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Citation for the original published paper (version of record):

Mahmoodi, F., Alderborn, G., Frenning, G. (2011)

Effect of spherical-agglomerate strength on the distribution of force during uniaxial compression.

Powder Technology, 206(3): 283-290

<http://dx.doi.org/10.1016/j.powtec.2010.09.031>

Access to the published version may require subscription.

N.B. When citing this work, cite the original published paper.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-147764>

Effect of spherical-agglomerate strength on the distribution of force during uniaxial compression

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We employ the carbon paper technique with the aim of investigating the effect of spherical-agglomerate (pellet) strength on force distributions, through confined compression of approximately 1 mm sized pellets formed from microcrystalline cellulose and polyethylene glycol. The carbon paper technique relies on the transference of imprints from compressed pellets onto white photo quality paper, which are digitised and processed via image processing software. The investigated pellets can both deform plastically and develop localised cracks in response to an applied stress, while remaining largely intact during confined compression. Our results indicate that such crack formation – henceforth referred to as fracture – has a decisive influence on force distributions. Previous work on non-fracturing systems has found that the distribution of normalised forces tends to narrow with increasing particle deformation. No narrowing is observed after the point of fracture in this study and the width of the distributions – as quantified by the standard deviation of non-normalised forces – is found to increase with the difference between non-normalised mean force and fracture force. Additional corroborative results show that spatial force–force correlations typically exhibit a marked change once the fracture force is exceeded.

Keywords: Granular materials; Compression; Force distributions; Carbon paper technique; Particle failure

1. Introduction

The compression of granular materials is performed in various industrial sectors. The typical approach in compression analysis has been the use of compaction equations which are empirical or semi empirical [1-3]. A common trend when investigating confined compression, has been to infer bulk behaviour from single-particle based investigations. The typical response of a powder in a die upon the application of force by a punch is to reduce in volume. The degree of powder volume reduction and the ability of it to form a coherent mass with a tensile strength once the force is removed, are termed compressibility and compactibility [4]. These two properties provide no information on how the applied force is distributed within the powder bed. Force transmission is inherently heterogeneous, as it is reliant on certain moieties spanning the bulk and forming chains through which the force can travel. An illustrative image displaying this phenomena has been presented by Liu et al. [5]. Force chains carry most of the axial load leaving areas which experience little or no load. Simulations of deformable “friction balls” demonstrated that the density of these chains increases with applied pressure, leading to a less heterogeneous transmission of forces [6]. Knowing the in die force distribution when tableting could help in developing tablets that are more homogenous in their binding strength. It could be hypothesised that this in turn may affect important tablet characteristics such as disintegration, friability and tensile strength.

The aim of this study was to investigate the effect of pellet strength on force distributions during confined compression. The carbon paper technique enables the capture of force distributions in die. The underlying premise is that the area and darkness of the

transferred imprint from the carbon paper are related to the force that was applied to it. It is from these imprints that a calibration fit is obtained and used in the determination of the force distributions.

Previous experimental work employing the carbon paper technique has relied on materials with well defined properties [5-9], however, as is commonly the case, it is rare to come across ideal systems in real world situations. The mm sized spherical agglomerates (pellets) used in this study were not externally sourced and were produced in house. The non ideal nature of these pellets stems from both intra and inter pellet type variations in porosity, yield stress and fracture force. To the best of our knowledge, this is the first study in which the carbon paper technique is used in the determination of force distributions of pharmaceutical materials with differing mechanical properties. Non ideal pellets of a single type were also used in previous carbon paper based studies [10, 11] conducted by our group.

