[Chem. Pharm. Bull. 18(8)1541—1547(1970)]

UDC 615.453.3.014.474

Granulating Processes. III.[1] The Effect of Properties of Binder Solutions on the Apparent Specific Volume and the Breaking Strength of Solid/Liquid Mixed System

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(Received January 8, 1970)

The effect of properties of binder solutions on the apparent specific volume and the breaking strength of solid/binder solution mixed systems was investigated in relation to the filling properties of the mixed system.

By the effect of additives, the apparent specific volume *vs.* amount of binder solution curves did not give a characteristic change as compared with the curve of powder/water mixed system. The work of adhesion between powder and binder solution decreased, the minimum apparent specific volume in Funicular-2 region decreased. The breaking strength of mixed systems may be composed of interparticle friction and interparticle adhesion force (tensile strength) by liquid pendular ring. The tensile strength (S) calculated from the equation $S=(1-\varepsilon)\ \sigma\ \mathrm{AB}/d_p g$ was compared with the strength found. It was supposed that the breaking strengths of mixed systems are multiplicable of interparticle friction and tensile strength. The higher the viscosity of binder solution, the larger the tensile strength. The effect of viscosity was minimized efficiently by the addition of detergent. In spite of the effect of properties of binder solutions, the critical points C_1 and C_2 were determined on the mean capillary diameter *vs.* amount of binder solution curves.

It was also found that the extrusion weight of granules through extrusion type granulator was inversely proportional to the breaking strength of the mixed system.

In the previous report,[1] the apparent specific volumes and the breaking strengths of l-$CaCO_3$/water and l-$CaCO_3$-fine/water mixed systems were investigated in relation to the filling properties. As the results, the two critical points, C_1 and C_2, were determined to be two inflection points, given on the apparent specific volume *vs.* water content curves and on the breaking strength *vs.* water content curves. Those changes of the extrusion weight and the pressure against basket wall with the lapse of time, especially through extrusion type granulators, were explained as the changes of the breaking strength of the mixed system in relation to the filling properties.

In the practical granulating processes, several kinds of binder solutions are used according to the purposes. As Awada, *et al.*[3] reported, the apparent density of granules mould increased as the amount of liquid added increased, and decreased as the surface tension of the liquid decreased. They[4] also pointed out that the amount of granules, extruded through extrusion type granulators, varied with the kinds of binder solutions and with the lapse of time.

As pointed out in the previous paper,[1] the breaking strength of a mixed system may be an important factor affecting the extrusion weight of granules. Knacke, *et al.*[5] carried out experiments to find out the factors affecting the breaking strength of granules mould, in com-

1) A part of this report was presented at the 85th Anual Meeting of the Pharmaceutical Society of Japan, Fukuoka, 1965; Part II: J. Mitsui, *Chem. Pharm. Bull.* (Tokyo), **18**, 1535 (1970).
2) Location: *No. 6–9, Narihira-5-chome, Sumida-ku, Tokyo.*
3) E. Awada, Y. Ikegami and A. Nakamura, *Yakugaku Zasshi*, **80**, 1567 (1960); E. Awada and Y. Ikegami, *Yakugaku Zasshi*, **82**, 555 (1962).
4) E. Awada, T. Morioka and Y. Ikegami, *Yakugaku Zasshi*, **80**, 721 (1960).
5) O. Knacke and H. Pohl, *Chemie Ing. Techn.*, **31**, 50 (1959).

parison with the Rumpf's theoretical tensile strength (S) of agglomerate,[6] as given by equation (1)

$$S=\frac{1.1k}{\pi}\ \frac{(1-\varepsilon)\sigma}{d_p} \tag{1}$$

where k is the contact number and d_p the diameter of particle, σ is the surface tension of inter particle liquid and ε the porosity of powder bed. From equation (1), the tensile strength of agglomerate must be proportional to the surface tension of the liquid and the compactness of particles, and be inversely proportional to the particle diameter. Knacke, *et al.*[5] reported that the breaking strengths of alumina/liquid mixed systems were qualitatively in good agreement with the tensile strength calculated from equation (1).

In this report, the effect of the properties of binder solutions on the apparent specific volume and the breaking strength of mixed systems was investigated in relation to the filling properties. The relationships between the breaking strength of mixed systems and the extrusion weight of granules were also examined.

