Chapter 3

Pore direction in relation to anisotropy of mechanical strength in a cubic starch compact

Abstract

The mechanical strength of bodies is strongly influenced by the porosity, a property that in uni-axially compressed bodies such as tablets displays an anisotropic behaviour. Earlier research providing SEM images of cross sections of tablets, suggested that this was caused by anisotropy in pore structure. In this case, the determination of the pore direction was done by the naked eye. In the present research, the preferential pore direction was quantified with image analysis. To better understand the consequences of the anisotropy in pore structure on the strength of a compact, the mechanical strength and the preferential pore direction was evaluated in cubic compacts of different porosities. Starch was chosen as a model compound for materials with ductile behaviour of which tablets with low porosities can be made and which shows some elastic recovery after compaction.

Image analysis showed that the pores are mainly oriented in the direction perpendicular to the direction of compression. This was accompanied by a lower crushing force in this direction compared to the crushing force in the direction parallel to the direction of compression. This could be explained by considering the pores as crack which propagate through the sample during crushing. For both directions the crushing force decreased with increasing porosity. The yield strength of the compacts also decreased with increasing porosity, but this parameter was not dependent on the direction of crushing when the porosity was below 10%.

The results show that pore direction significantly influences the crushing force but does not influence the yield strength.
3.1 Introduction

It is well known that porosity influences the mechanical strength of compacts [1-6]. It is also known that the mechanical strength of tablets compressed with uni-axial compression is an anisotropic property, i.e. it is not the same when it is measured in the direction of the compression or in the direction perpendicular to it [7-17]. In earlier research Ando et al [9] and Galen and Zavaliangos [16] determined the mechanical strength and made SEM images of cross sections of the tablets. Although they did not have a parameter to quantify the directions of the pores, the orientation of the pores and particles was distinguished visually by a human observer. This suggested that the (anisotropy in) pore structure is the cause of the anisotropy in mechanical strength. In the present paper attention will be paid to both the quantification of the preferential pore direction and the anisotropy in mechanical strength in a cubic starch compact to better understand the correlation between these two parameters. Starch was chosen as a model compound for materials with ductile behaviour of which tablets with extremely low porosities can be made and which show some elastic recovery after compaction. It was believed that studying the fracture behavior of compacts with an extremely low porosity would make it easier to evaluate the influence of the pore structure.

A previously described method was used to detect a preferential pore direction [18]. Previously, this method was applied to a cubic NaCl compact with a high porosity. In the present paper we modified this technique to make it suitable for the analysis of a compact made of starch with lower porosities. For the assessment of the mechanical strength a cubic compact was used. The cubic shape makes it possible to compare the properties in the horizontal direction with the properties in the vertical direction, since the outside dimensions of the compact are the same. The consequence of this way of breaking is that the tensile strength of the specimen can not be measured, as is done when a cylindrical body is subjected to the diametric compression test [19]. However, if the fracture shows ductile behaviour (i.e. the fracture has been preceded by considerable plastic deformation [20]) , it does provide an opportunity to measure the yield strength, which can also be used to describe the mechanical strength.
3.2 Materials and methods

3.2.1 Materials
To obtain bodies with a low porosity we chose to use pregelatinized starch, a visco-elastic material. By using a slow compression speed, a slow decompression speed, and a powder with a relatively high moisture content the powder shows plastic deformation with little relaxation. The 106-150 µm fraction of pregelatinized potato starch (Prejel JF, Avebe, Foxhol, The Netherlands) was obtained by 30 min. vibratory sieving (Fritsch analysette 3, Germany) followed by 12 min air jet sieving over a sieve of 106 µm (Alpine A200, Augsburg, Germany), to remove the fines. Before use the powder was stored at least three days at a relative humidity of 70%. The apparent particle density was measured with helium pycnometry (Quantachrome, Syosset, New York, USA). Corrected for the moisture content at a relative humidity of 70%, measured with a moisture analyzer (Sartorius MA40, Göttingen, Germany), this was found to be 1439 kg/m³.