The internal microstructure of the pellets under investigation can be viewed as a fabric or mesh of interweaving/interlocking polymer chains. Although the pellets primarily deform plastically, they all have a point beyond which they fail. Previous studies on similar pellets pointed out that localised cracks are formed but that fragmentation generally does not occur [12-14]. Other studies have focussed on employing the Discrete Element Method (DEM) to better understand agglomerate breakage [15-17]. The modelled agglomerates are composed of spherical particles bound together, whereas the pellets of this investigation have a mesh like microstructure, as mentioned above. This difference in

microstructure can result in variation of crack formation and propagation. The force–displacement behaviour of sodium benzoate granulates, as presented by Antonyuk et al. [18], was similar to that expected for plastically deforming pharmaceutical pellets. Thornton et al. [15] defined various breakage patterns of agglomerates, namely; fracture, shattering, disintegration and total disintegration. Although crack formation generally does not lead to fragmentation of the pellets investigated in this work, we adopt the term “fracture” to describe pellet failure.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC; Avicel PH101, FMC, Ireland), ethanol (Solveco Etanol A96%, Solveco AB, Sweden), polyethylene glycol 6000 (PEG; Fluka Chemie GmbH, Germany) and de-ionised water. Black carbon paper (Radex 1200, Kores, Austria) and white photo quality paper (Epson photo quality ink jet paper, S041068, Seiko Epson Corp., Japan).

2.2. Pellet preparation

Batches of low and high porosity MCC pellets (from hereon referred to as MLP and MHP respectively, see Table 1) and low and high porosity MCC combined with PEG (PEG; 5% of dry weight, from hereon referred to as MPLP and MPHP respectively) pellets were produced. The ethanol to water ratio of the agglomeration liquid used to produce the MHP and MPHP pellets was 70:30. The agglomeration liquid used to produce the MLP and MPLP pellets was de-ionised water only. MCC (400 g for MLP

and MHP, and 380 g for MPLP and MPHP) powder was aerated in a high shear mixer (QMM-II, Donsmark Process Technology, Denmark) at ≈ 500 rpm for 5 min. 20 g of PEG was dissolved in the agglomeration liquids used to produce the MPLP and MPHP pellets. The agglomeration liquid (110 % mass of MCC for MLP and MPLP, 100 % for MPHP and 107 % for MHP) was manually poured into the dry mass at a rate of approximately 100 ml/min while mixing. The resulting wet mass was mixed for a further 3 min at ≈ 500 rpm and immediately extruded (NICA System AB, model E140, Sweden; holes 1.0 mm in diameter and 1.2 mm long). The extrudate was spheronised (NICA System AB, model S 320-450, Sweden) for 3 min on a 32 cm diameter friction plate with a radially designed grid at a rotation speed of ≈ 850 rpm. Spheronisation time was started once all the extrudate had been transferred into the spheroniser. The ensuing pellets were spread into a thin layer on trays and allowed to dry at room temperature for at least 4 days. During the drying process the pellets adhered to each other forming clumps, and de-aggregation was accomplished by gentle tapping with a spoon. The desired pellet size fraction (800–900 μm) was obtained via sieving, through the vibration (Retsch, Type RV, West Germany) of square aperture sieves for 30 min at a relative intensity of 40 (on an arbitrary scale). All pellets were conditioned in a closed chamber at 40 % relative humidity and room temperature for at least 5 days prior to any tests.

2.3. Characterization

I. Powder

The apparent particle density of MCC (1.571 g/cm³) and PEG (1.227 g/cm³) were determined using a helium pycnometer (AccuPyc 1330, Micromeritics, USA). The apparent density of the combined MCC/PEG (1.549 g/cm³) was calculated via [19]

$$\rho_{mix} = \frac{w_1 + w_2}{w_1/\rho_1 + w_2/\rho_2} \quad (1)$$

where ρ_{mix} is the apparent binary mixture density, w_1 , w_2 , ρ_1 and ρ_2 are respectively the weight fraction and apparent densities of the two components in the mixture.

II. Pellets

Yield stress and single pellet fracture force: Pellets from each batch were compressed using a texture analyser (TA HDi texture analyser, Stable Micro Systems, UK) with a 6 mm diameter stainless steel rod. The compression profiles of the pellets (Fig. 1) were analysed (the number of independent measurements, n , was > 80 for each pellet type). The slopes of the initial linear region of the force displacement plots, which represent plastic deformation prior to fracture, were used in the calculation of yield stress through the equation [11, 20, 21]:

$$\sigma_y = \frac{4}{\pi D} \frac{dF}{dx} \quad (2)$$

where D denotes the mean pellet diameter and dF/dx is the slope of the linear region. These plots were also used in the determination of the single pellet fracture force ($n>80$).

