The relationship between solid fraction and mechanical properties of compacts – the percolation theory model approach

L.E. Holman and H. Leuenberger

School of Pharmacy, University of Basel, Basel (Switzerland)

Summary

A model based on percolation theory has been set up to elucidate the relationship between relaxed complex Young's modulus, hardness and normalized solid fraction of pharmaceutical compacts. The relationship between the variables is non-linear over the whole range of the solid fraction of the compacts. However, in a semi-logarithmic representation linear relationships could be established in certain ranges of the solid fraction of the compacts. The semi-logarithmic plot of Young's modulus or hardness against the solid fraction is comprised of segments of straight lines. The inflexions between the segments indicate a change in the consolidation behaviour as a function of the applied pressure, i.e. as a function of solid fraction of the compact. The number of these segments depends on the mechanical properties of the powder mix. In addition to the solid components, the mechanical properties are affected by the pore system. The straight line relationships allow extrapolations to be made to zero porosity thus furnishing the mechanical property of the solid components. The model has been illustrated with single and binary solid component compact systems. Single and binary solid component powder systems behave similarly.

Introduction

In order to gain an insight into the consolidation behaviour of powdered materials, it is desirable to study the physico-mechanical properties of the pure materials (or simple mixtures). Since it is difficult to use single powder particles for the determination of the physico-mechanical properties, the powder mass has to be compacted to zero porosity and the mechanical properties of the resulting compact determined. Assuming that the materials do not undergo work-hardening (most organic substances do not work-harden, Hiestand, personal communication) the mechanical properties of the compact at zero porosity represent the properties of the component materials.

It is common knowledge that it is impossible to compact a powder mass to zero porosity. A solution to the problem might be to establish a relationship between the mechanical properties and porosity of the compact and to extrapolate to zero porosity.

A difficulty which arises is that in a semi-logarithmic plot the apparent straight line relationship between the elasticity modulus, E, or hardness, H, and the porosity, ϵ, or solid fraction, ρ_r, of compacts does not hold over the whole range of porosity/solid fraction.

Correspondence: H. Leuenberger, School of Pharmacy, University of Basel, Totengässlein 3, 4051 Basel, Switzerland.

Hiestand et al. (1977) reported that "plots of logarithm of hardness against solid fraction are *nearly* linear" (our emphasis). With such plots as the solid fraction approaches unity (zero porosity) the hardness or elastic modulus values tend to deviate from the straight line relationship. It therefore makes it unreasonable to extrapolate to zero porosity.

In this present work it has been established that the relationship between the logarithm of elasticity/hardness and solid fraction, although obviously non-linear over the whole solid fraction range, consists of linear sections. These ranges of solid fraction where linearity exists between the logarithm of elasticity/hardness and solid fraction are definite and peculiar for each powder system. In these solid fraction ranges the following equations hold:

$$\frac{d \log F}{d\rho_r} = \text{constant} \tag{1}$$

that is

$$\frac{dE/E}{d\rho_r} = \text{constant} \tag{2}$$

$$\frac{d \log H}{d\rho_r} = \text{constant} \tag{3}$$

that is

$$\frac{dH/H}{d\rho_r} = \text{constant} \tag{4}$$

These relationships enable extrapolations to be made to a solid fraction of unity.

This behaviour of powdered material during compaction has been explained with the percolation theory. The fundamentals of the percolation theory can be found in Stauffer (1985), Stauffer et al. (1982) and Hoshen et al. (1979).

Percolation theory model for compaction of powders

For every powder system the pore network may be considered as one of the components. Thus a powder mass of a single solid material is a two-component system comprised of the solid powder particles of the material and pores.

The bonding of the particles during compaction can be explained with the bond percolation theory. The pores, however, go through phenomena which are best described with the site percolation theory. Thus a site-bond percolation problem can be envisaged for the compaction of particulate solids.

When particles lie loosely in a powder bed no bonds exist between the particles. P is then zero. P is the conversion factor (Stauffer et al., 1982) or percolation probability (Hoshen et al., 1979). It is defined as the fraction of bonds which have been formed and can thus have values between one and zero. P increases when bonds are formed between the particles (cluster formation) as a result of application of pressure. At a certain critical P the connecting bonds between the particles are such that a percolating cluster (infinite cluster) (i.e. a continuous network of bonds throughout the system in the *x-y-z* directions) of the particles result. This point is the percolation threshold of the solid particles, P_{c_s}, and is the point where a compact is just formed.

