Chapter 4

The influence of particles of a minor component on the matrix strength of sodium chloride

Summary

This chapter deals with the matrix strength of sodium chloride particles in pure sodium chloride tablets and in tablets compressed from binary mixtures of sodium chloride with low concentrations pregelatinised starch. Because this study concerns the strength of the sodium chloride matrix, the tablet strength is reflected as a function of the sodium chloride volume fraction in the tablet. Starch particles in the mixture tablets decrease the sodium chloride volume fraction-tensile strength relation compared with that of pure sodium chloride tablets. To determine the contribution of the sodium chloride matrix to the tablet strength, the starch particles are removed from the mixture tablets by a heat treatment. Determination of the strengths of these heat-treated tablets reveals that the sodium chloride matrix strength determines the tablet strength of mixture tablets containing a single matrix of sodium chloride particles. The decrease of the sodium chloride matrix density in the three different tablets (pure sodium chloride tablets, mixture tablets and heat-treated tablets) is reflected by an increase of the median pore size. The matrix in sodium chloride tablets shows a higher tensile strength to median pore size relation than the matrices in the mixture and heat-treated tablets. Calculations assuming elastic-brittle fracture suggest that the initial presence of starch particles during tablet compaction causes the pores in the matrices of the mixtures and heat-treated tablets to be relatively flat and long. These pores weaken the sodium chloride matrix in the mixture and heat-treated tablets to a larger extent than the shorter more spherical pores formed during compaction of pure sodium chloride.

Keywords: binary mixtures; tablet strength; matrix; median pore size; pore shape.

4.1 Introduction

The tensile strength of a tablet is often considered to be the result of the bonding between particles, which are the building blocks of tablets. Another property that is of relevance for the physical properties of the final tablet is the structure of the tablet. The structure is the resultant of the morphology of the compressed particles, which, together with the interactions between these particles, leads to a coherent tablet.

In a tablet compressed from a mixture of two materials, three different types of interparticle bonding are found: cohesive forces between particles of the first component, cohesive forces between particles of the second component and the adhesive forces between particles of the different components. A change in the ratio of particles of the components in a binary mixture consequently results into a change in interparticle bonding and into a change of the structure in the tablet. The percolation theory, introduced by Stauffer (1) and Leuenberger (2), is commonly used to describe the particle structure in tablets compressed from binary mixtures. Particles of a material form a continuous matrix or exist in finite clusters. The transformation from finite clusters to a continuous matrix at a certain concentration in the tablet is defined as the percolation threshold. The presence of a continuous matrix is of crucial importance for the final strength of a tablet (3).

Tablet compression and relaxation always results in the formation of pores. Fracture mechanics shows that not only pore size, but also pore shape and type of fracture are important factors for the tensile strength (4, 5) and are often as important as the interparticle attraction (6). This is because each individual pore is able to act as a stress concentrator (7, 8, 9).

Studies of tablet strength of binary mixtures have reported contradictory results as an effect of non-identical experimental set-ups (e.g. 10, 11). However, it is mostly found that tablets compressed from binary mixtures show lower strength than calculated from linear interpolation of the tablet strengths of the single components, provided that the porosity has a constant value (12, 13, Ch. 2). The decrease of the tablet strength as a function of the tablet composition is different for every mixture. Apparently, the alterations in either the interparticle attraction or in the total tablet structure are such that they virtually always result in a strength decrease. The objective of this chapter is to study (1) the relation between the structure of a matrix and its strength and (2) the effects of the presence of another, minor, component on the tablet structure. Sodium chloride with a small fraction of air is the material that forms the structure, while the minor compound is pregelatinised starch.
4.2 Materials and Methods

