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The effect of water content on the porosity and liquid saturation of extruded cylinders ☆

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Abstract

The preparation of isodiametrical and nearly monodispersed pellets by extrusion-spheronization requires an extruded mass which shows a complex balance between deformability and its ability to break up into smaller units. The possibility of extruding the mass through an orifice is mainly related to its plasticity or deformability. Such mechanical properties of moist compacts are related to both the porosity and the degree of liquid saturation. In this study the effect of water addition has been studied in this context. Mixtures of dicalcium phosphate dihydrate (DCPD) and Avicel PH 101 (70:30%) were massed with water (moisture contents of 50, 60, 70, 80 w/w %). The masses were extruded in a ram extruder (25.0 mm in diameter), initially with a 10.0 mm die and then without the die. The moist extrudates were cut to isodiametrical cylinders and the porosity and the degree of liquid saturation were determined. An increased moisture content decreased the extrusion force and increased the porosity of the extrudates. The degrees of liquid saturation were similar and high for all extruded masses. It is suggested that such a nearly complete filling of the pore space with a liquid component is a prerequisite for the wet mass to yield and thus extrude. The mechanism behind the yielding process is probably an enhanced possibility for particle movement and rearrangement due to a reduced particle-particle attraction when the pore space is filled with a liquid.

Keywords: Extrusion; Ram extruder; Microcrystalline cellulose; Dicalcium phosphate dihydrate; Water content; Porosity; Liquid saturation; Extruded cylinder

1. Introduction

A combination of extrusion and spheronization (Rowe, 1985) of wet powders has been used as one possible procedure for the production of nearly spherical particles to be used in oral multiple unit dose preparations. The success of this production procedure is dependent on the mechanical properties of the wet powder mass. During the extrusion process, the powder must be able to compress and flow through an orifice and additionally to this, the particles must cohere into cylindrical rods. During spheronization, those

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cylinders must break into specimens of suitable dimensions and subsequently deform into rounded agglomerates.

One approach to describe the mechanical properties of powders during extrusion is based on the measurement of the force needed to extrude the wet powder mass in a laboratory ram extruder under different conditions, e.g., for varying dimensions of the die (Harrison et al., 1985a) or at varying extrusion rates (Harrison et al., 1985b). By this procedure, the flow properties of wetted powders can be assessed quantitatively and used to predict the performance of the material during extrusion and spheronization in a production situation.

Extrusion of wetted powders involves two consecutive processes: Firstly, compression of the mass until a point is reached where the material starts to flow through an orifice and, secondly, the actual extrusion of the mass. Both compression and extrusion requires that the particles are able to slide or shear against each other. Hence, the extrusion behaviour of the mass is related to the fundamental interactions between the particles and how these interactions change as a force is applied on the mass.

Studies on the mechanical properties of compacts of wetted powders when stressed in compression (Kristensen et al., 1985a,b) have demonstrated the importance of both the porosity and the degree of liquid saturation of the agglomerate for its strength and deformability. Hence, it seems reasonable to assume that the behaviour of the mass during extrusion, i.e., the degree of compression of a powder mass before extrusion and the force needed to extrude the material, is related to changes in the porosity and degree of liquid saturation of the mass during the extrusion process. Furthermore, the properties of the extrudate formed with respect to the porosity and degree of liquid saturation will probably also be critical for the potential of the extrudate to break and deform during spheronization. Thus, the aim of the present paper was to study mechanistically the extrusion process in terms of the porosity and degree of liquid saturation of the extrudates formed. Such an understanding of the extrusion process constitutes a valuable complement to the analysis of the flow properties of materials described above. As model materials, a series of powder masses consisting of a mixture of microcrystalline cellulose and calcium phosphate mixed with varying amounts of water was used.

2. Materials and methods

Dicalcium phosphate dihydrate, DCPD, (Calipharm, Albright and Wilson, Ph. Eur., UK) and microcrystalline cellulose, MCC, (Avicel PH 101 FMC Corp., USA) in the proportion of 70:30% w/w were used as test materials.

2.1. Primary characteristics of the test materials

2.1.1. Apparent particle density

The density was measured by an air comparison pycnometer (Beckman model 930, USA) using ambient air as a gaseous medium. Presented results are mean values of three determinations.