In our proposed model the elasticity modulus and hardness of the compact at P_{c_s} is per definition zero. Above P_{c_s} increasing P as a result of increasing compressional pressure results in corresponding increases in the elasticity modulus, E, and hardness, H. We assume now that the following proportionalities hold for values of $P > P_{c_s}$:

$$\log E = k_1 P \tag{5}$$

$$\log H = k_2 P \tag{6}$$

where k = proportionality constant.

For P values close to P_{c_s} and E and H values close to zero these relationships are difficult to apply. Alternative relationships proposed by the theory of critical phenomena (Stauffer et al., 1982; Gauthier-Manuel et al., 1987) are:

$$E \propto \left(\frac{P - P_c}{P_c}\right)^{\mu_1} \tag{7}$$

$$H \propto \left(\frac{P - P_c}{P_c}\right)^{\mu_2} \tag{8}$$

where μ = critical exponent.

The evaluation of these models will be a topic of a subsequent paper.

Were the properties of the compact dominated only by the solid particles, then $\log E$ or $\log H$ would increase proportionally with increasing P until P reaches a value of unity. The truth is that the pores, the other component of the compact, affect the properties as well.

Now let us take a look at the second component, the pores. When the particles lie loosely in a powder bed, the pores are interconnected throughout the breadth, height and length of the system (infinite cluster). The pores continue to percolate the system after the compact is formed. At a certain P, far above the percolation threshold of the solid component, P_{c_s}, the pore clusters become finite, i.e. discontinuous and isolated. This is the percolation threshold of the pores P_{c_a}. According to the percolation theory, something peculiar should presumably happen at P_{c_a}. This

transition from infinite to finite clusters of pores manifests itself by effecting a change in the degree of change of $\log E$ or $\log H$ for P values above P_{c_a}.

That is:

$$\log E = k_3 P \tag{9}$$

$$\log H = k_4 P \tag{10}$$

where $P > P_{c_a}$, and k = proportionality constant.

Thus the change of $\log E$ or $\log H$ with changes in P is different for values of P below and above P_{c_a}.

A semi-logarithmic plot of E or H against P for all values of P should thus show an inflexion at P_{c_a} (see Fig. 1).

The conversion factor, P

P can be considered analogous to solid fraction or relative density, ρ_r, since both parameters are proportional to the amount of three-dimensional bonding. However, ρ_r, unlike P, cannot have a value of zero. To overcome this, the solid fraction has been normalized as follows:

$$P \approx \rho_{r(normalized)} = \frac{\rho_{r(com)} - \rho_{r(tap)}}{1 - \rho_{r(tap)}} \tag{11}$$

where

$\rho_{r(normalized)}$ = normalized relative density or solid fra(

$\rho_{r(com)}$ = relative density or solid fraction of con

$= \dfrac{\text{apparent density of compact}}{\text{true density of powder particle}}$

$\rho_{r(tap)}$ = relative tap density

$= \dfrac{\text{tap density}}{\text{true density of particle}}$

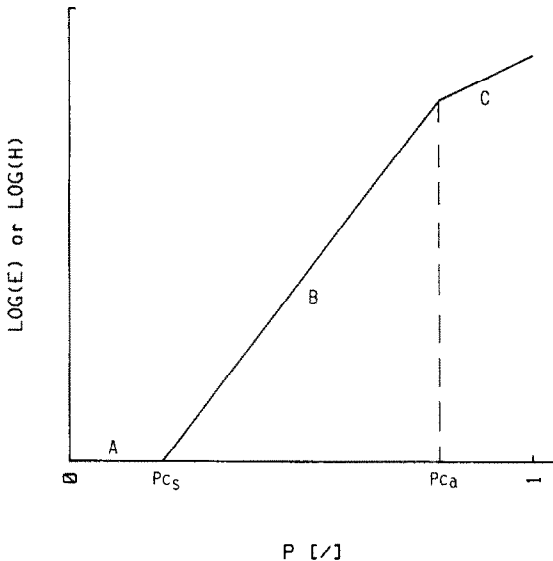In the foregoing discussion the normalized solid fraction has been referred to as P.