Experimental

Apparatous and Procedure——Apparatous and procedures were employed as described in the previous paper.[1]

Binder Solutions——The properties of binder solutions used, are given in Table I.

Table I. Properties of Binder Solutions

Binder solution	Surface[a] tension σ (dyne/cm)	Viscosity[b] η (cps)	$\cos\theta$[c] with 1-$CaCO_3$	S.V. of[d] 1-$CaCO_3$ (ml/g)
Water	73.2	1.00	0.475	3.4
20% EtOH	44.0	1.84	0.690	3.2
50% EtOH	33.0	2.85	0.728	3.4
0.3% HMP	68.8	1.04	0.551	2.0
0.5% DBS	34.1	1.05	1.000	1.9
0.5%T-80	43.4	1.03	0.777	2.9
50% S	64.0	6.35		
80% S	73.3	69.0		
80% S+0.5% T-80	48.8	66.8		

EtOH: ethyl aclohol
HMP: sodium hexameta phosphate
DBS: sodium dodecylbenzene sulfonate
T-80: Tween 80
S: sucrose

a) Surface tension was determined by De-Nöuy type tensiometer at 22± 0.5°.
b) Viscosity was measured by Ostwald type capillary viscometer at 22± 0.2°.
c) $\cos\theta$ was determined by Kuno's penetrating method and calculated from the following equation and assumed that the contact angle of 1-$CaCO_3$ with 0.5% DBS was zero.

$$L^2=\frac{r\sigma\cos\theta}{2\eta}\ t$$

where L is the distance of pnetrating in a time t, σ the surface tension and η the viscosity of the liquid.
d) Sedimentation volume was measured in 25 ml stoppered graduated glass cylinder with 2.0 g of powder and 20 ml of binder solution. Shake vigorously for 2 min and allowed to stand at 22± 0.5°. The volume of sediments was measured after 2 days.

Powders Used——The powders used were commercially available light calcium carbonate (abbreviated as l-$CaCl_3$) and precipitated calcium carbonate (abbreviated as p-$CaCO_3$), and the properties of powders are given in Table II. The measurements were carried out as described in the previous paper.[1]

6) H. Rumpf, *Chemie Ing. Techn.*, 30, 144 (1958).

Table II. Properties of Powders used

Powders	Specific gravity (g/ml)	Median diameter (μ)	Apparent specific volume after tapping (ml/g)
1-$CaCO_3$	2.55	4.5	1.64
P-$CaCO_3$	2.75	6.5	0.72

Result and Discussion

The Effect of Properties of Binder Solutions on the Filling Properties of Mixed Systems

As pointed out by several workers,[5,6] the breaking strengths and the apparent specific volumes of powder/liquid mixed systems are affected by the properties of liquid used. From these results, the filling properties of mixed systems are supposed to be varied with the kinds of liquid added. Fig. 1 shows the breaking strength *vs.* apparent specific volume curves of 1-$CaCO_3$/binder solution mixed systems, in which the amount of binder solution was varied. Though the breaking strength *vs.* apparent specific volume curves of mixed systems varied with the kinds of binder solutions, they had fundamentally the same tendency to have two critical points.

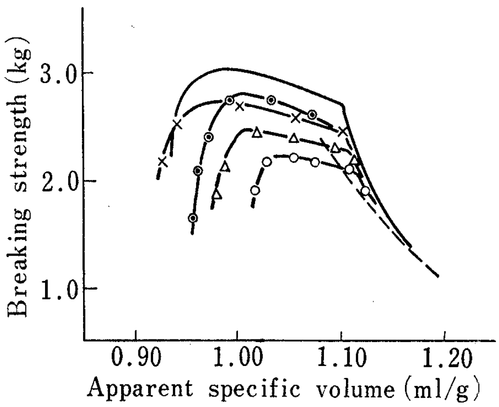

Fig. 1. Breaking Strength *vs.* Apparent Specific Volume Curves with Different Binder Solutions (1-$CaCO_3$)

moulding pressure : 30 kg mixing time : 1 min
— : H_2O
△ : 20% EtOH
○ : 50% EtOH
⊙ : 0.5% T-80
× : 0.3% HMP