2.1.2. External specific surface area

The weight specific surface areas were determined by permeametry using a Blaine apparatus as described by Blaine (1943) and Alderborn et al. (1985). Results given are mean values of three determinations. The primary characteristics of the untreated materials are listed in Table 1.

2.2. Dry and wet mixing

The materials were dry mixed for 3 min in a convective mixer (Braun Multipractic Plus, UK 20, Braun AG, Germany), at 700 rpm with a specially constructed mixer blade (Pharmacia AB,

Table 1
Primary characteristics of test materials, mean and standard deviation

Material	Apparent particle density (g/cm^3)	Specific surface area (cm^2/g)
Dicalcium phosphate	2.31 (0.06) [a]	4644 (580)
Avicel PH 101	1.51 (0.07)	3563 (209)

[a] Standard deviations are given in parentheses.

Uppsala, Sweden). The batch size was held constant at 400 g. Water was thereafter added by atomisation at a flow rate of 50 ml/min followed by wet mixing for 1 min. Four wet powder masses were produced with water contents of 50, 60, 70, and 80% w/w in relation to the dry powder weight. The wet powder masses were allowed to equilibrate for at least 12 h before extrusion measurements were performed.

2.3. Ram extrusion

For the extrusion experiments a laboratory ram extruder described by Harrison et al. (1985b) was used. In order to be able to characterise accurately the extrudates with respect to both weight and dimensions, a special die was made with an orifice diameter of 10.0 mm. Forces were recorded and samples collected both with and without this die in place, thus resulting in cylindrical samples with diameters of 10 and 25 mm, respectively (25 mm equals the inner diameter of the barrel.) Prior to extrusion, approx. 50 g of the wet mass was packed manually into the barrel to a constant volume, whereafter the piston was inserted into the barrel and placed in a material testing instrument. (Overload dynamics, The Netherlands). A ram speed of 150 mm/min was used in all experiments.

During extrusion both the force exerted on the piston and the displacement of the piston were monitored as a function of time.

As soon as a steady-state flow stage was detected, extrusion was stopped, the die removed, and the plug of material remaining within the barrel ejected by applying pressure to the piston. The force to remove this compressed plug was recorded and samples were collected. Results given are mean value of three determinations.

2.4. Preparation of isodiametrical extrudate specimens

From the untreated extrudates (10.0 mm) and plugs (25.0 mm) isodiametrical cylinders, were prepared by cutting the extrudates with a specially constructed device.

2.5. Determination of porosity and degree of liquid saturation of moist extruded cylinders

To estimate the porosity and degree of liquid saturation the weight and volume of the extruded cylinders and the plug were determined. Densities of the wet powder masses were calculated from the apparent particle densities of the powder excipients and water. Results given are mean value of three determinations.

The porosity of the cylinders (extrudate and plug) was calculated in the following way:

$$E = 1-(4W/t\pi d^2\rho) \qquad (1)$$

where E is the porosity of moist extrudate (–), W denotes the weight of dry extrudate (g), t is the length of moist extrudate (cm), d represents the diameter of moist extrudate (cm), and ρ is the density of dry powder mixture (g/cm^3) (from Eq. 3).

The degree of liquid saturation of the cylinders, i.e., the ratio of pore volume occupied by liquid to the total pore volume, was calculated in the following way:

$$S = H(1-E)\rho/E \qquad (2)$$

where S is the degree of liquid saturation (–), H denotes the water content (–), weight of water/weight of dry components, E is the porosity of moist extrudate or plug (–) (from Eq. 1), and ρ represents the density of dry powder mixture (g/cm^3) (from Eq. 3).

The densities of the powder mixtures needed for porosity and liquid saturation calculations were calculated as follows:

$$\rho = \frac{w_1 + w_2}{w_1/\rho_1 + w_2/\rho_2} \quad (\mathrm{g/cm^3}) \qquad (3)$$

where w_1 and w_2 are the weights of the mixture components 1 and 2 respectively, and ρ_1 and ρ_2 denote the densities of the mixture components 1 and 2, respectively.

For both porosity and liquid saturation, values determined were expressed as percent values.