Fig. 1. The relationship between the logarithm of elasticity or hardness and P. P_{c_s} = percolation threshold of solid component. P_{c_a} = percolation threshold of pores. In region A there is a percolating cluster of pores and isolated clusters of solid particles. In region B pores and solid component percolate the system. In region C pore clusters are finite and randomly dispersed in an infinite cluster of solid component.

Experimental

Materials

Avicel PH 102 (Microcrystalline cellulose) FMC, Philadelphia, U.S.A.

Emcompress (Di-calcium phosphate dihydrate) Edward Mendell Co., Carmel, New York, U.S.A.

Lactose β-anhydrous De Melkindustrie Veghel, (D.M.V.) B.V., Veghel Holland.

Methods

Materials were conditioned at 45% relative humidity by placing them over saturated potassium carbonate solution for a minimum of 7 days.

The substances were deagglomerated by passing them through a sieve and mixed with 0.5% w/w magnesium stearate for 5 min. For mixtures, the deagglomerated components were mixed for 15 min, re-deagglomerated and mixed for another 15 min. They were further mixed with 0.5% w/w magnesium stearate for 5 min. All the mixing was done in a Turbula (model T2C-WA Bachofen, Basel, Switzerland).

Tap density was determined with a mechanical tapping device (tap volumeter; manufacturer: J. Engelmann AG., Ludwigshafen a. Rh., F.R.G.).

The compression was done on a Korsch EK-0 single punch instrumented tablet machine (manufacturer: Korsch, Berlin, F.R.G.), fitted with strain gauges. When not stated, the compression speed was 25 tablets/min.

Tablet weights were chosen such that the diameter to thickness ratio fell between 0.264 and 0.363. The punches were circular and flat-faced with a diameter of 11 mm. The environmental conditions during compression and identation tests were kept constant at $40 \pm 10\%$ relative humidity and $21 \pm 3°C$. The powder systems were compressed at varying pressures to give varying compact porosities.

The tablets were stored at 45% relative humidity over saturated potassium carbonate solution for a week to allow the tablets to reach a completely relaxed state before being tested.

The hardness and elasticity values were derived from static indentation tests using a machine developed by Galli (1983).

Load was applied onto a spherical indenter with a diameter of 1.50 mm onto the centre of the upper surface of a tablet and left in contact for 30 s. A preload amounting to a tenth of the test load when the test load is below or equal to 24.5 N; or a preload of 2.5 N when the test load was more than 24.5 N; was applied before the tablet was subjected to the test load. For precision purposes the forces were chosen such that the indentation depth after load release was 60 ± 10 μm. The indentation depth after this period, h_1, was noted and the load released by moving the indenter away from the tablet surface at a rate of 7.2 mm/min. The indentation depth immediately after load release, h_2 was also noted. The indentation depth under load was corrected for the elastic deformation of the machine.

$$\Delta h = h_1 - h_2 = \text{Elastic recovery} \qquad (12)$$

The hardness values were calculated from the equation

$$H = \frac{F}{\pi D h_1} \qquad (13)$$

where $F =$ force applied; $D =$ diameter of indenter; $h_1 =$ depth of indentation under load, obtained by substituting for the diameter of indentation in the Brinell (1900) equation.

The elasticity values were calculated from the equation

$$\frac{1}{E_2^*} = \frac{8}{3} \cdot \frac{\Delta h \left(D h_1 - h_1^2 \right)^{1/2}}{F} - \frac{1}{E_1^*} \qquad (14)$$

where

$$\frac{1}{E^*} = \frac{1 - \nu}{E}$$

$E^* =$ complex Young's modulus; $E =$ Young's modulus; $\nu =$ Poisson's ratio. E_1^* and $E_2^* =$ complex Young's Modulus of indenter and test material resp.

Eqn. 14 was obtained from Hertz's (1896) classical equation (Eqn. 16) describing the elastic deforma-

tion of spherical surfaces by substituting for $r_1 r_2 / (r_2 - r_1)$ and d.

$$d = 2\left[\frac{3}{4} \cdot F \frac{r_1 r_2}{r_2 - r_1}\left(\frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}\right)\right] \qquad (16)$$

where d = chordal diameter of indentation; r_1 = radius of curvature of indenter; r_2 = radius of curvature of the recovered indentation. ν_1 and ν_2 = Poisson's ratio for indenter and test material, respectively.