4.2.1 Materials and mixtures

The materials used in this study were sodium chloride (glidant-free material, Akzo Nobel, Hengelo, The Netherlands) and pregelatinised potato starch (Paselli WA4, Avebe, Foxhol, The Netherlands). Because the sodium chloride batch contained coarse particles, the sodium chloride powder was milled (Moulinex, Birmingham, UK). The sodium chloride and pregelatinised starch samples were sieved with an Alpine Air Jet Sieve (Alpine, Augsburg, Germany) using USA Standard testing sieves (W.B. Tyler Inc., Mentor, OH, USA) in order to obtain the particle fraction between 106 and 212 µm. Prior to use or measurements, the powders were stored at 20°C and 60% RH for at least 4 days. The true densities of the conditioned 106-212 µm fractions were measured at a temperature of 20°C by helium pycnometry (Quantachrome, Syosset, NY, USA). The true densities of the 106-212 µm fraction of sodium chloride was 2239 kg·m⁻³ and of pregelatinised starch 1486 kg·m⁻³. The binary mixtures (2.5-80% v/v) were blended in a Turbula mixer (Model 2P, W.A. Bachofen, Basle, Switzerland) at 90 rpm for a period of 15 min.

4.2.2 Tablets

Flat-faced compacts of 500 mg and a diameter of 13 mm were prepared on a compaction simulator (ESH, Brierley Hill, UK) at a temperature of 20 °C and a relative humidity of 60%. The applied compaction pressures varied between 10 and 350 MPa. The die and punches were lubricated by dusting with magnesium stearate. While the lower punch was stationary during compaction, the upper punch displacements were sine waves with different amplitudes to vary the applied compaction pressures. The average punch speed during compaction was 3 mm·s⁻¹. After a constant ejection time of 10 s, the relaxation period was at least 14 hours in a controlled climate chamber (Heraeus, Hanau, Germany) at 20°C and 60% RH.

The final dimensions of the tablets were measured with an electronic micrometer (Mitutoyo, Tokyo, Japan) and the weights were determined with an analytical balance (Mettler-Toledo, Greifensee, Switzerland). Tablet strength was measured with a Schleuniger 6D strength tester (Dr. Schleuniger Productronic, Soloturn, Switzerland). The tensile strength of tablets was calculated according to Fell and Newton (14). The relation between the tensile strength and the tablet porosity was determined for both pure materials and for every binary mixture containing a different percentage...
pregelatinised starch. The porosity-tensile strength relation was fitted using the Ryshkewitch-Duckworth relation (15, 16) using data of at least 40 tablets with different porosities. Using this fit, a tensile strength of tablets with a porosity of 15% was calculated for each different blend.

4.2.3 Heat treatment

To determine the structure formed by sodium chloride particles inside the tablet structure, three tablets of each mixture with a porosity of 15% (± 0.5%) were put in a muffle furnace (Naber Industrieofenbau, Bremen, Germany). In tablets compressed from pregelatinised starch and sodium chloride, the difference between the self-ignition temperature of starch at 300°C and the melting temperature of sodium chloride at 800°C (17) enables the starch particles to be burned out, leaving the sodium chloride particles behind inside the tablet structure. Details of the heat treatment are described in Ch. 3. Dimensions, masses and tablet strengths of the tablets after the burning experiment were determined as described in sec. 4.2.2.

4.2.4 Pore size distributions

The pore size distributions of tablets compressed from the single materials and the binary mixtures and of the heat-treated tablets were measured by mercury intrusion porosimetry (Micromeritics, Model Autopore 9220, Norcross, GA, USA). Three tablets with a porosity of 15% (± 0.5%) or three heat-treated tablets were used for the determination of the pore size distribution of each binary mixture. Three tablets with equal porosity were used to measure the pore size distributions of sodium chloride tablets at each different sodium chloride volume fraction. Conditions and pressure ranges used during mercury intrusion measurements are described in Ch. 3.