3. Results and discussion

3.1. Extrusion of wet powder masses

The extrusion of wet powder masses gave force-displacement curves with three stages: compression, steady state and forced flow (Harrison et al., 1985b). During the compression stage, the wet powder mass from the beginning packed into the barrel by hand pressure consolidated further with only a slight increase in pressure. Eventually, the pressure rapidly increased until the material in the barrel and the die of the ram extruder began to flow. This was followed by the steady-state stage in which the force required to maintain the extrusion remained constant as the displacement increased. The duration of steady-state flow was found to be relatively short but increased with moisture content (Fig. 1) for all formulations tested, except the one with the highest water content. This particular formulation was overwetted and contained excess, free water, which was squeezed out of the system and moved through the plug towards the die exit of the ram extruder just before extrusion took place.

The steady-state force during extrusion was found to decrease with increasing moisture content (Fig. 2), for the extrudate produced both

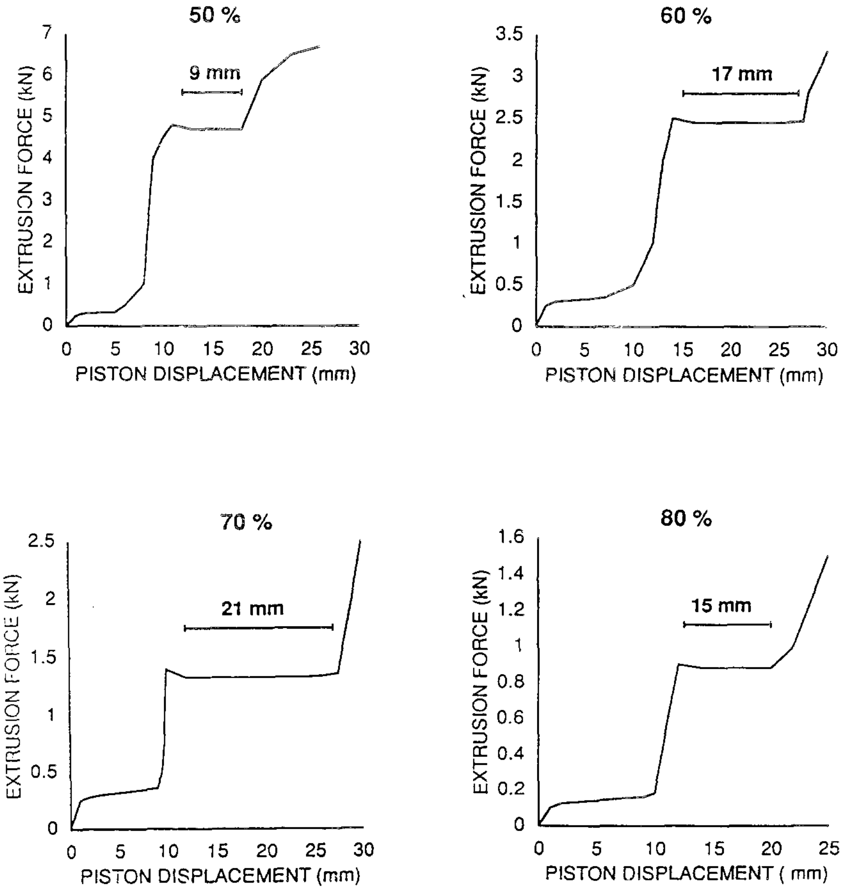

Fig. 1. Force-displacement curves during extrusion. The corresponding water content is given in each respective panel. The steady-state flow stage is denoted by an arrow together with its length in mm.

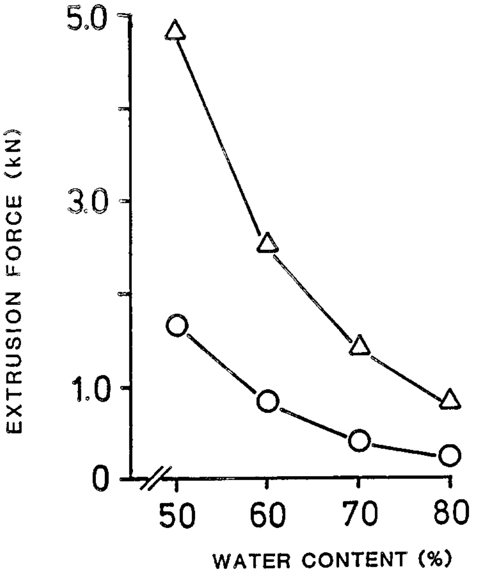

Fig. 2. Extrusion force at steady state for extruded cylinders: (△) with the die of diameter 10.0 mm; (O) without the die (barrel of diameter 25.0 mm).