To a first approximation (Tabor, 1951):

$$\Delta h = \frac{d^2}{8}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \frac{d^2}{8}\left(\frac{r_2 - r_1}{r_1 r_2}\right) \qquad (17)$$

Thus $r_1 r_2 / r_2 - r_1$ can be substituted in Eqn. 16 from geometrical considerations:

$$d = 2\left(Dh_1 - h_1^2\right)^{1/2} \qquad (18)$$

The complex Young's Modulus E^*, which incorporates Poisson's ratio, was used because Poisson's ratio of the pharmaceutical materials used were unknown.

A minimum of 8 tablets was tested at any one solid fraction value.

Generally, for viscoelastic materials, Young's modulus is time-dependent. (All pharmaceutical materials are viscoelastic to a greater or lesser extent.) Differentiation is therefore made between instantaneous Young's modulus and relaxed Young's modulus (Johnson, 1976). For such slow methods like the static indentation tests the derived elasticity parameter is the relaxed Young's modulus. What is referred to as the complex Young's modulus in this test is in effect the relaxed complex Young's modulus.

The complex Young's modulus values varied greatly for substances which undergo relatively little elastic recovery on load release. This was partly due to the accuracy of the depth measurement gauge.

The solid fraction or the relative density, ρ_r, was calculated from the true density and apparent density of the compact.

Solid fraction or relative density,

$$\rho_r = \frac{\text{apparent density}}{\text{true density}} \qquad (19)$$

$$= 1 - \text{porosity} \qquad (20)$$

The apparent density was determined from the dimensions and weight of the tablet and the true density determined with a Beckman's gas pycnometer (model 930; Beckman Instruments, Fullerton, CA, U.S.A.).

Results and Discussions

The results presented in this paper were chosen to illustrate typical relationships between E^* or H and the solid fraction of compacts for single and binary component compacts.

Single-solid component compact systems

Plastic materials

This is illustrated with Avicel. Figs. 2 and 3 show plots of log E^* and log H as a function of the normalized solid function, P. Both plots exhibit the same profile confirming the correlation between elasticity and hardness.

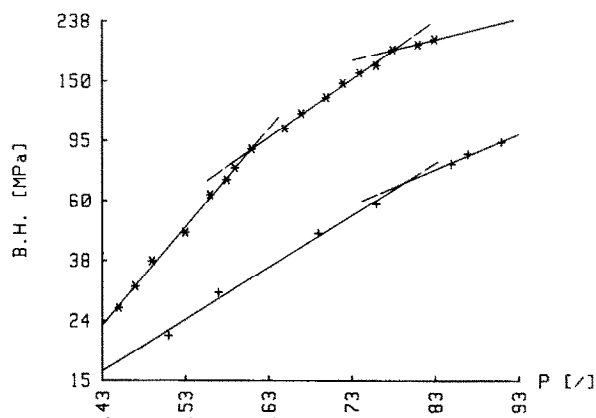The inflexion points signify the percolation thresholds of the pores. Below the points of inflex-