The first peak preceding a drop on the force displacement plots was chosen as the point where the pellet begins to fracture.

Density/Porosity: Pellets were weighed in a 25 ml measuring cylinder. The volume occupied by the pellets was estimated after applying 1000 taps on the tap density tester (Pharma Test PT-TD, Hainburg, Germany), and the ratio of weight and volume was calculated to give the tapped density ($n \geq 3$). Pellet porosity ε was estimated through calculation:

$$\varepsilon = 1 - \rho^{bulk} / (\phi_c \rho^{solid}) \quad (3)$$

where ρ^{bulk} is tapped density, ρ^{solid} is apparent particle density and ϕ_c is the packing fraction for random loose packing [6], where the interaction is composed of both normal forces and transverse frictional forces, with a value of 0.6284, which is within the range generally obtained for spherical particles [22].

Pellet size and shape: Pellets were spread out on a flatbed scanner (Epson Perfection 1640SU Scanner, Seiko Epson Corp., Japan) and covered by a black background. 1600 dpi images of the pellets were captured. The images were analysed via ImageJ [23], a public domain image analysis programme. The projected-area diameter was calculated through the equation ($n > 2000$):

$$D = \sqrt{4A / \pi} \quad (4)$$

where A is the projected area of the pellet. The ImageJ parameter “fit ellipse” produced the outputs “minor” and “major”, which correspond to the primary and secondary axes derived from fitting an ellipse around the pellet. The ratio minor/major was used to determine circularity.

2.4. Calibration, bulk compression and carbon paper analysis

The carbon paper technique relies on transferred imprints which are related to force. Hence a calibration curve is necessary in order to create a relationship between imprint area and force. Once bulk compression is carried out the resulting imprints are analysed through image analysis and the calibration curve is applied to convert the imprint areas into forces. As calibration, bulk compression and carbon paper analysis methodologies have been described in a previous article [11], only a brief description will be given here. Circular pieces of carbon and white photo quality paper were cut out using a stencil tool designed for the purpose (diameter 11.3 mm). These were placed in a double layer, with the carbon paper on top of the white paper. This arrangement was used for both the calibration and bulk compression procedures. Calibration was carried out on single pellets placed in a rig specifically designed to mimic a physically constraining environment (cylindrical die of diameter ≈ 1 mm with teflon walls) [11], with compression being applied via the Stable Microsystems TA HDi texture analyser equipped with a 50 N load cell. Forces between 2 and 50 N were applied with 10 repetitions for each step. Single pellet compression data at 100 N was derived from a Zwick Z100 materials tester (Zwick/Roell, Zwick GmbH & Co. KG, Germany) equipped

with a 1 kN load cell, and included in the calibration (non-constrained at a compression rate of 1 mm/min).

Bulk compression was carried out via the Zwick Z100 materials tester, equipped with a mobile upper punch attached to a 100 kN load cell and a stationary lower punch (diameter 11.3 mm) and die. Prior to all bulk compression events the die wall was lubricated with 1% w/w magnesium stearate suspension in ethanol. Pellets were poured into the die and the weights were adjusted based on bulk density, so as to maintain similar initial column heights (~ 12 mm). Three pressure steps between 10 and 30 MPa were applied, with 20 replications for each. Digital images of the resultant imprints caused by the layer of pellets on the lower punch were captured via the Epson Perfection flatbed scanner at a resolution of 1600 dpi. Images were processed via Photoshop Elements 5 (Adobe Systems Incorporated) prior to analysis. ImageJ was employed as analysis software and a threshold range of 1–220 was applied for all images. Bulk compression analysis was based on implementation of a watershed algorithm [24] in imageJ.

2.5. Statistics

From the analysis described above, a large dataset consisting of single particle forces and corresponding spatial locations was obtained. To obtain force distributions, the population mean force $\langle F \rangle$ was calculated at each pressure step, as an arithmetic average. This was used to normalise forces within each pressure step to give $f = F/\langle F \rangle$. The data for each pressure step and pellet type was pooled into one file. Each of these files was analysed via the R statistical software programme [25]. The force data was binned (bin

width 0.1) and the probability densities $P(f)$ and standard errors for force distributions were estimated from bin counts in a standard manner, utilising the fact that the number of observations falling within a single bin is expected to follow a binomial distribution.

