder/liquid mixed systems, Umeya[4] proposed a classification according to the liquid content in the system, named Pendular (abbreviated as P), Funicular-1 (abbreviated as F-1), Funicular-2 (abbreviated as F-2) and Capillary (abbreviated as Cap.). Those critical points between P and F-1, named C_1, between F-1 and F-2, named C_2, *etc.* were determined by analysing the relationship between the apparent specific volume of wet system and that after dried, against water content.

In the previous report,[1] it was tried to find out the filling properties of aluminium silicate synth./water and calcium carbonate/water mixed system by Umeya's method,[4] and it was suggested that those critical points of a mixed system were determined by analysing the relationship between the breaking strength and the apparent specific volume of the binary system in which the liquid content was varied.

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1) A part of this report was presented at the 85th Annual Meeting of the Pharmaceutical Society of Japan, Fukuoka, 1965 [Part I: J. Mitsui, R. Aoyama and S. Kaga, *Yakuzaigaku*, **25**, 251 (1966)].
2) Location: *No. 6-9, Narihira-5-chome, Sumidaku, Tokyo.*
3) E. Awada, T. Morioka and Y. Ikegami, *Yakugaku Zasshi*, **80**, 721 (1960).
4) K. Umeya, *Kagaku To Kogyo* (Tokyo), **14**, 349 (1961).

In this report, the apparent specific volume and the breaking strength of calcium carbonate/water mixed system were examined in detail, varying the liquid content and moulding pressure. As the results, two inflection points were given both on the breaking strength *vs.* water content curves, and on the apparent specific volume *vs.* water content curves. The air permeability method was adopted to examine the relationship between two inflection points and two critical points. The mean capillary diameter of a mixed system may vary with the liquid content, typically with the filling properties of the system. Two inflection points were found on the mean capillary diameter *vs.* water content curves, being in fairly good accordance with those on the breaking strength *vs.* water content curves. Thus the above mentioned two inflection points were certified to correspond to the two critical points, C_1 and C_2.

In the process of granulation, especially through extrusion type granulator, it is assumed that the mixture is gradually compressed with successive force between basket wall and extruder, resulting in a change of the filling properties. The compressed powder bed is then deformed to be pushed out through holes in the basket wall by continued extrusive force, and in these cases, the breaking strength of the mixture under compression, is a factor affecting the extrusion weight of granules and the pressure against wall. Experiments were carried out to examine the above mentioned hypothesis.

Experimental

Powders Used——Commercially available light calcium carbonate (abbreviated as 1-$CaCO_3$) and 1-$CaCO_3$-fine which was gained by pulverizing 1-$CaCO_3$ in pot mill. Properties of powders used are given in Table I.

Table I. Properties of Powders Used

Powders	Specific gravity[a] (g/ml)	Median diameter[b] (μ)	Apparent specific volume after tapping[c] (ml/g)
1-$CaCO_3$	2.55	4.5	1.64
1-$CaCO_3$-fine	2.55	3.5	1.25

a) Specific gravity was measured using picnometer and ethyl alcohol as the medium on 2 g of powders.
b) Shimazu sedimentographer was adopted using 10 g of powder and 0.3% sodium hexa-metaphosphate as the dispersion medium.
c) 2 g of powders was put into a 20 ml mess-cylinder and tapped for 200 times from the height of 2 cm.

Moulding of Sample Piece——Fourty grams of powders were put into a mortar. A given amount of water was added scatteringly on the powder, and then mixed for one minute by electromotive pestle. Powder bed was then scarified and lumps were crushed softly. Mixture was weighed and put into a mould accompanied by tapping. The mixture was pressed uniaxially at 30, 40 or 50 kg, then pressed sample piece was pushed out, and the height and weight was measured accurately. Those sample pieces whose height deviated from 15.0 ± 0.2 mm, were not used for measurements. Diameter of the sample piece was 12 mm.

Apparent Specific Volume——Apparent specific volume of a sample piece was calculated from the height and weight of the sample piece and the amount of liquid added, as apparent volume per 1 g of powder.