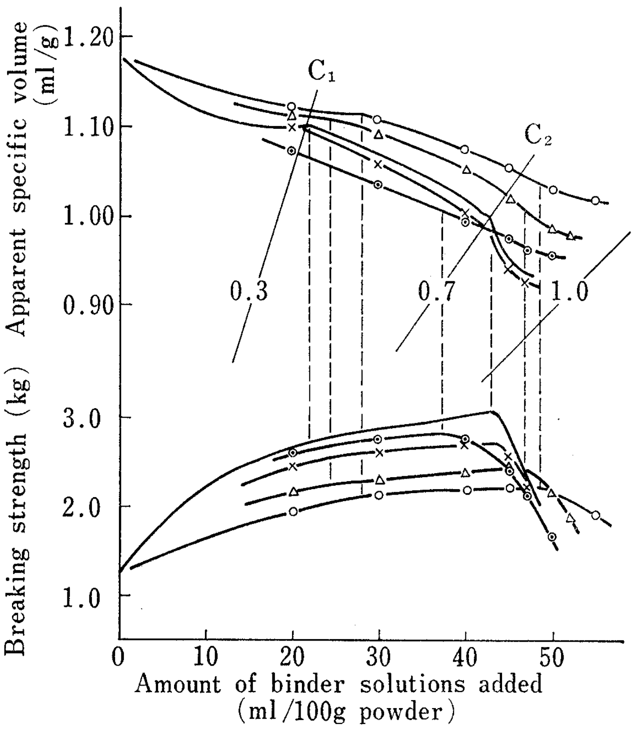

Fig. 2. Effect of Binder Solutions on the Filling Properties of 1-$CaCO_3$/Binder Solution Mixed Systems

moulding pressure : 30 kg mixing time : 1 min
— : H_2O
△ : 20% EtOH
○ : 50% EtOH
⊙ : 0.5% T-80
× : 0.3% HMP

The apparent specific volume *vs.* amount of binder solution curves and the breaking strength *vs.* amount of binder solution curves are presented in Fig. 2, to analyse the two critical points. By the effect of additives, the apparent specific volume *vs.* amount of binder solution curves did not give a characteristic change as compared with the curve of powder/

water mixed system. Especially in the detergent solution system, it was difficult to determine the two critical points on the apparent specific volume *vs.* amount of binder solution curves.

The amount of liquid required to give C_1 point is calculated as 25 per cent of the internal void space for the theoretical fillings of uniform sphere.[7] From the results given in Fig. 2, the amount of liquid required to give C_1 point and C_2 point were nearly 30 per cent and 70 per cent, respectively. In the detergent solution system, the amount of binder solution to give C_2 point which is determined on the breaking strength *vs.* amount of binder solution curves, deviated in low liquid content region as compared with the other systems. To explain the extraordinariness given in the breaking strength *vs.* amount of binder solution curve of the detergent solution system, mean capillary diameters of the mixed system were measured in order to determine the critical points.

As presented in Fig. 3, the amount of binder solution required to give C_2 point in the detergent solution system was nearly the same as in the water system. From these results, the breaking strengths of powder/detergent solution mixed systems in Funicular regions are supposed to be decreased effectively by the lubricating effect of the detergent, diminishing the interparticle friction.

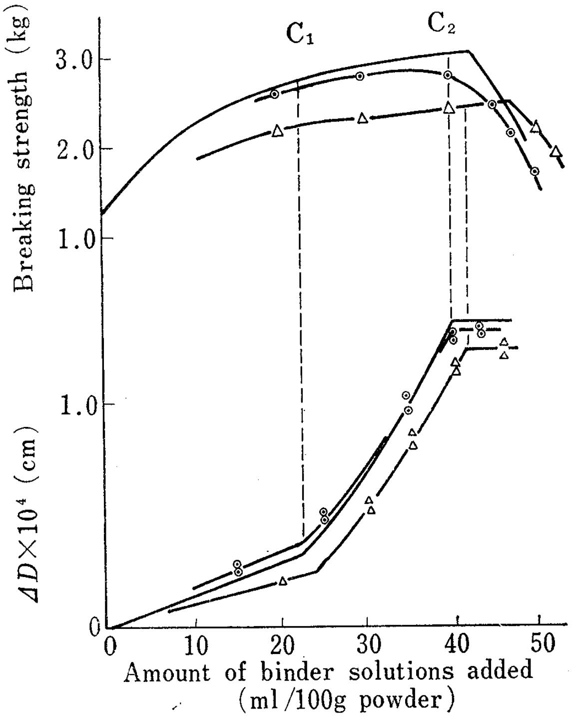

Fig. 3. Relationship between Mean Capillary Diameter and Critical Points of 1-$CaCO_3$/Binder Solution Mixed Systems