Twenty separate files were produced for each pressure step and pellet type combination in the calculation of the 2D pair distribution and mark correlation functions. The pair distribution function $g(r)$ is defined as

$$g(r) = \frac{1}{N n_0 \pi r} \sum_{i=1}^N \sum_{j=i+1}^N \delta(r_{ij} - r) \quad (5)$$

where N is the total number of imprints, n_0 is the average number density of imprints, and r_{ij} is the distance between the centres of imprints i and j . The pair distribution function quantifies the probability of finding a particle at a distance r from an arbitrarily selected particle, normalized so that a value of unity is obtained for a uniform distribution.

Calculation of the mark correlation function $K_{mm}(r)$ was based on the estimated normalized force of an imprint (i.e., the mark $m = f$). Due to this normalisation, $K_{mm}(r)$ is defined as

$$K_{mm}(r) = \frac{\sum_{i=1}^N \sum_{j=i+1}^N \delta(r_{ij} - r) m_i m_j}{\sum_{i=1}^N \sum_{j=i+1}^N \delta(r_{ij} - r)} \quad (6)$$

The mark correlation function quantifies the dependence between marks (in this case normalized forces) a distance r apart, and may hence be referred to as the spatial force–force correlation function. A value of unity indicates that the marks are uncorrelated, whereas values > 1 are obtained for positively correlated marks (forces).

The position of each imprint (derived from the “centre of mass” parameter of ImageJ) was used to determine the $g(r)$ and $K_{mm}(r)$ through the R package and its SPATSTAT algorithm. A translation edge correction was applied to this (see [26] and references therein).

3. Results and Discussion

3.1. Pellet characteristics

Production parameters are a factor in determining pellet porosities and mechanical properties. Previous experience [14] has demonstrated that addition of ethanol to the granulation liquid increases the porosity of ensuing pellets. It is apparent from Table 2 that the porosities of MHP and MPHP are higher than those of MLP and MPLP, thus validating their categorical division into two distinct groups (high porosity and low porosity) based on quantitative similarities.

Figure 1 shows representative force distance curves for each pellet type. It is apparent from these curves that the region prior to the first peak is predominantly linear. It is also apparent that the initial peak does not coincide with the fragmentation of the pellet, but rather to crack formation within it. Analogous observations were made in Ref. [12], where similar pellet systems as are presented here were used. The yield stress and the single pellet fracture forces – extracted from curves of the type shown in Fig. 1 – rank in the same order (Table 1), with the lowest values being obtained for the MPHP pellets followed by the MHP, MPLP and the MLP pellets. Hence the mechanical characteristics

of the pellets are influenced by their porosity and addition of PEG, which is thought to act by facilitating the repositioning of primary particles in the pellet [13, 14, 27].

In what follows, we will refer to pellets characterized by low values of yield stress and fracture force as being “weak”, and those characterized by high values as being “strong”. It can finally be noted that all pellets are of similar size and shape.

3.2. Calibration and transmitted force

The results of the calibration procedure are presented in Fig. 2, which displays applied single-particle forces plotted against imprint areas. The solid lines represent fits of a rational function of the form shown in Eq. (7) to the experimental data:

$$y = \frac{a_0 + a_1x + a_2x^2 + a_3x^3}{1 + b_1x + b_2x^2 + b_3x^3} \quad (7)$$

In the above equation, x is the independent variable (area), y is the dependent variable (force) and a_i and b_j are coefficients. Coefficients that did not improve the quality of the fit were put to zero. It is apparent that in the 5–20 N range the curves inflect. These inflection points are of interest as they represent the vicinities where the various pellet types begin to fracture (see Table 2). Overall the presented calibration curves provide an adequate fit to the data.