Fig. 2. Semi-logarithmic plot of Brinell hardness and normalized solid fraction for compacts of single substances. * = anhydrous lactose; +, = Avicel.
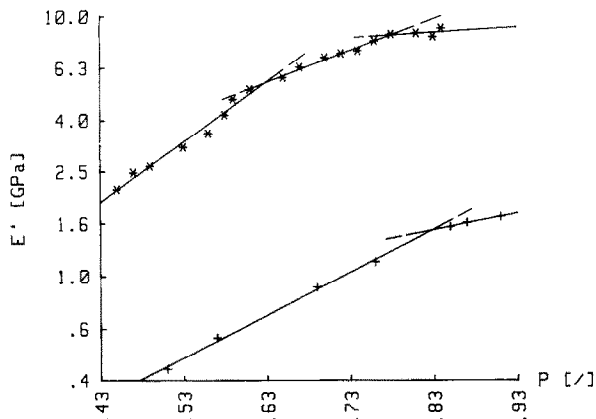
Fig. 3. Semi-logarithmic plot of relaxed complex Young's modulus vs normalized solid fraction for single solid component compacts. * = anhydrous lactose; + = Avicel.
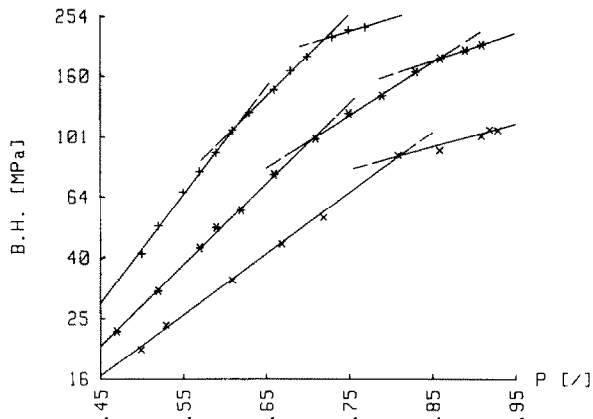

Fig. 4. Semi-logarithmic plot of Brinell hardness against normalized solid fraction for binary composite compacts. x = Avicel/anhydrous lactose 8:2 w/w; * = anhydrous lactose/Avicel 8:2 w/w; + = Emcompress/anhydrous lactose 6:4 w/w.

ion continuous structures/infinite clusters of Avicel and pores co-exist. Above these points the pores are closed and dispersed in the infinite clusters of Avicel.

Brittle substances

Anhydrous lactose has been used to elucidate the behaviour of this class of materials. The compacts were compressed at a speed of 20 tablets/min. Figs. 2 and 3 exhibit the corresponding plots for indentation hardness and elasticity.

The plots for anhydrous lactose manifest two inflexion points signifying two transition points. The inflexion point at the lower P-value indicates a change in the consolidation behaviour from a state where the particles are undergoing predominantly fragmentation to a condition where plastic deformation dominates. This point therefore denotes a crossover from a brittle to a plastic behaviour. Kendall (1978) has pointed out that below a certain critical particle size brittle materials respond in a ductile manner to stress application. The second inflexion represents the percolation threshold of pores signifying, as already mentioned, the transition from a continuous network of pores to isolated, discrete, randomly distributed pores.

The elasticity values showed high coefficients of variation. Nevertheless, the graphical representation of log E^* as a function of the normalized

solid function exhibited a similar shape as that for the indentation hardness plot.

Binary solid component compacts

The binary mixtures behaved essentially the same as the single substances. Binary mixes which are brittle; for example, anhydrous lactose/Avicel 8:2 w/w and Emcompress/anhydrous lactose 6:4 w/w (Figs. 4 and 5) depict the same profile as a single brittle substance. Compare these plots with that of anhydrous lactose (Figs. 2 and 3). Corroboratively, a binary mix which is plastic in
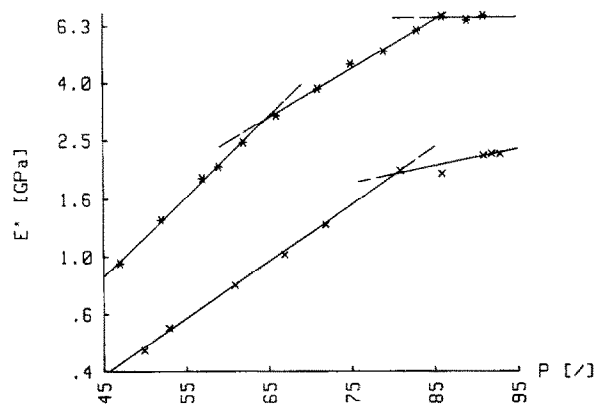

Fig. 5. Semi-logarithmic plot of relaxed complex Young's modulus and normalized solid fraction for binary composite compacts. Symbols are the same as in Fig. 4.