4.2.5 Disintegration

The disintegration times of tablets were tested with a disintegration test unit according to the USP 24 test <701> (Model ZT 42, Erweka, Heusenstamm, Germany). To determine the disintegration time of tablets compressed from each blend containing a different percentage pregelatinised starch, the disintegration time of 5 tablets with a porosity of 15% (± 0.5%) was measured: the mean value is presented. The tests were conducted in 1 L tap water maintained at 37°C and with no discs in the individual test compartments.
4.3 Results and Discussion

4.3.1 Structure-strength relationships

The tensile strength of a tablet is the consequence of its structure created by consolidation and relaxation. A frequently used comparison between the tablet structure and its strength is the porosity-tensile strength relation. Fig. 4.1a depicts this relation for tablets compressed from pure sodium chloride and from binary mixtures of sodium chloride with low concentrations of pregelatinised starch, respectively. All profiles show the same shape, but are numerically different. The pure sodium chloride tablets consisting of only a matrix of sodium chloride particles give the highest strength. The addition of the minor component (starch) to sodium chloride decreases the strength. Larger amounts of the minor component weaken the structure of the tablets to a larger extent.

![Graph](image_url)

*Fig. 4.1a. Tensile strength as a function of the tablet porosity of tablets compressed from (◊) sodium chloride, (Δ) binary mixtures of sodium chloride and 2.5% pregelatinised starch and (×) binary mixtures of sodium chloride and 15% pregelatinised starch.*

This study is performed to determine the effect of the presence of a minor component on the sodium chloride structure. Therefore, it has been decided to correlate the alterations in strength to the volume fraction of sodium chloride rather than to total relative density or to porosity. The sodium chloride volume fraction is calculated as the fraction of the whole tablet volume, including air.
Fig. 4.1b. Tensile strength as a function of the tablet’s sodium chloride volume fraction. Symbols as in Fig. 4.1a.

Fig. 4.1b shows this sodium-chloride-volume-fraction to tensile strength relation of the tablets given in Fig. 4.1a. As described for the porosity-tensile strength relation, the sodium-chloride-volume-fraction to tensile strength relations show lower tensile strengths as a result of the addition of starch to the sodium chloride structure. Fig. 4.1b shows that the tensile strength becomes a function of the sodium chloride only when the sodium chloride volume fraction is higher than about 0.82. It is not possible to make a clear distinction between these three types of tablets. In contrast, when the sodium chloride volume fraction is lower than about 0.82, the tablets that were compressed in the presence of starch show equal tensile strengths. Apparently, starch has no concentration-dependent influence on the strength of the sodium chloride matrix in this density range. However, starch must have had an effect during compression, because the tablets that were compressed in the presence of starch are always weaker than the tablets compressed from pure sodium chloride at equal sodium chloride fraction.

In order to study the effects of starch on the matrix strength of sodium chloride in more detail, the starch particles were removed from tablets compressed from mixtures containing low amounts of starch. The individual tablet structure formed by the sodium chloride particles was obtained by burning out the starch particles in an oven. Because sodium chloride is a material that always forms a tablet structure containing a fraction of air, the air fraction before removal of the starch particles was fixed at 0.15 for all tablets compressed from mixtures. Removal of increasing amounts of starch...
from the mixture tablets results in heat-treated tablets consisting of only the sodium chloride matrix and increasing air fractions.

The sodium chloride volume fraction-tensile strength relation of these heat-treated tablets is given in Fig. 4.2 and is compared with the relation of the pure sodium chloride tablets (same as depicted in Fig. 4.1b). The tensile strength of the heat-treated tablet with a sodium chloride volume fraction of 0.85, i.e. no starch particles were present in the tablet before the heat treatment, shows hardly any difference with that of the sodium chloride tablet with equal sodium chloride volume fraction. This indicates that the heat treatment has a negligible effect on the sodium chloride matrix and its strength. This is supported by the mercury intrusion porosimetry measurements of the pure sodium chloride tablets reported in Ch. 3.