Figure 3 displays the transmitted force estimated from carbon paper analysis plotted against applied bulk compression force for all pellet types. It is apparent from Fig. 3 that the estimated fraction of force being transmitted increases as pellet strength decreases. This may be due to the harder pellets penetrating the lubricant layer on the die wall

thereby increasing die wall friction and reducing the transmitted force. It may also be noted, that the estimated transmitted force for the MPHP pellets was greater than the applied compression force at 20 and 30 MPa. The exact cause of this observation is unclear. However, it seems that it is related to how the compression response of MPHP is conveyed through the carbon paper. It could possibly be attributed to smearing effects (due to the softness of the pellets) and/or to neighbouring pellets having deformed/fractured to the extent that they leave larger indivisible imprints. Alternatively, the calibration of the MPHP pellets may have overestimated the single-pellet forces. As such, the results for MPHP should be interpreted with caution. They are however included in the following discussion, as they appear to follow the overall trends identified from the behaviour of the other three pellet types.

3.3. Force distributions

The force distributions obtained for the different pellet types are summarized in Fig. 4 and the statistics of the distribution are provided in Table 3. In addition to the mean force $\langle F \rangle$, the standard deviation (SD) and coefficient of variation (CV) of the non-normalized forces are given in the table. In the figure, we have presented f (where $f = 1$ corresponds to mean force) values up to 3. In real terms, any values exceeding 3 are very few in number compared to the global count of imprints. Semilog plots are the conventional way to present this type of data [5-9] as they highlight the post peak exponential tail. On a qualitative level, all the $P(f)$ profiles generally exhibit similar features. There is a peak (the mode), followed by an approximately exponential decline. A reduction in the slope of the post peak tail on a $P(f)$ profile is indicative of larger probabilities of forces

considerably exceeding the average being transmitted (i.e. a less homogenous force distribution). The $P(f)$ plots of MLP generally exhibit the steepest tails, whereas the plots for MPHP display the converse of this.

A general widening of force distributions with increasing compression pressure is observed within each pellet type except for MLP, which is exemplified when viewing Fig. 4 and the CV values of Table 3. It must be mentioned here that the slope and CV are not equivalent, but rather that they are indicative of the same trends when viewed in this context. At the two higher pressure steps the CV values indicate that the weaker the pellet the wider the distribution.

Volume reduction due to particle rearrangement has been found to be limited for these types of systems [12] and inter-particle friction and cohesion are known not to significantly affect the force distributions at these pressure steps [11]. Blair et al. also found that the force distributions of their rough and smooth beads were not significantly different and that packing order causes a very little change in the $P(f)$ profiles [9]. Assuming the exclusion of these factors, the observed differences between pellet types and pressure steps could be related to; the ease and extent of pellet deformation, which are governed by their fracture resistance and yield stress, both of which in turn are influenced partly by porosity.

Frenning and Alderborn [10] conducted force distribution studies on ductile MCC pellets of low porosity and found that much like the studies mentioned above, their force

distributions became more homogenous with increasing applied pressure from 10 to 50 MPa. Although the pellets used in this study predominantly deform plastically, it is of interest to compare our results with those obtained for elastic particles; as long as loading is monotonic, one would expect qualitative similarities between the results obtained for plastically and elastically deforming particles. Erikson et al. [8] conducted experiments on rubber beads with varying hardnesses and soda lime glass beads. They found that when comparing the force distributions for soda lime glass beads, hard, medium and soft rubber beads at similar average forces, the more deformable the material was, the steeper its post peak tail. They also found that with increasing applied force (and consequently increasing bead deformation) the tails of the force distributions of their soft beads became steeper. From their simulations of deformable “friction balls” Makse et al. [6] found that at low stresses of 21 and 46 kPa their force distributions were exponential, whereas at higher compressions of 10 and 100 MPa there was a gradual change toward a Gaussian form. This finding implies an increase in the homogeneity of the force distribution with increasing deformation.

In summary, seeing as the most probable factors influencing the force distributions in this study are pellet deformation and/or fracture, it seems that, based on previous findings [6, 8, 10], which only took deformation and not fracture into account, the influence of deformation on MLP is greater than the other pellet types, as it was the only one to somewhat follow the trends seen in these studies, by exhibiting the least homogenous distribution within its pellet type at 10 MPa.