TABLE 1

Percolation thresholds and transitional points obtained from semi-logarithmic plots of relaxed complex Young's modulus, E*, and hardness, H, against normalized solid fraction of single and binary component compacts

| Substances | Percolation thresholds and transition regions | | | | | |
| | P_{c_s} | | P_T | | P_{c_a} | |
	E^*	H	E^*	H	E^*	H
Avicel	–	–	–	–	0.83	0.79
Lactose, anhydrous	–	–	0.63	0.61	0.78	0.78
Emcompress	–	–	–	0.67	–	–
Avicel/anhydrous lactose 8 : 2 w/w	–	–	–	–	0.80	0.81
Anhydrous lactose/Avicel 8 : 2 w/w	–	–	0.65	0.71	0.86	0.86
Emcompress/anhydrous lactose 6 : 4 w/w	–	–	–	0.62	–	0.72

P_{c_s} = percolation threshold of the solid component.
P_T = P-value at which the consolidation behaviour changes.
P_{c_a} = percolation threshold of pores.

mechanical character; for example, Avicel/anhydrous lactose 8 : 2 w/w (Figs. 4 and 5) shows the same form as a single substance which is plastic in nature, for example, Avicel (Figs. 2 and 3).

The plot of log E^* as a function of normalized solid fraction for Emcompress/anhydrous lactose 6 : 4 w/w was not shown because the values exhibited very high coefficients of variation.

The linearity of the straight line regions were confirmed with an F-test for lack of fit and residual plots (Draper and Smith, 1981; Bolton, 1984).

Percolation thresholds

Percolation theory is supposed to be applied to infinitely large systems. Since compacts are not infinitely large, boundary effects come into play and affect the value of the percolation threshold. The percolation threshold values obtained from compacts are thus effective percolation threshold values. Generally, any effective threshold values determined experimentally need to be extrapolated to infinite system size by using finite-size scaling techniques (Stauffer, 1985).

The estimates of the effective percolation thresholds for the substances used in this work are summarized in Table 1. There do not seem to be significant differences between the percolation thresholds derived from the relaxed complex Young's modulus data and the indentation hardness data.

The percolation thresholds differ for different substances and are dependent on the way the particles are arranged relative to each other. The arrangement of the particles in turn depends on the particle shape and size distribution.

The percolation threshold of the solid particles, P_{c_s}, which is the P value when E^* or H is zero cannot be determined from the semi-logarithmic plots. To obtain P_{c_s}, the data analysis discussed in Stauffer et al. (1982) would have to be used. Such determinations are beyond the scope of this publication. It will be the subject of a subsequent publication.
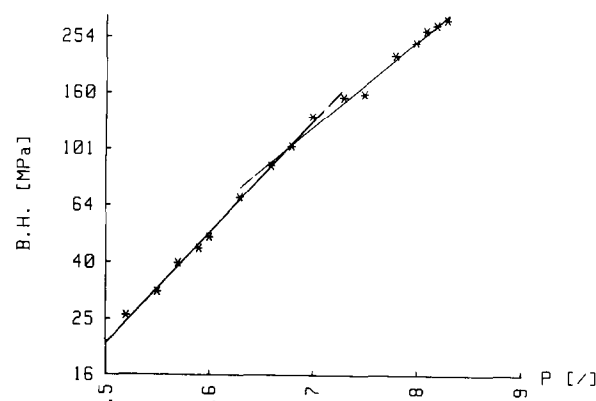

Fig. 6. Plot of log Brinell hardness against normalized solid fraction for Emcompress compacts. Speed of compression = 20 tablets/min.

TABLE 2

Slopes of semi-logarithmic plots ± S.E. of relaxed complex Young's modulus and hardness as a function of normalized solid fraction of the below listed substances and binary mixtures

Substances	Slopes, k					
	k_{s_1} Slope for $P_{c_s} < P < P_T$		k_{s_2} Slope for $P_T < P < P_{c_a}$		k_a Slope for $P > P_{c_a}$	
	E^*	H	E^*	H	E^*	H
Avicel	1.63 ± 0.07	1.73 ± 0.11	–	–	0.62 ± 0.06	1.18 ± 0.16
Lactose, anhydrous	2.32 ± 0.15	3.27 ± 0.09	1.22 ± 0.05	1.95 ± 0.05	0.21 ± 0.33	0.68 ± 0.10
Emcompress	–	3.92 ± 0.09	–	3.03 ± 0.21	–	–
Avicel/anhydrous lactose 8 : 2 w/w	1.97 ± 0.03	2.01 ± 0.04	–	–	0.58 ± 0.18	0.77 ± 0.12
Anhyd. lactose/Avicel 8 : 2 w/w	2.76 ± 0.08	2.67 ± 0.05	1.69 ± 0.06	1.75 ± 0.06	0.02 ± 0.32	0.93 ± 0.01
Emcompress/anhyd. lactose 6 : 4 w/w	–	3.57 ± 0.09	–	2.70 ± 0.05	–	0.83 ± 0.22

