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Paper

# Effect of water on deformation and bonding of pregelatinized starch compacts

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## Abstract

This paper evaluates the tabletting process of pregelatinized starch with different moisture contents on the basis of the stress deformation curve. Simplification of the stress deformation curve enables the amount of elastically stored energy to be calculated. That stored energy, which is the driving force for relaxation of tablets, increases with compaction speed and decreases with increasing water activity of the material. This paper suggests a relation between absorbed water and stored energy. Interparticle bonding, however, also decreases with increasing amounts of adsorbed water. The decrease in stored energy with increasing water activity of the pregelatinized starch tends to produce stronger tablets at higher water activities, whereas the decrease of particle bonding with increasing water activity tends to produce weaker tablets at higher water activities. Given these two counteracting effects, the final tablet strength is a balance between viscoelasticity and bonding, resulting in a water activity where tablet strength has a maximum. In this case, the optimum water activity is about 0.70. © 1997 Elsevier Science B.V.

*Keywords:* Moisture; Particle bonding; Pregelatinized starch; Relaxation; Strength; Tablet; Viscoelasticity; Water activity

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## 1. Introduction

The ability of particulate materials to form tablets depends on their deformation and bonding characteristics. Materials are usually classified as either brittle or plastic, depending on their predominant deformation behaviour. Plastic materials are basically viscoelastic, which is apparent from their sensitivity to changes in strain rate [1]. This means that their consolidation is affected by the speed of compaction. Here, elastic deformation at higher tabletting speeds leads to additional stress relaxation of tablets.

An important group of plastically-deforming materials is represented by amorphous and partially-crystalline polymers like modified starches and modified cellulose. The deformation properties of these materials are often influenced by water, because water acts as a plasticizer in these materials [2]. Bos et al. [3] Rees and Tsardaka [4] studied this effect on some native starches and modified maize starch, respectively. It has been found that a maximum tablet strength exists at a certain water content. It has been suggested that this phenomenon is the result of viscoelastic properties of the material [4]. However, not only does water have an effect on deformation characteristics of particulate materials, but it may have an effect on bonding between particles due to water adsorption by the particles.

This paper expands on the results of a previous publication [5], which demonstrated that the properties

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of a final tablet are predominantly a result of the relaxation phenomena. The elastic energy built up during compression is regarded as the driving force for relaxation. Interparticle bonding is considered the counteracting parameter, preventing a new tablet from extensive expansion. Both the deformation properties and the particle bonding depend on the water content of the material. This study plans to quantify separately, the stress relaxation and bonding of tablets compacted from a model excipient, pregelatinized potato starch.

## 2. Theory

Fig. 1 shows a representative stress–strain curve for a solid in tension (thick solid line) [6]. For an elastic solid, the stress is directly proportional to the strain which represents deformation. The proportionality constant ($E_0^*$) is called Young's modulus, also referred to as the elastic or complex modulus. The modulus is a measure of rigidity or resistance to deformation. The material behaves predominantly in an elastic manner up to a yield point, where the stress is termed the yield stress ($\sigma_c$). Beyond this point the material behaves as a plastic, rather than as an elastic—solid—it flows under practically constant stress. The complex modulus ($E_0^*$) of a compacted material can be measured as a function of the deformation rate using Dynamic Mechanical Analysis (DMA) [7]. The yield stress ($\sigma_c$) of a particulate solid can be derived from compaction experiments by applying Heckel's equation [8,9] to the data.

DMA also enables a distinction to be made between elastic and viscous deformation, quantified by the storage and loss moduli, respectively. The ratio of loss to storage moduli is called damping, which is a measure of the viscoelasticity of the material at small deformations. Usually, small deformations of glassy and crystalline materials are elastic, and values of damping are consequently low. This paper ignores the effects of viscous deformation at small strains.

Knowing both Young's modulus and the yield stress, a simplified stress-deformation curve can be derived by plotting a linear portion with tangent $E_0^*$ up to the yield stress $\sigma_c$, followed by a horizontal portion from a point of 'critical deformation'($\gamma_c$) where yielding starts (thin solid line in Fig. 1) [5].