Determination of Breaking Strength——Leverage was used to break a sample piece. Load was continuously increased along the axial direction by pouring water into a reservoir hung at the end of the lever. Span ratio of leverage was 1:10. Friction at the bearing was equivalent to 0.1 kg load. Mean velocity of loading was 1.2 kg/min. Breaking strength was defined as the load (kg) when a sample piece undergoes an abrupt deformation (destruction). Mean value of three trials (3 to 5 sample pieces being used under each compressional force, at each trial) was taken to the calculations of the data.

Mean Capillary Diameter——Before pushing out the sample piece, the mould was fixed to an air permeation apparatous. Mean capillary diameter (D) in a sample piece was calculated as Nogami, *et al.*[5)]

5) H. Nogami, H. Fukuzawa and Y. Nakai, *Chem. Pharm. Bull.* (Tokyo), **11**, 1389 (1963).

$$D=\frac{2}{7}\sqrt{\frac{\eta LQ}{\Delta pAt\varepsilon}}$$

where η is the viscosity of air (poise). L the height (cm) and A the cross section area (cm^2) of a sample piece. Q is the volume (ml) of air passed through the sample piece during a time t (sec), Δp the pressure difference at both ends of the sample piece, ε the porosity of the sample piece in which the volume of liquid was neglected.

Granulation——0.8 kg of powder was put into a mortar. A given amount of liquid was added scatteringly on the powder and then mixed for two minutes by electromotive pestle. The mixture was then put into a small scale rotary granulator and granulated for each one minute. The granules obtained were dried at 50° for one hour and weighed. The diameter of the basket used was 12.7 cm. The revolution number of extruder was 50 rpm. The diameter of the holes in the basket wall was 0.8 mm.

Result and Discussion

Relationship between Apparent Specific Volume and Breaking Strength

The relationship between the apparent specific volume and the breaking strength of a mixed system, in which the moulding pressure was varied, were nearly rectilineal as given by solid lines in Fig. 1. In spite of large shifts of the apparent specific volume *vs.* breaking strength curves, the slopes of those curves were nearly equal, independently of liquid content, a little larger than that of mono system (dried powder). Broken lines were obtained by linking up the points at the same moulding pressure, and it was found there two inflection points at under each moulding pressure. These results were in accordance with those which was pointed out in the previous paper.

In P region, the breaking strength of solid/liquid mixed system increased as liquid content increased. The breaking strength of powder bed is mainly composed of friction (shear stress required to break the adhesion) at the shearing surface. In P region, the tensile strength caused by the capillary adhesive force may be added to the original adhesive force. According to the calcula-

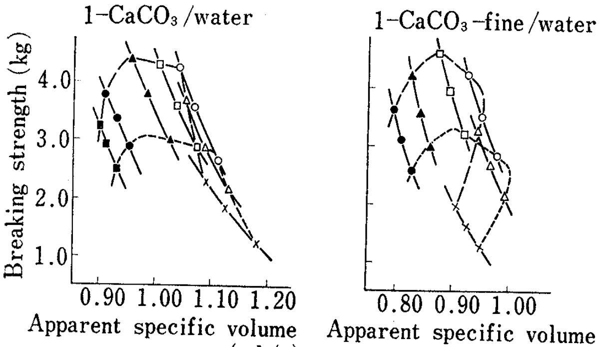

Fig. 1. Effect of Moulding Pressure on the Apparent Specific Volume and the Breaking Strength of Granule Mould

amount of water added 0 ml/100 g powder : ×; 10 ml: △; 20 ml: ○; 30 ml: □; 40 ml: ▲; 45 ml: ●; and 47 ml: ■ for 1-$CaCO_3$, 35 ml: ▲; and 37 ml: ● for 1-$CaCO_3$-fine, moulding pressure 30 kg: ----; and 50 kg: — —