The P_{c_a} is easily reached experimentally for plastic substances. However, for substances that are brittle and possess very little plastic properties, and thus have an inclination to cap, the percolation threshold of the pores may not be reached. For example, Emcompress capped under our experimental conditions before reaching P_{c_a} (see Fig. 6). To obtain compacts with high solid fractions, the powder may be hot-pressed (Janowski and Rossi, 1967; Blattner, 1987) or a triaxial decompression die may be used to reduce capping (Hiestand and Smith, 1984).

Slope, k

The slopes of the various linear sections of the plots are summarised in Table 2.

The slope, k is a measure of the relative change of the elasticity module or indentation hardness with change in solid fraction.

$$\frac{d \log E}{dP} = k \qquad (21)$$

$$\frac{d \log H}{dP} = k \qquad (22)$$

Janowski and Rossi (1967) propose that the slope of the relationship between elasticity and porosity or, for that matter, solid fraction, above P_{c_a}, where the pores are isolated and closed, depends on the shape of the pores.

The significance of the different ks, of the linear sections, and of the ks obtained from the elasticity module and hardness data is not clear at

the moment. However, a trend is easily noticeable. k_{s_1} is always larger than k_{s_2} which is in turn always larger than k_a.

The elasticity module and hardness values of the "as compacted" material

The elasticity module or hardness of the "as compacted" material can be obtained by extrapolating the straight-line relationship of the mechanical property and the normalized solid fraction above the percolation threshold of the pores, P_{c_a}, to a normalized solid fraction value of one. In this region the pore clusters would be finite; in other words, they would be isolated in the continuous matrix of the solid phase. Thus the equation for the elasticity module is:

$$\log E^* = \log A + k_a P \qquad (23)$$

where $P > P_{c_a}$; A = constant

Similarly,

$$\log H = \log A_H + k_a(H)P \qquad (24)$$

when $P = 1$

$$\log E^* = \log A + k_a$$

$$= \log E_0^* \qquad (25)$$

and

$$\log H = \log A_H + k_a(H)$$

TABLE 3

Mechanical properties ± S.E. of pharmaceutical substances and mixtures used in the present study

Substances	Relaxed complex Young's modulus E_0^* [GPa]	Hardness H_0 [MPa]
Avicel	1.924 ± 0.033	119.942 ± 5.489
Lactose, anhyd.	8.671 ± 1.036	268.895 ± 11.771
Avicel/anhyd. lactose 8 : 2 w/w	2.521 ± 0.126	122.242 ± 3.981
Anhyd. lactose/Avicel 8 : 2 w/w	6.733 ± 0.001	247.423 ± 0.569
Emcompress/anhyd. lactose 6 : 4 w/w	–	363.057 ± 45.572

$$= \log H_0 \tag{26}$$

where E_0^* and H_0 = elasticity modulus and hardness value at a solid fraction of unity, respectively.

Alternatively, when porosity, ϵ, is used instead of the normalized solid fraction, P

$$\log E^* = \log A + k_a(1 - \epsilon) \tag{27}$$

or

$$\log H = \log A_H + k_a(H)(1 - \epsilon) \tag{28}$$

$$\epsilon < 1 - \rho_{rc_a}$$

where ρ_{rc_a} = the relative density/solid fraction of tablet which corresponds to P_{c_a}.

$$\log E^* = \log A_p + k_a - k_a\epsilon$$

where $\log A_a + k_a = \log E_0^*$

$$\log E^* = \log E_0^* - k_a\epsilon \tag{29}$$

similarly

$$\log H = \log H_0 - k_a(H) \tag{30}$$

Equation 14 is similar to that suggested by Spriggs (1961). The only modification is that the equation is valid when used for porosity values below $\epsilon = 1 - \rho_{rc_a}$.

Using Eqns. 25 and 26 we obtained the relaxed complex Young's modulus and hardness values for the materials tested. They are given in Table 3.