![Fig. 4.2. Tensile strength as a function of the sodium chloride volume fraction of (⊙) sodium chloride tablets, (△) heat-treated tablets and (×) tablets compressed from binary mixtures of sodium chloride and pregelatinised starch. Error bars are the 95% confidence intervals of the heat-treated tablets.](image)

As can be observed from Fig. 4.2, the tensile strengths of the heat-treated tablets are systematically lower than the tensile strengths of the sodium chloride tablets. Apparently, the sodium chloride matrix in the heat-treated tablet has been weakened by the initial presence of starch particles. The heat-treated tablets with sodium chloride volume fractions of 0.60 and lower did not retain their original dimensions and showed no strength. Apparently, the sodium chloride particles cannot form a continuous matrix any longer in these tablets compressed from mixtures. For this reason, in tablets compressed from blends of sodium chloride and pregelatinised
starch, a sodium chloride volume fraction between 0.64 and 0.60 can be considered as the percolation threshold of the sodium chloride matrix.

The third type of tablets shown in Fig. 4.2 are the tablets compressed from the mixtures of sodium chloride and starch with an air fraction of 0.15 without the heat treatment; the starch particles are still present in the tablets. Tablets consisting of high volume fractions sodium chloride (and consequently low volume fractions starch) have the same decrease in tensile strength as the heat-treated tablets. The tablet strengths are comparable and are independent of the presence of the starch particles in the tablet structure. From this observation it can be concluded that the strength of the sodium chloride matrix entirely determines the tablet strength. The contribution of the adhesion forces of the starch particles to the matrix strength and the tablet strength can be considered as zero.

In contrast, tablets compressed from mixtures with a sodium chloride volume fraction lower than 0.76 show higher tensile strengths than the heat-treated tablets with the same initial composition. Obviously, the tensile strength of these tablets is not determined anymore by the strength of sodium chloride matrix. A change in tablet structure terminates the domination of the matrix strength of sodium chloride particles. A disintegration test of tablets can support this suggestion. Luginbühl and Leuenberger (18) showed that the minimum disintegration time for tablets containing starch as a disintegrant is found for tablets in which starch particles start to form a matrix. Table 4.1 lists the disintegration times of tablet compressed from the mixture of sodium chloride and pregelatinised starch with an air fraction of 0.15.

<table>
<thead>
<tr>
<th>Sodium chloride volume fraction (-)</th>
<th>Average disintegration time (s). Standard deviation in parentheses.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>206 (7)</td>
</tr>
<tr>
<td>0.83</td>
<td>200 (11)</td>
</tr>
<tr>
<td>0.81</td>
<td>99 (13)</td>
</tr>
<tr>
<td>0.79</td>
<td>69 (10)</td>
</tr>
<tr>
<td>0.76</td>
<td>34 (3)</td>
</tr>
<tr>
<td>0.72</td>
<td>49 (5)</td>
</tr>
<tr>
<td>0.68</td>
<td>75 (11)</td>
</tr>
<tr>
<td>0.64</td>
<td>323 (64)</td>
</tr>
<tr>
<td>0.60</td>
<td>1930 (200)</td>
</tr>
<tr>
<td>0.51</td>
<td>5102 (250)</td>
</tr>
</tbody>
</table>
The table shows the shortest disintegration times for tablets with a sodium chloride volume fraction of $\pm 0.76$. Both the end of the influence of the sodium chloride matrix on the tablet strength (Fig. 4.2) and the disintegration test prove that the percolation threshold of the starch matrix is found in tablets with a sodium chloride volume fraction of $\pm 0.76$.

Chapter 3 of this thesis states that besides the changes in particle structure, the pore size distributions in tablets compressed from mixtures also change as a function of the tablet composition. Because of the pores’ ability to concentrate stress, pore characteristics are very important for changes in tablet and matrix strength.

### 4.3.2 Pore size-matrix strength relationships

Tablets consist of a fraction solids and a complementary fraction of air (porosity). The air fraction is built up from pores with different sizes and is represented by the pore size distribution.