with and without the die. However, extrusion through the die required generally higher forces. According to extrusion studies by Ovenston and Benbow (1968) and Benbow et al. (1987), the extrusion pressure is equal to the sum of two terms: the first due to the change in cross-section undergone by the material (describes the flow from the barrel into a die), and the second due to the frictional resistance to be overcome in the die (describes the flow along the die), as expressed by the equation:

$$P = 2Y \log(D_0/D) + 4\tau_R L/D \qquad (4)$$

where P is the extrusion pressure, Y denotes the yield stress, D_0 is the diameter of the barrel, D represents the diameter of the die exit, L is the length of the die, and τ_R denotes the wall shear stress.

In agreement with Eq. 4, the results thus indicate that increased moisture content reduced both particle-particle interaction in the mass (first term in Eq. 4) and the friction between powder plug and the die wall (second term in Eq. 4).

The steady-state flow stage was followed by forced flow, resulting in an increased extrusion force with displacement. This is due to the inability of the system to retain a constant convergent angle of entry into the die (Harrison et al., 1985a). The end point of this stage was the cessation of flow, when the resistance to flow reached a limiting value.

3.2. *The effect of moisture content on the porosity of extruded cylinders*

When a wet powder mass is extruded in the ram extruder, it undergoes volume reduction before the flow begins. As the interparticulate voidage (gas phase) is gradually eliminated, the volume of the plug changes and thus the porosity. In contrast to the granulation system where the mixture of solid, liquid and air is not constrained within an enclosed volume, the extrusion process restricts the volume available with the barrel and application of pressure will induce the extrusion of the mobile phase via the die. Hence, air is expelled, and if the solid/liquid structure does not yield by flow through the die, then water would be expelled. The ability of the structure to expand, to accommodate more water, is associated with its ability to flow due to the ease of flow, as represented by the lower steady-state values associated with increased water content (Fig. 2).

In contrast to other granulation methods, especially granulation in high-speed mixers (Kristensen et al., 1985a,b), the porosity of extruded cylinders increased with increased water content (Fig. 3). The porosity values for extrudates (10.0 mm) and plugs (25.0 mm) were similar. This clearly indicates that no further consolidation of the wet powder mass occurred during the flow through the die.

3.3. *The effect of moisture content on the degree of liquid saturation of extruded cylinders*

Liquid saturation, i.e., the degree of filling intragranular voids with binder solution (Kristensen et al., 1985a), depends on the amount of water and the intragranular porosity. Kristensen et al., (1985a) have shown that the effect of increased liquid saturation is a reduction of the work required to separate the particles. The effect of the moistening liquid may be compared to that of a lubricant which reduces particle interactions and facilitates densification of the moist agglomerates during granulation. The process of pressing a wet powder out of the container through an orifice with a smaller diameter than the container, i.e., extrusion, involves two consecutive stages: compression and extrusion. In both processes, particles will slide against each other. In this study, it has been found that during extrusion in a ram extruder, the wet powder will compress until 100% degree of liquid saturation is reached without the incidence of any extrusion. Thus, repositioning of particles causing the powder to compress requires relatively low applied forces compared to the establishment of a shearing zone in the material allowing extrusion. Moreover, when the powder mass approaches 100% degree of liquid saturation, i.e., when compression became more or less impossible, a drastic increase in applied force is needed in order to initiate extrusion of the material (Fig. 1). Thus, extrusion seems, compared to compression, be a much more demanding process in terms of force requirement. It therefore appears reasonable to hypothesise that specimens prepared by extrusion, generally and independent of extrusion method, posses a high degree of liquid saturation. In addition, extrusion requires probably low particle-particle interactions meaning that extrusion becomes impossible without a large amount of liquid present in the interparticulate pores.