Consequently, it is possible to calculate the stored elastic energy ($W_{\mathrm{rev}}$) in the deformed material as a function of the deformation rate, this elastic energy being the area under the line with slope $E_0^*$ and strain between 0 and $\gamma_c$ by:

$$W_{\mathrm{rev}} = \frac{1}{2}\cdot\frac{\sigma_c^2}{E_0^*} \qquad (1)$$

A previous study has indicated that the amount of stored energy is the driving force for stress relaxation of tablets [5]. As a result of stress relaxation, there is an increase in porosity after compression. The same paper also reported that the porosity and the stored energy are interrelated by interparticle bonding—the stronger the particle bonding, the smaller the increase in porosity at fixed values of stored energy. Particle bonding can be quantified by relating the tensile strength to the porosity of tablets by means of the Ryshkewitch–Duckworth relation [10]:

$$S = S_0\cdot e^{-k\cdot\epsilon} \qquad (2)$$

where $S$ is the tensile strength of the tablet, $\epsilon$ its porosity, and $S_0$ is the tensile strength at zero porosity. The constant $k$ is a fit constant related to particle bonding, and for this reason called 'bonding capacity'. Tablet porosity completely determines tablet strength, and this relation is not affected by compaction speed and other process parameters [5]. Consequently, both $k$ and $S_0$ are regarded as material constants.

## 3. Materials and methods

The material used was a pregelatinized potato starch (Paselli® WA4, Avebe, Foxhol, The Netherlands). After a drying period of at least 24 h, the material was stored in a climatic test chamber (Heraeus-Vötsch, Balingen, Germany) under controlled humidity for a period of at least 3 days. After this storage time, it was assumed that the water activity ($a_w$) of the starch was equal to the relative humidity of the air.

True density of the material was measured as a function of the moisture content by helium pycnometry using a Quantrachrome pycnometer (Syosset, OH). Moisture content appears to, only slightly affect the true density of the materials (Table 1).

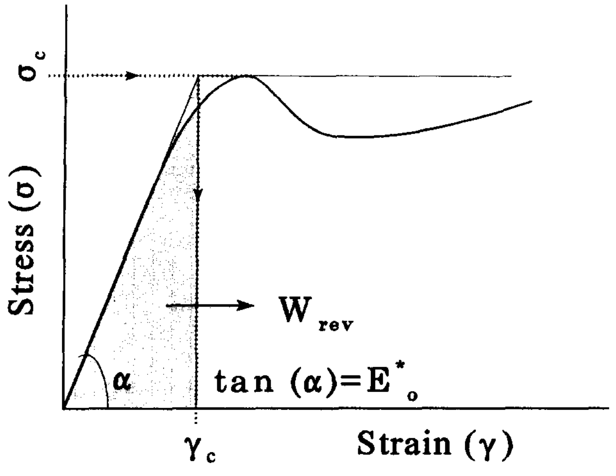

Fig. 1. Stress–strain relation (thick solid line) and simplified relation (thin solid line) of a viscoelastic solid, with yield stress ($\sigma_c$), elastic modulus ($E_0^*$), critical deformation ($\gamma_c$) and stored energy ($W_{\mathrm{rev}}$).

Table 1
True density of pregelatinized potato starch as a function of water activity

| Water activity (-) | True density (kg/m$^3$) |
|---|---|
| 0.22 | 1472 |
| 0.35 | 1461 |
| 0.50 | 1457 |
| 0.60 | 1452 |
| 0.70 | 1438 |
| 0.95 | 1407 |

Viscoelastic properties were assessed by Dynamic Mechanical Analysis (DMA) with a Rheometrics Solids Analyzer (Piscataway, NJ), using the dual cantilever method. The method was previously described in detail [11]. Strips of the test material (60 × 6 × 1 mm) were prepared with a hand press (Paul Weber, Stuttgart, Germany) in a specially designed punch-and-die set. The maximum applied pressure, which was varied experimentally between 15 and 370 MPa, was held constant for about 10 s. After ejection, followed by a relaxation period of at least 16 h the size of the strips were measured with a micrometer and weighed on an analytical balance. The maximum strain in the experiments was 0.01%. Measurements were started at a frequency of 0.5 rad/s and discontinued at a frequency of 100 rad/s. The elastic moduli at zero porosity were calculated as previously described [11].