3.2.2 Tablet compaction
A hydraulic press (ESH compaction apparatus, Hydro Mooi, Appingedam, The Netherlands) was used to compress the starch in a square shaped die with sides of 7 mm. Before compaction, the die was lubricated with magnesium stearate using a brush. Varying quantities of powder were used to obtain cubic shaped compacts with different porosities. The rate of compression was 0.1 kN/s and the rate of decompression varied between 0.001 kN/s for the compacts with low porosity and 0.1 kN/s for the compacts with higher porosities. Compact dimensions were measured after 24 hours with an electronic micrometer (Mitutoyo, Tokyo, Japan) and the weight of the compacts was measured with an analytical balance (Mettler-Toledo, Greifensee, Switzerland). The porosity of the compacts was calculated from these data and the true density. The porosity calculated in this way will be referred to as ‘porosity’ while the porosity calculated with image analysis will be referred to as ‘local porosity’.

3.2.3 Determination of mechanical properties
The mechanical properties of the cubes were determined by compressing them between the punches of a compaction simulator (ESH , Brierley Hill, UK) while registering the force- displacement curve on an X-Y recorder (Kipp & Zonen, Delft, The Netherlands). The upper punch moved downwards with a linear speed of 0.75 mm/s. The strength in the x – direction was determined by placing the cube between the upper punch and the lower punch in such a way that the direction of the original compression was perpendicular to the direction of
crushing. The strength in the z-direction was determined by placing the compact in such a way that the direction of the compression was parallel to the direction of crushing. In this way the force at which fracture occurred (crushing force) was registered. The yield point was defined as the maximum in the stress-strain curve or as the point where the two tangents of the initial and final parts to the stress strain curve intersect [21]. By dividing the force at which yielding occurred by the area of one of the sides of the cube (49 mm$^2$) the yield strength was calculated.

3.2.4 Imaging of planes in the compact
Compacts were embedded with glycolmethacrylate resin. After hardening of the resin, several planes in the compact were smoothed using a microtome as described earlier [18]. The planes in the compact that have been imaged are depicted in figure 1. Two sets of images were defined, plan and elevation images. Plan images provide a top view and elevation images provide a side view. Of each plane 9 images were taken. Figure 1 also clarifies the nomenclature of the different directions. The z-direction is the direction of compression and the x- and y-direction lie perpendicular to this direction.

SEM BEI (Backscattered Electron Imaging) images were made using a JEOL scanning electron microscope (JEOL, type JSM-6301F with standard paired semiconductor element detector, Japan) operated at an accelerating voltage of 10 kV. The diaphragm was 50 µm and the working distance was 15 mm. The
magnification was 60x. Before SEM images were made, the compacts were stored overnight in a closed container with a few Osmium tetroxide crystals for evaporation to obtain in a better contrast between the resin and the starch in the images.

### 3.2.5 Image analysis

Matlab 7.0.232 R2006a (The MathWorks Inc, Natick, USA) and the DIPimage toolbox version 1.5.3 (Quantitative Imaging Group, Faculty of Applies Sciences, Delft University of Technology, The Netherlands) [22] were used for the image analysis.

The first step in image analysis was the removal of small irregularities in the starch grains so that the borders between the grains and the pores would be clearly defined, while small artefacts caused by the use of the microtome were removed. This was done by using a separable bilateral filter [23]. The bilateral filter replaces each pixel value by a weighted sum of its neighbours. The weighting depends on the product of a proximity measure in space (x,y distance) and intensity (pixel value). Both proximities use a Gaussian weighting that decay from the current pixel. The scales (standard deviations) of the two Gaussians were set to respectively 3 pixels and 0.7 times the full-width at half its maximum (FWHM) of the distribution of the pixel values. The FWHM was measured in the grey-value histogram of the image. The histogram shows one great Gaussian shaped peak, with tails to the left and right representing respectively the dark (empty) and with (filled) pore space. The tails have no effect on the measured peak width. The filter’s spatial scale is set just large enough to cover the scratches and the intensity scale is set such to encompass noise and scratches in the grains, but to exclude pixel values from across the grain boundary. Hence, the noise is suppressed, but the transitions between grain and pores are preserved (unaltered).

Secondly, the local porosity of the images was determined by counting the white pixels and the black pixels. The segmentation relies on the histogram of the bilateral filtered image. We again measured the position of the peak and its FWHM. We then labelled all pixels that were respectively lower or higher than 1.25 times the FWHM of the peak as black (empty pores) or white (filled pores).