moulding pressure: 30 kg
— : H_2O
△ : 20% EtOH ⊙ : 0.5% T-80

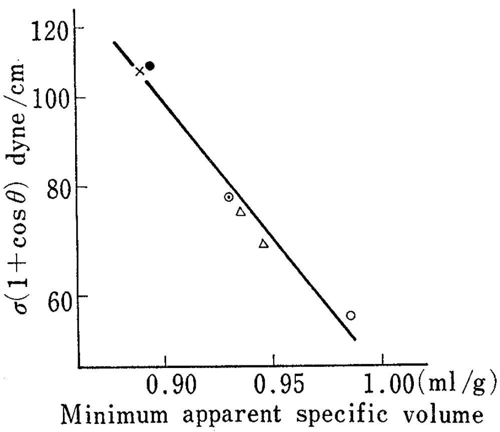

Fig. 4. Effect of Properties of Binder Solutions on the Minimum Apparent Specific Volume (1-$CaCO_3$)

● : H_2O × : 0.3% HMP
△ : 20% EtOH ○ : 50% EtOH
⊙ : 0.5% T-80 △ : 0.5% DBS

The Effect of Properties of Binder Solutions on the Apparent Specific Volume of Mixed System

As pointed out previously, the apparent specific volume of mixed systems have changed with the amount of liquid, with the mixing time and others. So complicated as to the changes of the apparent specific volume of mixed systems that it is difficult to find out the effect of the properties of binder solutions on the apparent specific volume. As given in Fig. 1 and Fig. 2,

7) K. Shinohara and T. Tanaka, *Kagaku Kogaku*, **32**, 88 (1968).

the apparent specific volume of mixed systems in F-2 region tend to have a minimum value respectively. These minimum values are practically very important to be informed of the maximum amount of binder solutions to be added. The relationships between the minimum apparent specific volume and several properties of binder solutions were investigated under a moulding pressure of 50 kg. As presented in Fig. 4, there was found a rectilinear relationship between the minimum apparent specific volume and the work of adhesion [$Wa=\sigma(1+\cos\theta)$] between l-$CaCO_3$ and binder solutions, in log scale. From these results, the work of adhesion may be the factor for determining the minimum apparent specific volume of powder/binder solution mixed system.

The Effect of Properties of Binder Solutions on the Breaking Strength of Mixed System

Theoretical interparticle adhesion force by liquid pendular ring and theoretical tensile strength of powder bed by the interparticle liquid has been calculated by several workers.[6,7] From Rumpf's equation[6] and Shinohara's equation,[7] the tensile strength (S) of powder/liquid mixed system is calculated by the following equation (2),

$$S=\frac{(1-\varepsilon)\sigma}{d_P g}AB \qquad (2)$$

where ε is the porosity of powder bed, σ the surface tension of interparticle liquid, d_P the particle diameter and g the gravity constant. A is a factor relating to the contact number of particle in the shearing surface and B a factor relating to the amount of interparticle liquid. In the practical mixed systems, A and B in equation (2) cannot be calculated as in the theoretical fillings. In this study, the value of A and B are assumed to be 2.0 and 1.0, at the same particle compactness and at the same liquid composition.