Flat-faced compacts of 500 mg and a diameter of 13 mm were prepared on a high-speed compaction simulator (ESH, Brierley Hill, UK). During compression the powders were exposed to different climatic condition of 20°C and 50% relative humidity. This short time exposure to other conditions did not lead to weight variations of the powders investigated. Consequently, this did not affect the moisture content of the powders. The maximum applied pressures were from 5 to about 350 MPa. The upper punch displacement profiles were sinewaves with different amplitudes in order to reach different maximum compression pressures. As sinusoidal profiles were used, a complete profile corresponds to $\pi$ rad. Knowing both the compression speed ($v$) and the penetration depth ($A_{\mathrm{comp}}$), it is possible to calculate the angular frequency of the compression ($f$):

$$f = \frac{\pi \cdot v}{2 \cdot A_{\mathrm{comp}}} \quad (3)$$

This makes it possible to correlate DMA to compaction experiments. The average compaction speeds were 3, 30 and 300 mm/s, respectively. The lower punch was stationary during compression. The ejection time was always 10 s. Both the force and the displacement of the upper punch and the lower punch displacement and force were recorded. The resolution of the analogue-to-digital conversion was 0.3 $\mu$m. Punch-to-punch measurements at pressures ranging from 0 to 400 MPa gave variations smaller than 10 $\mu$m. This led to the conclusion that the total error of measurement was less than ± 10 $\mu$m. Corrections were made for elastic punch deformation. The yield stress of the test materials was measured according to Heckel [8,9]. Linear interpolation was performed in the porosity range between 35 and 8%. After a relaxation period of at least 16 h, tablet dimensions were measured with a micrometer and the tablets were weighed on an analytical balance. The crushing strength of the tablets was measured with a compaction simulator. Profiles with a linear speed of 0.25 mm/s were created, and the maximum applied pressure was recorded on an $XY$-recorder (Kipp and Zonen, Delft, The Netherlands). The tensile strength of the tablets was calculated according to Fell and Newton [12].

## 4. Results and discussion

Tablets were compressed from pregelatinized potato starch with a range of moisture contents—at compaction pressures from 10 to 350 MPa at three different compaction speeds. Fig. 2 shows the relation between tensile strength and compaction pressure of tablets with water activities of 0.50 and 0.95. Tablets compressed from powders with other water activities gave similar profiles, but were numerically different. Up to a certain compaction pressure value (depending upon water activity), the strength of all tablets increased with compaction pressure. At higher pressures, a constant (maximum) value was obtained, that depended on compaction speed and water activity of the material (Fig. 2). A previous study has indicated that the final strength of a tablet compressed from this material is principally a result of the relaxation phenomena: the minimum volume of a tablet under pressure is much lower than that of the same tablet after relaxation [11]. The minimum attainable porosity, and hence the maximum strength, of tablets is primarily a result of material compression during consolidation leading to values of tablet porosity which are independent of the compaction pressure. The values of the maximum attainable tensile strength are plotted versus water activity at three different compaction speeds in Fig. 3. The figure shows the effect of both compaction speed and water activity of the material on maximum attainable tablet strength. The dependence upon speed of compaction illustrates that viscoelastic properties play a role.