In the images of the compacts with a low porosity (i.e. values approaching 0%) it could be seen that the resin had not penetrated the pores of the compacts. Therefore, the local porosity in these compacts was calculated as the percentage of black pixels only. In the compacts with the intermediate porosity (approx. 13%) and high porosity (approx. 22%), the resin had penetrated the pores, at least partly. Therefore, the local porosity in these compacts was calculated as the percentage black and white pixels of the total number of pixels in the image.
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The principle of the quotient of the number of transitions (Q) was described earlier [18]. In the present research we made use of the same principle. However, the number of transitions was calculated in the filtered gray-scale image. By doing so, the pores with a higher contrast between the pore and the grain are more important for the calculation of Q than the pores with only a small contrast between the pore and the grain. This method was chosen since it was believed that pores with a higher contrast between the pore phase and the grains, were deeper pores i.e. larger in the third dimension and are considered to have a more pronounced effect on the mechanical strength. The number of transitions was calculated as the sum of the (absolute) change in pixels value between all adjacent pixels in one direction (either y and x or z and x). The quotient number of transitions was then calculated according to the following equations. For the

plan images: \[ Q_P = \frac{N_{Ty}}{N_{Tx}} \] (1)

for the elevation images:

\[ Q_E = \frac{N_{Tz}}{N_{Tx}} \] (2)

\( Q_P \) or \( Q_E \) Quotient of the number of transitions in [Plan or Elevation] image(s)

\( N_{Ty} \) Sum of the absolute change in pixel value between all adjacent pixels in the y-direction

\( N_{Tx} \) Sum of the absolute change in pixel value between all adjacent pixels in the x-direction

\( N_{Tz} \) Sum of the absolute change in pixel value between all adjacent pixels in the z-direction

3.3 Results

3.3.1 Mechanical strength

Figure 2 shows some force-displacement curves of the crushing of starch cubes with different porosities. Some images of the fractured cubes are also shown to illustrate the result of the different behaviour during fracture. Figure 2a shows the curves for crushing in the x-direction and figure 2b shows the crushing in the z-direction. It is indicated which points are defined as yield point (the first maximum or the intersection of the regression lines of the first and the second linear part of
the curve) and at which points fracture occurred. The shapes of the curves change dependent on the porosity. With increasing porosity, the yield point becomes less

Figure 2: a. Force displacement curves of crushing in the x-direction of cubes with a porosity of 0%, 6%, 11%, 15%, and 22%. Arrows indicate yield points and the ‘x’ indicates where fracture occurred. The images depict cubes of a porosity of 0%, 11%, and 22% after crushing. b. Force displacement curves of crushing in the z-direction of cubes with a porosity of 0%, 6%, 10%, 15%, and 22%. Arrows indicate yield points and the ‘x’ indicates where fracture occurred. The images depict cubes of a porosity of 0%, 10%, and 22% after crushing.
and less pronounced and fracture occurs at lower forces. Figure 3 shows the crushing force (figure a) and the yield strength (figure b) in the x-direction and the z-direction at different porosities. The crushing force decreases with increasing porosity. However, at all porosities the crushing force was higher when the tablets were crushed in the z-direction. For both directions the relation between crushing force and porosity showed an exponential relation with an R-squared value of 0.99. The yield strength of the specimen also decreases with increasing porosity. However, at porosities below 10% there is no difference in the yield strength measured in the x- or z-direction. Below a certain porosity the compacts do not break anymore, but only yield.

Figure 3: a. Crushing strength versus porosity, calculated out of weight and volume, in the x-direction and the z-direction. b. Yield strength versus porosity, calculated out of weight and volume in the x-direction and in the z-direction.
3.3.2 Image analysis

Figure 4 shows some original plan and elevation images from compacts with low, intermediate and high porosity. All images are taken from the 0 mm plane. Pores that are filled with resin are white, unfilled pores are black, and the starch grains have an intermediate gray intensity. Resin has not penetrated all the pores, especially in the compacts with the lowest porosity. The local porosity determined with image analysis was slightly higher than the porosity determined out of weight and volume (figure 5). Due to a lower surface roughness on the 3.5 mm plane, the local porosity was lower than at the 0 mm plane (note that the 3.5 mm plane was made visible by removal of material and subsequently polished, whereas for the 0 mm plane only the microtome was used). Tablets with a porosity of 0% as calculated out of volume and weight of the tablet were not completely transparent indicating that the actual porosity was not zero. This is in agreement with the results found with image analysis that also indicate that the porosity of the densest compacts is somewhat above 0%.