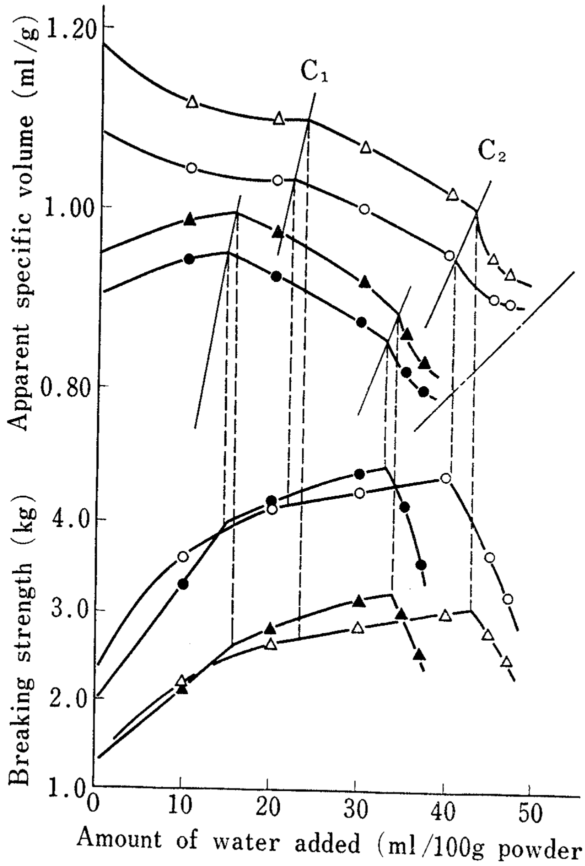

Fig. 2. Apparent Specific Volume/Water Content Curves and Breaking Strength/Water Content Curves in Relation to the Filling Properties

△ : 1-$CaCO_3$, 30 kg ○ : 1-$CaCO_3$, 50 kg
▲ : 1-$CaCO_3$-fine, 30 kg ● : 1-$CaCO_3$-fine, 50 kg

tions[6] of capillary adhesive forces between nonspherical solid particles with liquid pendular ring, the force increases as the amount of liquid increases. Those results given in Fig. 1 were qualitatively in good agreements with the results of calculations. In F-1 region, however, particle compactness changes were the main effect, and in F-2 region, the breaking strength decreased and the effect of moulding pressures on the apparent specific volume and the breaking strength diminished. These might be the lubricating effects of interparticle liquid, diminishing the interparticle friction.

Filling Properties of Calcium Carbonate/Water Systems

To analyse the two critical points in detail, Fig. 2 will be helpfull. Concerning 1-$CaCO_3$-fine/water system, the critical points were easily determined both on the apparent specific volume *vs.* amount of liquid curves and on the breaking strength *vs.* amount of liquid curves. As for 1-$CaCO_3$/water system, C_1 points could not be decided so distinctly as C_2 points, especially on the breaking strength *vs.* amount of liquid curves. Umeya[4] described that those critical points from the apparent specific volume *vs.* liquid content curves under several moulding pressures fall on a straight line passing the origin. The same relation was obtained from the results given in Fig. 2.

To confirm the two critical points by another experimental method, the air permeability method was adopted to determine the mean capillary diameter in a binary system. From Umeya's classification,[4] it is expected that, in a mixed system belonging to P region, the

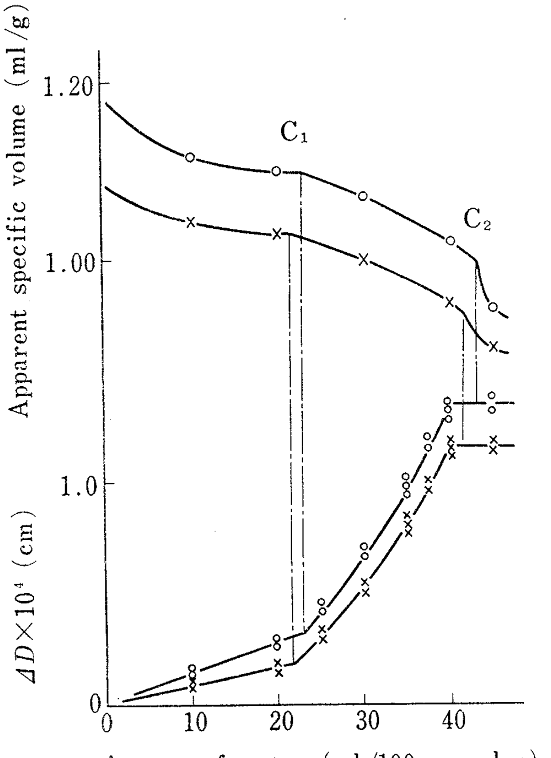

Fig. 3. Relationship between Mean Capillary Diameter and Critical Points of 1-$CaCO_3$/Water System