Having seen that deformation does not fully explain the trends observed in Fig. 4 and Table 3, the focus of attention will be turned to fracture. It was previously found [12] that the initial stages of compression involving pellets with similar properties as those used here, were governed by crack/fracture formation. This ties in well with our investigation, as the applied pressures are in the range that can be thought of as the initial stages of compression when viewed in the context of tableting, where much higher pressures than were used here are applied. Due to this, the force standard deviations at each compression pressure were plotted against the difference between the mean force and the individual pellet fracture force ($\langle F \rangle - F_{frac}$) at that pressure (Fig. 5). This highlighted a correlation, which was evident for all pellet types, where the width of the force distribution (as expressed by the standard deviation of the non-normalized forces) increases linearly with $\langle F \rangle - F_{frac}$, when the average force exceeds the fracture force. Moreover, the data for the different pellet types seem to follow a common relationship when displayed in this manner. Although the data do not permit general conclusions for average forces smaller than F_{frac} , it can be inferred that the standard deviation of MLP is less dependent on fracture force in this region.

The data in Table 3, when presented as in Fig. 5, suggests that fracture has a decisive influence on the width of the distributions. The importance of fracture is further highlighted in Fig. 4 by the reduction of slope that is observed once the fracture force has been exceeded. Our interpretation is that the additional randomness introduced by fracture is translated into a wider force distribution.

3.4. Robustness

In order to test the calibration sensitivity, a different set of fits of the form:

$$y = a_1x + a_2(e^{a_3x} - 1) \quad (8)$$

were determined which captured the data points reasonably well, but without the inflection observed in Fig. 2. The clarity of the trends in Fig. 4, seems to be dependent on the capture of this region. However, even if the inflecting region is overlooked, the resulting force distributions do not display a clear homogenisation with increasing applied pressure. Furthermore, it was found that the relationship between standard deviation and $\langle F \rangle - F_{frac}$ remained robust and that the mark correlations could still be interpreted in terms of fracture force. Blair et al. [9] identified the fitting of data to be a significant problem, and found that their two fitting methods produced significant differences in force determinations, while at the same time being uncertain as to which of the two methods produced the more accurate calibration. They also found that uncertainties in the calibration form the largest contribution to systematic error, even though they were working with soda lime glass beads, which most likely exhibit less intra batch variability than the pellets used in this investigation.

3.5. Spatial and force correlations

Pair distribution functions are presented in Fig. 6. It is apparent that all pellet types follow similar trajectories and that differences between pellet types are not as clear as they were in the force distribution plots. All the pellet types display three peaks with a progressive reduction in amplitude with increasing r , indicating a degree of order up to

approximately three imprint diameters. It may be concluded that the spatial arrangement of particles is largely independent on their mechanical properties.

Mark correlation functions for the normalized forces are presented in Fig. 7. As may clearly be seen, the spatial force–force correlation function $K_{mm}(r)$ deviates significantly from unity at some interparticle distances and exhibits pronounced oscillations. Hence the location of the particles and the normal forces they exert on the bottom punch are not independent in general. The forces acting on the pellets during compression are expected to have components that are both parallel to and normal to the bottom surface. It appears plausible that the magnitude of the parallel component is related to the normal component, and that the parallel component may have caused a lateral motion of the particles during the compression process. Conversely, it is also conceivable that the spatial arrangement of the particles may have affected their normal forces in a non-random manner. Oscillations in the correlation function have previously been observed experimentally for plastically deforming particles [10] and have also been seen in simulations of granular shear flow [28], but no solid explanation appears to have been offered this far. On the contrary, when they measured the correlations between pairs of normal forces, Blair et al. [9] found no significant correlations for their amorphous arrangements. Mueth et al. [7] found no simple correlations between forces within the plane of any confining walls. In order to investigate spatial force–force correlations in more detail, simulations may be useful, for instance by using the DEM.

A glance across Fig. 7 reveals that the primary peaks at the pressure steps where the fracture force of each pellet type is exceeded are generally more pronounced relative to prior fracture. This observation further corroborates the importance of fracture.

The novel nature of and experience gained through this and a previous study [11] demonstrated that the use of carbon paper is not an exact technique, particularly so, when working with very soft pellet types as has been performed here. However, this should not diminish the value of the technique, as it does highlight consistent relative trends. Accordingly, the scope of our article has been directed toward comparing general relative trends within and between pellet types. A way to improve the sensitivity of force capture could be to do the experiments with more accurate force sensors.