It can also be seen in figure 4 that there is no orientation in the plan images, while the pores in the elevation images seem to be mainly oriented along the x-direction. For the plan images no preferential direction of the pores was expected since the direction in which the image was taken was the same as the direction of compression. Visual inspection of the images confirmed that there was no preferential direction of the pores. This would mean that the quotient of transitions equals unity. However, this is not the case as can be seen in figure 6 which shows the quotient number of transitions for the plan and the elevation images. This can be caused by the fact that the images are made with a scanning electron microscope. The transitions in the scanning direction could be less sharp than the transitions perpendicular to this direction. This could mean that even in images of an isotropic structure a quotient of transitions lower than unity is found.

There is a significant difference in the quotient of transitions between the plan and the elevation images (p< 0.01, Mann-Whitney test, SPSS 12.0.1). This applies to all porosities and at both locations in the tablet except for 0% at the 3.5 mm plane (from this plane, only three elevation images could be used because of technical problems with the other six images). A higher quotient in the elevation images than in the plan images means that the elevation images have relatively more transitions in the z-direction (see equation 1 and 2). This means that the pores are preferentially oriented in the x-direction (perpendicular to the direction of compression) which can also be seen with the naked eye in the images in figure 4.
Figure 4: Original plan (a.) and elevation (b.) images of starch cubes with 0% porosity (upper), 13% porosity (middle), and 24% porosity (lower). All images are taken from the 0 mm plane.
3.4 Discussion

3.4.1 Pore direction
The observation that the pores are mainly oriented in the x-direction is probably caused by stress relaxation. Pregelatinized starch is a ductile material which shows both visco-elastic deformation during compaction and always some elastic recovery afterwards [24]. The high moisture content facilitates deformation of the material [25, 26]. This deformation behaviour combined with uni-axial compression will result in pancake like shaped particles. When the decompression speed is extremely low, the porosity expansion is very little [24], keeping the pancake like stacking intact. In images of tablets with a low porosity a large number of transitions in the z-direction (direction of compression) can therefore be seen, corresponding to a large difference in quotient of transitions between the plan and the elevation images. For the higher porosities the structure is less dense, resulting in a lower number of transitions in the z-direction and consequently a smaller difference in quotient of transitions between the plan and the elevation images.

3.4.2 Crushing force
It is known that when a body containing fine cracks is subjected to compressive stress, the fine cracks extend parallel to the compression axis causing failure planes parallel to the compressive stress [27]. If the cracks are slightly off with respect to the direction of the applied load, wing cracks appear along the loading direction, splitting the material into slender columns which then fail [27, 28]. It is therefore not difficult to imagine that the larger the dimensions of the cracks along the compaction direction, the lower the crushing force will be when crushed in compression. This is why the crushing force of the starch cubes in the x-direction is much lower than the crushing force in the z-direction (see figure 3a). Apparently, the pores in the cubes (which are mainly oriented in the x-direction) act as some sort of quasi cracks.

Another observation supporting this hypothesis is that the fracture of the starch cubes when crushed in the x-direction showed failure planes parallel to the compressive stress especially at the highest porosity (see figure 2a). These are probably caused by the opening of the pores in the x-direction. When the cubes were crushed in the z-direction the fragments of the cube after fracture more looked like slender columns after failure (figure 2b). This could indicate wing crack development during crushing in the z-direction.
3.4.3 Yield strength

There was no difference in yield strength between the x-direction and the z-direction of the cube. There was neither a difference in porosity measured in the plan images and in the elevation images (figure 5). Since yielding is a material property, yielding does not depend on the direction of the pores, but on the pore fraction (porosity) in the cross section. Because the porosity in the plan images is similar to the porosity measured in the elevation images, it is not surprising that there was no difference in yield strength between the x-direction and the z-direction. The explanation for the observation that the yield strength decreases with increasing porosity is the same. With increasing porosity, the cube consists of less material resulting in a lower yield strength of the cube.

At porosities higher than 12% the values for the yield strength in the x-direction and z-direction deviate more from each other, but it is questionable whether at these high porosities a yield strength is present at all, because the fracture shows more brittle behaviour with increasing porosity. In case of brittle fracture no plastic deformation takes place and thus no yielding point can be defined.

Figure 5: Local porosity as calculated with image analysis in the images taken from 0 mm from the size and from images taken from 3.5 mm from the side.
3.5 Conclusion

The anisotropy in pore structure in a cubic starch compact could be detected with image analysis. The different compressive forces at which fracture occurred in the x-direction and in the z-direction could be explained with these results. The yield strength of the cube was not dependent on the pore direction. It was thus shown that the pore direction influences the force at which fracture occurs, but does not influence the yield strength of the compact.
3.6 References


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