○ : moulding pressure 30 kg
× : moulding pressure 50 kg

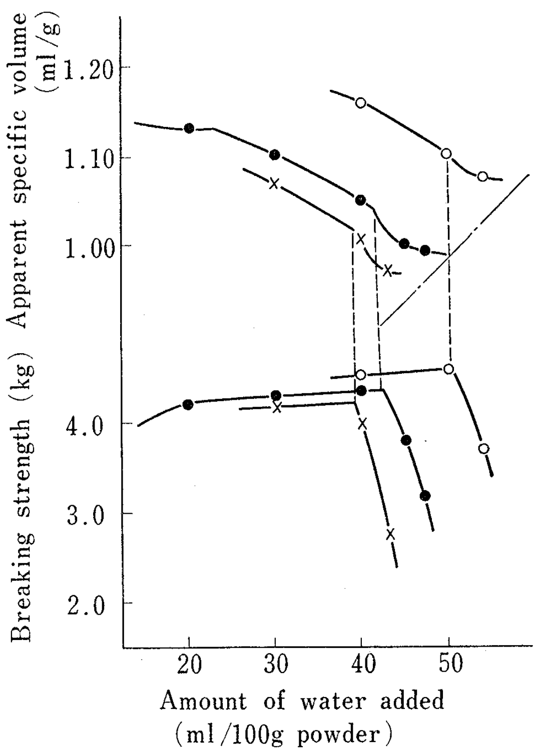

Fig. 4. Effect of Mixing Time on the Apparent Specific Volume and the Breaking Strength of Granule Mould (1-$CaCO_3$)

(moulding pressure: 50 kg)
○ : mixing time 0.5 min
● : mixing time 1.0 min
× : mixing time 1.5 min

6) K. Iinoya and H. Muramoto, *Zairyo*, **16**, 352 (1967); Yu. V. Naidich and I.A. Lavrienko, *Poroshkovaya Metalurgia*, **9**, 32 (1967).

liquid exists as bridge water and mean capillary diameter in the system is not largely affected by the existence of liquid. But in F-1 region, the liquid enters into the interparticle gaps, and as the results, mean capillary diameter in the system decreases as the liquid content increases. Finally in F-2 region, as air is locked into large volume of liquid, mean capillary diameter reduces to zero. The disposition of particles in a sample piece may vary with the liquid content, mixing time and others, even under a same moulding pressure, resulting in the variation of the mean capillary diameter values. Therefore the difference (ΔD) between the mean capillary diameter in a wet sample piece and that after dried was adopted as the parameter.

As given in Fig. 3, two inflection points were given on ΔD *vs.* amount of liquid curves, and so far as C_1 point concerns, the results were consistent with those on the apparent specific volume *vs.* amount of liquid curves. But as for C_2 point, the results deviated from those on the apparent specific volume *vs.* amount of liquid curves. The reason to give such shifts of C_2 point to low liquid content region, from the results of ΔD curves, is explained as follows; the dispositions of particles by uniaxial compression were extraordinarily compact at the upper surface of a sample piece resulting changes from F-1 region to F-2 region in those teritories.

Changes in the Filling Properties with the Lapse of Time through a Granulating Process

In a practical granulating process, especially through extrusion type granulator, the properties of powder/liquid mixed system are empirically known to change with the lapse of time. Such a phenomenon may be explained by considering that the apparent specific volume and the breaking strength of mixtures in a granulator vary gradually with the pressure between basket wall and extruder, applied continuously in the granulator. Experiments were carried out varying the amount of liquid added and the mixing time. In the process of mixing, powder bed is compressed by the pestle and the filling properties of the mixture may vary as those in a granulator.