As stated previously [11], viscoelastic properties of materials have been characterized with dynamic mechanical analysis. Fig. 4 indicates decreasing complex modulus ($E_0^*$) with increasing water activity of the material and an insignificant effect of compaction speed on the complex modulus. The adsorption isotherm of

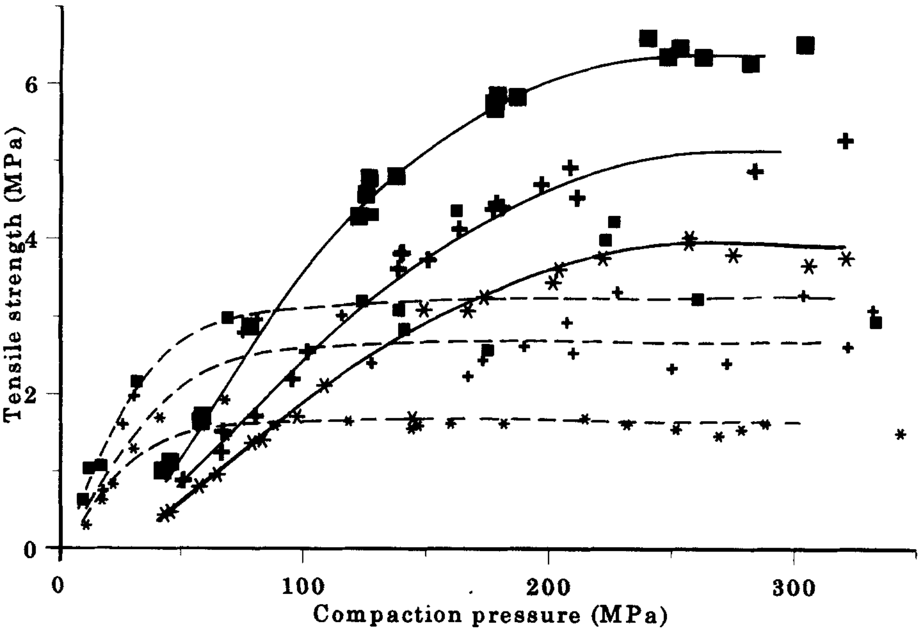

Fig. 2. Tensile strength of pregelatinized potato starch tablets as a function of compaction pressure at three different compaction speeds. Symbols: (■), 3 mm/s; ( + ), 30 mm/s; (*), 300 mm/s. Large symbols represent the relation of the material with a water activity of 0.50, small symbols that of the material with a water activity of 0.95.

pregelatinized potato starch (Fig. 5) provides an explanation for the effect of water on the elastic modulus of the material. Sorption data were analysed using the equation developed by Guggenheim, Anderson and De Boer [13], which is frequently applied to describe sorption of water by starches:

$$\frac{\omega}{\omega_m} = \frac{C_g \cdot K \cdot a_w}{(1 - K \cdot a_w) \cdot (1 - K \cdot a_w + C_g \cdot K \cdot a_w)} \tag{4}$$

where $\omega$ is the amount of sorbed water, $\omega_m$ the amount of sorbed water present as a monolayer, and $C_g$ and $K$ constants. Least-square fit of the sorption data with Eq. (4) shows that there is monolayer adsorption when the weight fraction of water equals 0.09. According to Fig. 5, this corresponds to a water activity of 0.35. At lower water content, there are a larger number of hydrogen bonds between particles, giving larger particle attractions and strong bonds. Consequently, the complex