4. Conclusion

Our results indicate that consideration of fracture is necessary when viewing force distributions for non ideal systems during confined compression. The findings presented here suggest that within the pressure range of 10–30 MPa, in systems where fracture occurs, the force distributions do not increase in homogeneity after the point of fracture. The width of the distributions, as quantified by the standard deviation of the non-normalized forces, appears to depend on how much the average force exceeds the fracture force, in a manner that is largely independent of particle type. Moreover, marked changes are observed in the spatial force–force correlations once the fracture force has been exceeded. The processes of deformation and fracture upon compression of a pellet bed

are not mutually exclusive, and as such it is not possible to exclude the contributory influence of deformation. Further work in this field could include DEM analysis and the use of more accurate force sensors, to help shed more light on the observed trends.

5. Acknowledgements

We would like to acknowledge Aleksi Takala for his experimental contributions to this work. This study is part of a research program in Pharmaceutical Materials Science at Uppsala University. We would like to convey our gratitude to the Swedish Research Council (Project numbers 621-2005-3372 and 621-2007-3854) for financing this project.

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Figures

Fig. 1. Representative force vs. distance curves for each pellet type.

Fig. 2. Applied force vs. area of imprints. The symbols represent experimental data, with error bars indicating standard deviations, and the solid lines are fits of Eq. (7) to the data.

Fig. 3. Estimated transmitted force vs. applied compression force (error bars indicate 95 % confidence intervals).

Fig. 4. Force distributions for all pellet types and pressure steps (error bars indicate standard errors).

Fig. 5. Correlation between the standard deviation of force and single pellet fracture force. The lines are presented as a guide only.

Fig. 6. Pair correlation functions (error bars indicate 95 % confidence intervals).

Fig. 7. Mark correlation functions for normalized forces (error bars indicate 95 % confidence intervals).

Tables

Table 1. Components and proportions used in making pellets.

Pellet type	Mass of MCC/PEG (g)	Mass of water/ethanol (g)	Total agglomeration liquid mass (g)
MLP	400/0	440/0	440
MPLP	380/20	418/0	418
MHP	400/0	128.4/299.6	428
MPHP	380/20	114/266	380

Table 2. Pellet characteristics, values in parentheses indicate standard deviations.

Characteristic	MLP	MPLP	MHP	MPHP
Tapped bulk density (g/cm^3)	0.877(0.0024)	0.851 (0.0039)	0.619 (0.0173)	0.625 (0.0078)
Estimated porosity (-)	0.111(0.0024)	0.126 (0.0040)	0.373 (0.0175)	0.358 (0.0080)
Diameter (mm)	0.919 (0.0867)	0.920 (0.0752)	0.884 (0.0907)	0.901 (0.0833)
Single pellet fracture force (N)	14.8 (2.20)	10.2 (2.04)	7.61 (2.174)	4.19 (0.836)
Yield stress (MPa)	114 (15.1)	99.7 (13.79)	75.2 (16.10)	57.3 (7.84)
Circularity (-)	0.858 (0.0995)	0.865 (0.0873)	0.852 (0.1000)	0.852 (0.0940)

Table 3. Statistics of non-normalized force distributions for all pellet types and pressure steps: Mean $\langle F \rangle$, standard deviation (SD), and coefficient of variation ($\text{CV} = \text{SD}/\langle F \rangle$).

	MLP			MPLP			MHP			MPHP		
	10	20	30	10	20	30	10	20	30	10	20	30
$\langle F \rangle$ (N)	7.61	12.30	17.58	6.84	13.45	21.14	7.35	13.87	20.55	7.22	17.33	27.03
SD (N)	3.29	3.47	5.20	2.47	5.61	9.30	2.14	7.54	12.67	3.64	10.84	17.98
CV (-)	0.43	0.28	0.30	0.36	0.42	0.44	0.29	0.54	0.62	0.50	0.63	0.67
Count	2166	2481	2480	2322	2377	2420	2475	2548	2677	2460	2539	2576