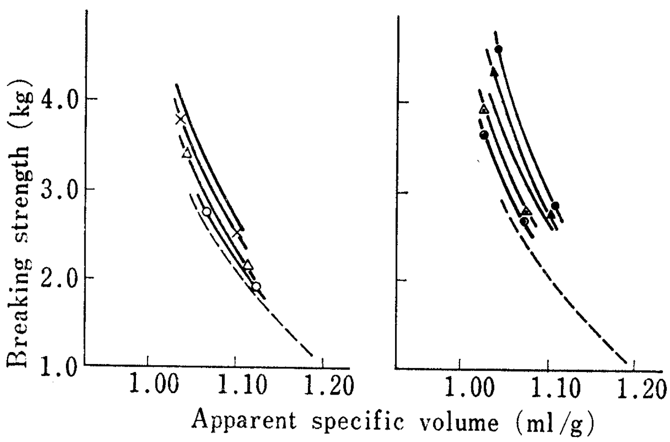

Fig. 5. Effect of Binder Solutions on the Breaking Strength at C_1 Point

moulding pressure: 30, 50 kg
— : no binder
▲ : 50% sucrose
△ : 20% EtOH
○ : 50% EtOH
◬ : 80% S+0.5% T-80

× : 0.3% HMP
— : water
● : 80% S
⊙ : 0.5% T-80

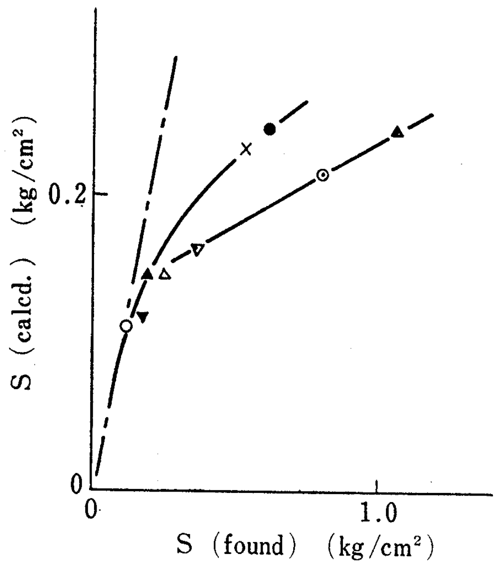

Fig. 6. Relationship between Tensile Strength Calculated and Found

● : water
○ : 50% EtOH
▼ : 0.5% DBS
⊙ : 50% S
▽ : 80% S+0.5% T-80

△ : 20% EtOH
× : 0.3% HMP
▲ : 0.5% T-80
◬ : 80% S

The relationships between the breaking strength and the apparent specific volume of mixed systems are given in Fig. 5, in different moulding pressure at C_1 point. The shearing area in which the interparticle adhesion is broken, may usually be irregular and the area cannot practically be determined. Thus, the tensile strength (found) was defined as the difference between the breaking strength of a mixed system at C_1 point, and that of dried (no binder) system at constant apparent specific volume of 1.09 ml/g, calculating the shearing area to be equal to the base area of the granule mould.

The relationships between tensile strengths found and calculated are presented in Table III and in Fig. 6. As given in Fig. 6 the tensile strengths found were not proportional to the tensile strength calculated. From these results, the breaking strengths of powder/binder solution mixed systems may not be additional of interparticle friction and tensile strength, but multiplicable. The breaking strengths of mixed systems were increased as the viscosity of the binder solution increased, but decreased as the surface tension of the binder solution decreased.

Table III. Tensile Strength Calculated and Found

Binder solution	σ (dyne/cm)	S(calcd.) (kg/cm^2)	S(found)(kg)	S(found)(kg/cm^2)
Water	73.2	0.246	0.69	0.61
20% EtOH	44.0	0.148	0.28	0.25
50% EtOH	33.0	0.110	0.14	0.12
0.3% HMP	68.8	0.232	0.60	0.53
0.5% T-80	43.4	0.146	0.22	0.19
0.5% DBS	34.1	0.114	0.20	0.18
50% S	64.0	0.214	0.90	0.80
80% S	73.3	0.246	1.20	1.06
80% S+0.5% T-80	48.8	0.164	0.42	0.37

General Discussion

In the previous report, it was suggested that the breaking strength of a mixed system is a factor affecting the extrusion weight of granule. As shown in Fig. 7, the extrusion weight *vs.* extrusion time curves had same tendency to have a minimum value. The minimum points are supposed to corespond to the C_2 point. The plots of minimum extrusion weight against maximum breaking strength give a straight line as presented in Fig. 8.