As it is given in Fig. 4, the apparent specific volume of a binary system varied largely with mixing time and C_2 point deviated to low water content region. From these facts, the relationship between the apparent specific volume and the breaking strength of a mixed

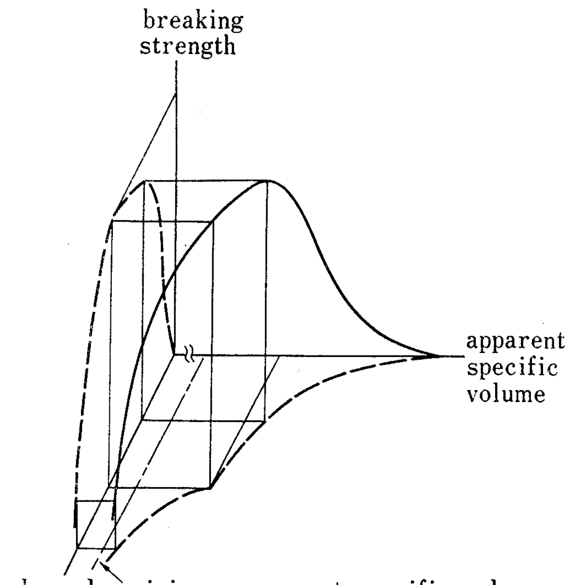

Fig. 5. Illustration of the Effect of Elapsed Time on Apparent Specific Volume and Breaking Strength of a Binary System

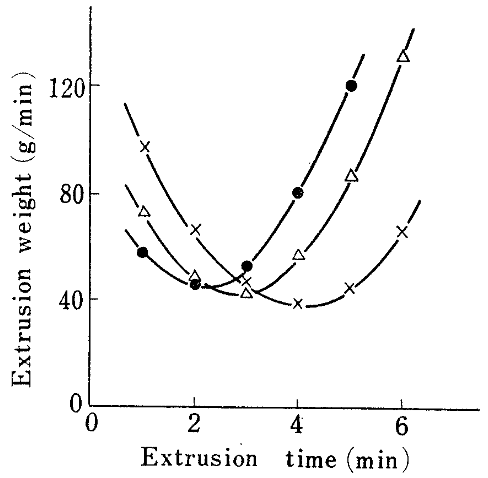

Fig. 6. Relationship between Extrusion Weight in each One Minute and Extrusion Time (1-$CaCO_3$)

× : amount of water: 40 ml/100 g
△ : amount of water: 42 ml/100 g
● : amount of water: 43 ml/100 g

system with the lapse of time, in the case of fixed weight powder and fixed volume liquid, is given in Fig. 5 as a typical illustration.

In the early stage, the apparent specific volume of a binary system decreases largely with the lapse of time, accompanied by increasing of the breaking strength. In the next stage, the apparent specific volume and the breaking strength varies gradually approaching to C_2 point. Then in F-2 region, the breaking strength decreases markedly accompanied by decreasing of the apparent specific volume.

General Discussion

Awada, *et al.*[3] carried out rheological studies on the granulating process by rotary granulator, and found that the extrusion weight of granules and the pressure against basket wall varied irregulary with the lapse of time through a granulating process. In the extrusion type granulator, it is assumed that mixtures are first compressed between basket wall and extruder, and then the compressed powder bed is deformed to be pushed out through the holes in the basket wall by continued extrusive force. In these case, the breaking strength of the mixture may be the factor affecting the extrusion weight of granules and the pressure against basket wall. Thus the extrusion weight are expected to be inversely proportional to the breaking strength of the binary system.

Granulations were carried out using a small scale rotary wet granulator. As given in Fig. 6, the extrusion weight decreased gradually reaching to a minimum point and then changed to increase. Granules obtained in the early steps gave a powder rich properties after drying but granules obtained after the minimum point made good granules. These results are consistent with the above mentioned hypothesis. Thus, the breaking strength and the apparent specific volume of powder/liquid mixed system, in relation to the filling properties, gives informations not only for the properties of granules but also for the extrusion weight of granules.

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