![Fig. 4.3. Pore volume size distributions of sodium chloride tablets with sodium chloride volume fractions of (Φ) 0.85, (Δ) 0.83 and (×) 0.79.](image)

In Fig. 4.3, the pore size distributions measured by mercury intrusion porosimetry are given for sodium chloride tablets containing different volume fractions of sodium chloride. Upon decreasing sodium chloride volume fractions, the pore size distributions of tablets show a shift to larger pores while the distribution of the small pore sizes ($< 5 \, \mu m$) hardly changes in size and number. The pore size distributions of tablets compressed from mixtures of sodium chloride and pregelatinised starch also show a change in the larger pores, while the smaller pores stay constant in size and...
number (Ch. 3). To express this change in pore size distribution in a single value, the median pore diameter was calculated for all tablets containing a sodium chloride matrix.

Fig. 4.4a shows the sodium chloride volume fraction-median pore diameter relation of the pure sodium chloride tablets, tablets compressed from the mixtures and heat-treated tablets, all containing a single matrix formed by sodium chloride particles. Tablets containing also a matrix of starch particles are not shown in Fig. 4.4a in comparison with Fig. 4.2. Every type of these tablets shows an increase of the median pore diameter as an effect of the decreased sodium chloride volume fraction. The sodium chloride tablets have higher median pore diameters than the tablets compressed from the mixtures and the heat-treated tablets, proving the presence of larger pores in the sodium chloride matrix. Although the heat-treated tablets and the tablets compressed from the mixtures have identical sodium chloride matrices, the heat-treated tablets show a higher median pore diameter than the tablets compressed from the mixtures. Apparently, the removed starch particles are slightly larger than the original pores, causing an increase of the median pore diameter. This is confirmed by Ch. 3.

![Graph](image_url)

*Fig. 4.4a. Median pore diameters measured by mercury intrusion porosimetry as a function of the sodium chloride volume fraction. Symbols as in Fig. 4.2.*

The theory of fracture mechanics describes that the combination of size, orientation and shape of the pores determines their influence on the tensile strength of the tablet. In general, pores with the largest length perpendicular to the stress profile in the tensile strength measurement cause the failure of the material, as these pores give the highest stress concentration. Unfortunately, the exact pore dimensions (length and
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diameter) cannot be determined by mercury intrusion porosimetry. This technique measures the opening to the pore volume; thereby it underestimates in many cases the actual pore dimensions. However, closer packing of the particles in the tablet will decrease the pore opening as well as the pore dimensions (19). As a consequence, a decrease of the median pore diameter mainly reflects a decrease of the dimensions of the larger pores.

The relation between the median pore diameter and the strength of the tablets depicted in Fig. 4.4a is shown in Fig. 4.4b. The decreasing effect of larger median pore diameters on the sodium chloride matrix strength is valid for all three types of tablets. This phenomenon has also been reported for compacts compressed from other materials (20) and from ceramic materials (21). The heat-treated and mixture tablets show a similar relation between the median pore diameter and the tensile strength. These two types of tablets have the same sodium chloride matrices that determine the tablet strengths (Fig. 4.2). On the contrary, the sodium chloride tablets show higher tensile strengths at comparable median pore diameters. This indicates that the initial presence of starch particles during compaction of the binary powder mixtures affected the influence of the median pore size on the sodium chloride matrix strength.

![Graph showing the relationship between median pore diameter and tensile strength](image)

*Fig. 4.4b. Tensile strength of sodium chloride matrix as a function of the median pore diameter. Symbols as in Fig. 4.2.*
4.3.3 Pore shape in sodium chloride matrix

The effective influence of the median pore diameter on the sodium chloride matrix strength was found to be different for the sodium chloride matrices in the different tablets (Fig. 4.4b). The effective influence on the tensile strength is not only dependent on the size, but also on other factors, like pore shape.

It would be interesting to calculate the effective pore dimensions in the different sodium chloride matrices and compare the results with Scanning Electron Microscopy photographs. However, as already mentioned, mercury intrusion data are interpreted as round pore openings based on mercury intrusion pressures. The median pore diameter gives an interpreted size of the large pores rather than the real large pore dimensions, i.e. length and diameter. Implementation of the median pore diameter as the large pore dimension results in unreliable and imprecise effective pore dimensions. However, the median pore diameter still is a useful indication of the size of the large pores.