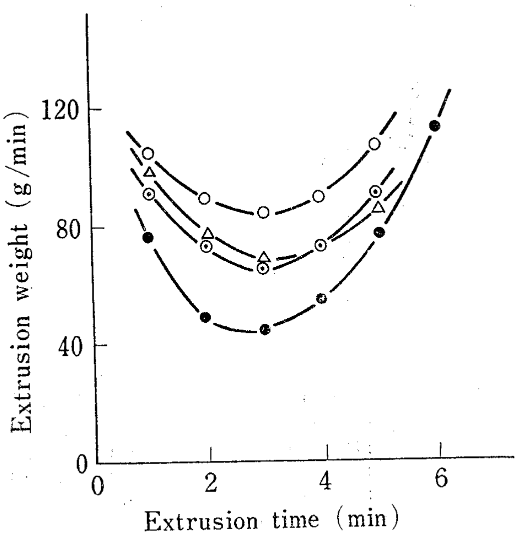

Fig. 7. Effect of Binder Solutions on the Extrusion Weight in each One Minute

●: water, 42 ml/100 g powder
△: 20% EtOH, 45 ml/100 g powder
⊙: 0.5% T-80, 42 ml/100 g powder
○: 50% EtOH, 47 ml/100 g powder

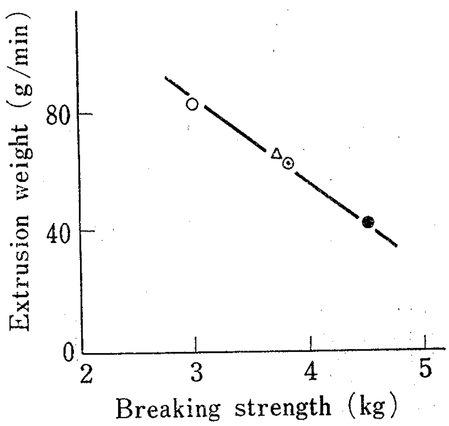

Fig. 8. Relationship between Minimum Extrusion Weight and Maximum Breaking Strength

Table IV. Relationship between Breaking Strengths and Extrusion Weights

Binder solution	Amount of liquid added (ml/100 g powedr)	Breaking strength A (kg)	Extrusion weight B (kg/min)	A·B
Water	17.5	2.30	0.26	0.60
	20.0	2.10	0.29	0.61
50% EtOH	15.0	2.00	0.30	0.60
	20.0	1.75	0.35	0.63
	22.5	1.60	0.39	0.62

In the l-$CaCO_3$/binder soluton miixed systems, the apparent specific volumes and the breaking strengths of the mixed systems varied with the lapse of time through the granulating processes. In the p-$CaCO_3$/binder solution mixed systems, however, the filling properties of of the mixed systems did give little change with the lapse of time, because the particle compactness of p-$CaCO_3$ is near the compact packings. In these systems, the relationship between the extrusion weight and the breaking strength in Funicular-2 region may easily be examined.

As presented in Table IV, the extrusion weights and the breaking strengths of p-$CaCO_3$/binder solution mixed systems were inversely proportional. From these results, the breaking strength of a mixed systems was certified to give an important information of the extrusion weight of granules through extrusion type granulators.

In the pratical granulating processes, however, the mixtures are fed successively into the basket and the changes of the properties of mixed systems around the extruder are not so speedy as given in Fig. 7. Moreover, the changes of the filling properties of mixed systems with the lapse of time are largely affected by the type and scale of granulators, the distance between extruder and basket wall and others.

For the practice of granulation, the mixture shall be changed into Funicular-2 region as soon as possible and not exceed the C_3 point, varying into Capillary or Slurry region, untill the end of granulation. From these points of view, the breaking strength of mixed systems in Funicular-1 region and the changes of the apparent specific volume in Funicular-2 region shall preferably be decreased by the addition of detergent or others.

Acknowledgement The authors wish to express their deep gratitude to Dr. Tsuneji Nagai of Faculty of Pharmaceutical Sciences, University of Tokyo for his encouragement. Thanks are also due to Dr. Masao Shimizu, Director of the Laboratories, and to Dr. Takeo Naito, Director of this Laboratory for their encouragement and for the permission to publish this work.