It is interesting to note that several mathematical theoretical equations proposed to predict the effect of porosity on elastic constants presume that the pores are isolated (Mackenzie, 1950; Hashin, 1962).

Conclusion

It is clear from the plots that the relationship between relaxed complex Young's modulus or hardness and normalized solid fraction is non-linear over the whole range of solid fraction of compact. However, in certain definite solid fraction ranges, the relationships can be linearized. The semi-logarithmic plots of elasticity or hardness against normalized solid fraction consists of segments of straight lines. The points at which crossovers occur from one linear region to another signify changes in the consolidation behaviour of the compacts. In addition to the pore structure, the mechanical properties of the powder determine the number of segments that may be obtained.

Binary mixtures of powders behave similarly to single substances when subjected to stress.

It has been shown that to obtained the Young's modulus or the hardness of the "as compacted" material one has to use the semi-logarithmic linear relationship of that segment of the graph above the percolation threshold of the pores to extrapolate to a normalized solid fraction of unity.

The experimental work has confirmed the model set up. It can therefore be said that the percolation theory can be applied to the compression of powder systems.

References

Blattner, D. *Untersuchungen über das Komprimierverhalten binärer, pulverförmiger Haufwerke*, Ph. D. thesis, University of Basel, Basel, Switzerland, 1897.

Bolton, S., *Pharmaceutical Statistics*, Marcel Dekker, New York, 1984.

Brinell, J.A., *Cong. Int. Méthodes d'Essai*, Paris (1900). Through Tabor (1951).

Draper, N. and Smith, H., *Applied Regression Analysis*, Wiley, New York, 1981.

Galli, B., *Entwicklung einer Härteprüfmethode für Tablette*, M. Sc. thesis, University of Basel, Basel, Switzerland, 1983.

Gatto, F., Influence of small cavities on velocity of sound in metals. *Aluminio*, 19 (1950) 19–26. Through Spriggs (1961).

Gauthier-Manuel, B., Guyon, E., Roux, S., Gits, S. and Lefaucheux, F., Critical viscoelastic study of the gelation of silica particles. *J. Physique*, 48 (1987) 869–875.

Hashin, Z., Elastic moduli of heterogenous materials. *J. Appl. Mech.*, 29 (1962) 143–150.

Hertz, H., *Miscellaneous Papers* (1896). Through Tabor (1951).

Hiestand, E.N., personal communication.

Hiestand, E.N. and Smith, D.P., Indices of tabletting performance. *Powder Technol.*, 38 (1984) 145–159.

Hiestand, E.N., Wells, J.E., Poet, C.B. and Ochs, J.F. Physical processes of tabletting. *J. Pharm. Sci.*, 60 (1977) 510–519.

Hoshen, J., Klymke, P. and Kopelman, R., Percolation and cluster distribution. III. Algorithms for the site-bond problem. *J. Statist. Phys.*, 21 (1979) 583–600.

Janowski, K.R. and Rossi, R.C., Elastic behaviour of MgO matrix composites. *J. Am. Ceram. Soc.*, 50 (1967) 583–600.

Johnson, K.L., Adhesion at the contact of solids. Proc. 14th IUTAM Congress, Delft, The Netherlands, Aug.–Sept. 1976. In W.T. Koiter (Ed.) *Theoretical and Applied Mechanics*, Elsevier, Amsterdam, 1976, pp. 133–143.

Kendall, K., The impossibility of comminuting small particles by compression. *Nature (Lond.)*, 272 (1978) 710–711.

Mackenzie, J.K., Elastic constants of a solid containing spherical holes. *Proc. Phys. Soc.*, 63B (1950) 2–11.

Spriggs, R.M., Expression for effect of porosity on elastic modulus of polycrystalline refractory materials, particularly aluminium oxide. *J. Am. Ceram. Soc.*, 44 (1961) 628–629.

Stauffer, D., *Introduction to Percolation Theory*, Taylor and Francis, London, 1985.

Stauffer, D., Coniglio, A. and Adam, M., Gelation and critical phenomenon. *Adv. Polymer Sci.*, 44 (1982) 103–158.

Tabor, D., *The hardness of Metals*, Oxford University Press, London, 1951.