To give an estimation of the pore shapes in the individual sodium chloride matrices, the pore shapes were calculated according to the Inglis-Griffith theory of elastic-brittle fracture (4, 22). Although sodium chloride and starch are known as plastically deforming materials, compacted powders behave brittle under tensile loading (23). This means that the tablet fracture is not preceded by any significant plastic deformation.

The relation between the pore shape and decrease of the material strength derived by Inglis and Griffith is reflected by the equation:

\[ \frac{\sigma_{\text{max}}}{\sigma_{\text{measured}}} = 1 + 2\sqrt{\frac{l}{\rho}} \]  

(1)

where \( \sigma_{\text{max}} \) is the theoretical maximum tensile strength, \( \sigma_{\text{measured}} \) is the measured tensile strength, \( l \) is the total length of the pore and \( \rho \) is the diameter of the curvature of the pore tip. The pores are taken to be as ellipsoidal holes with the mathematical equation:

\[ \rho = \frac{d^2}{l} \]  

(2)

in which \( d \) is the diameter of the pore. The advantage of taking pores to be ellipsoidal holes is that the pore shape can vary from a spherical hole \( (l = d) \) to a sharp crack \( (l >> d) \).
By rewriting eq. 1, it is possible to describe the pore shape, expressed by the length-to-diameter ratio of the pore, \( l/d \):

\[
\frac{l}{d} = \left( \frac{\sigma_{\text{max}}}{\sigma_{\text{measured}}} - 1 \right) / 2
\]  

(3)

To be able to calculate the pore shapes in the different sodium chloride matrices, \( \sigma_{\text{max}} \) has to be determined. The theoretical maximum tensile strength \( \sigma_{\text{max}} \) is the failure of atomic bonds across an atomic plane. A fracture plane will arise when the stress at the tip of the pore reaches \( \sigma_{\text{max}} \). The theoretically correct value of \( \sigma_{\text{max}} \) would be the tensile strength of a single sodium chloride crystal. Since this value is hard to obtain, the tensile strength at zero tablet air fraction from the Ryskewitch-Duckworth equation of the sodium chloride tablets (\( \sigma_{\text{max}} = 11.4 \text{ MPa}, r^2 = 0.976 \)) is considered to provide a good approximation of the maximum theoretical tensile strength. This single value of the maximum theoretical tensile strength was used as maximum tablet strength for all tablets containing the different sodium chloride matrices.

Using this information, the shapes of the pores have been calculated as a function of the sodium chloride volume fraction. Fig. 4.5 gives these pore shapes of the sodium chloride, heat-treated and mixture tablets, all containing a single sodium chloride matrix. The mixture and heat-treated tablets show higher values of the pore shape than the sodium chloride tablets. This suggests that the pores in the first-mentioned tablets are relatively flatter and/or have sharper tips at the endpoints (eq. 2).

![Fig. 4.5. Pore shape expressed as l/d-ratio as a function of the sodium chloride volume fraction in tablets containing a single matrix of sodium chloride particles. Symbols as in Fig. 4.2.](image-url)
The development of these pores can be explained by examining the compaction behaviours of mixtures. As a result of the difference in yield pressure, the softer starch particles are flattened between the rigid sodium chloride particles during the densification of the mixtures (Ch. 2). Relaxation of tablets compressed from these mixtures results in larger pores (Ch. 3), which can be considered to adopt the shape of relatively flat holes. It is expected that these relatively flat pores weaken the sodium chloride matrix to a larger extent than the more spherical shaped pores (eq. 3) formed in tablets compressed from sodium chloride only.

The consequence of this finding is that the extent of particle deformation of softer materials is of importance on the pore shape in the main structure formed by more rigid materials. This difference in rigidity (difference in yield pressure) influences the matrix formation (24) as well as the creation of the pore shape.

### 4.4 References

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