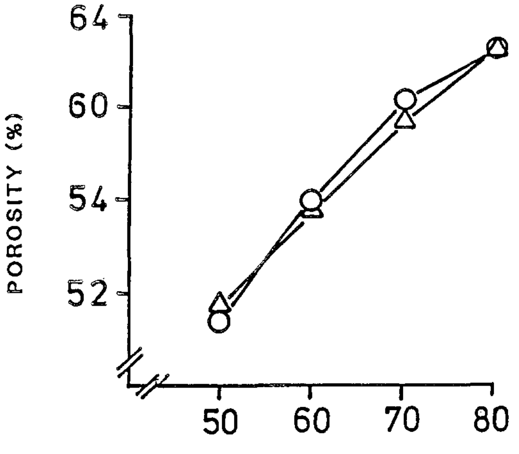

Fig. 3. Porosity as a function of water content for extruded cylinders: (△) extruded cylinders of diameter 10.0 mm; (○) extruded plug of diameter 25.0 mm.

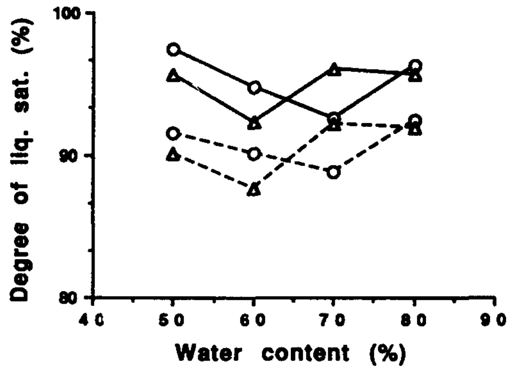

Fig. 4. Degree of liquid saturation as a function of water content for extruded cylinders. Calculation of $S\%$ based on simplified assumption that no water was sorbed into the MCC structure (continuous line) and corresponding values of $S\%$ reduced approx. 4% (dashed line). (△) extruded cylinders of diameter 10.0 mm; (○) extruded plug of diameter 25.0 mm.

The results show that an increased moisture content facilitated the extrusion process and increased the porosity, but did not effect the degree of liquid saturation (Fig. 4) which was similar and high for all extruded masses.

The presented calculation of degree of liquid saturation (Fig. 4, continuous line) was based on a simplified assumption that no water was sorbed into the Avicel PH 101 structure during the wet mixing and extrusion process. However, if some of the added water was taken up and included in the cellulose structure, a reduced amount of water should be available for the filling of the void volume and would subsequently lead to a reduction of the degree of liquid saturation.

To calculate the lowest possible value of degree of liquid saturation, $S\%$ (Eq. 2), it was assumed that 10% w/w of water (Angberg et al., 1991) was taken up by the MCC fraction during wet mixing and extrusion, in comparison with the amount of water, initially present in the microcrystalline cellulose. This situation representing the maximum possible uptake of water would then correspond to approx. 4% reduction of $S\%$ (data presented in Fig. 4, dashed line). However, such a reduction of the water present in the void structure is probably counteracted by the swelling of cellulose due to the presence of water (Khan et al., 1988). Irrespective of how the $S\%$ values were calculated, the general conclusion remains that almost complete filling of the interparticulate void space is needed before extrusion occurs.

In studies on tabletting it has been shown that intermolecular forces, mainly of the London-Van der Waals type, dominate in compressed powders (Karehill et al., 1990). It was shown that with increasing dielectric constant of the void medium a reduction in specimen strength was obtained (Karehill et al., 1990). It could thus be suggested that the process of volume reduction (i.e., pressing out the gas phase during the compression stage) requires a relatively low force and is, compared to tabletting, facilitated by the presence of high amounts of water. In fact, the increase in degree of liquid saturation during the compression stage enhances nearly complete volume reduction. The start of extrusion seems to coincide with the moment when volume reduction is almost finished and that nearly all pore voids are filled with water. Obviously, a substantial reduction of the particle-particle attraction is needed before yielding and extrusion can occur.

4. Conclusions

Due to the fact that extrusion occurred generally at near 100% degree of liquid saturation, an increased water content of the powder mass corresponds to an increased porosity during the extrusion phase. An increased porosity corresponds to an increased separation distance between particles and thus, reduced particle-particle attractions. This will explain the reduction in extrusion force with an increased water content of the powder. In addition, the possible prerequisite that extrusion requires low particle-particle interactions means that a low separation distance between particles, e.g., as a result of a low water content of the powder mass, prevents extrusion although near 100% degree of liquid saturation can be reached.

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