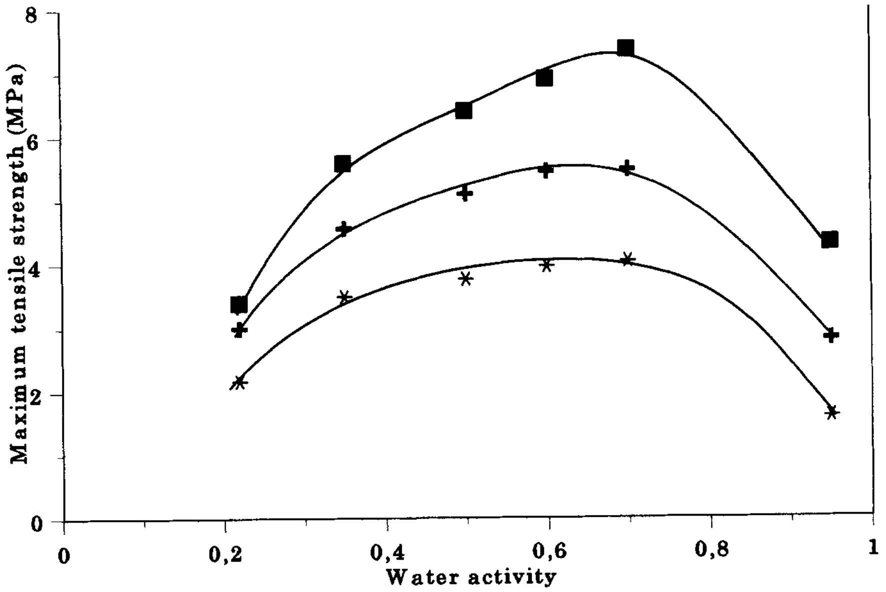

Fig. 3. Maximum attainable tensile strength as a function of water activity at different compaction speeds. Symbols: (■), 3 mm/s; ( + ), 30 mm/s; (*), 300 mm/s.

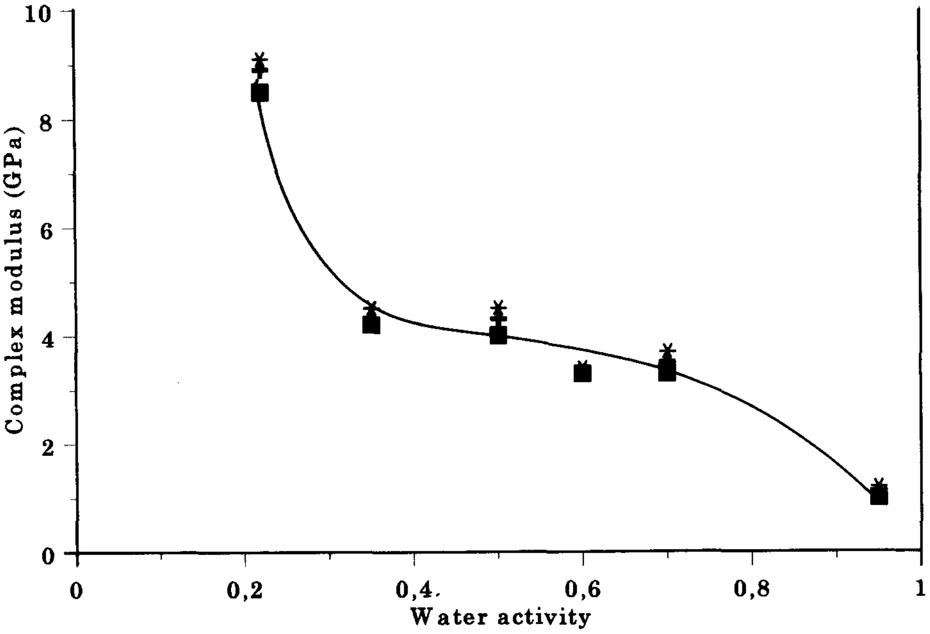

Fig. 4. Complex modulus at different water activities and compaction rates. Symbols as in Fig. 3.

modulus of the dry material is larger. At higher water activities fewer hydrogen bonds exist between powder particles, resulting in lower values for the complex modulus. Therefore, the measurement of the elastic modulus of compacts of different water activities essentially measures the rigidity of bonding.

According to the Gordon–Taylor equation [14], the glass transition temperature of starch equals room temperature (20°C) when the water fraction is 0.19 which, according to Fig. 5, corresponds to a water activity of 0.80. This means that material with a water activity of 0.95 is in the rubbery state—such material would possess a low elastic modulus as illustrated in Fig. 4.

Deformations recorded in DMA experiments are small, causing reversible, elastic strains, expressed by low values of damping. During compaction of powders, however, materials are forced to yield. A frequently-used parameter that gives information about large deformation of solids is the yield stress ($\sigma_c$). Fig. 6 depicts yield stress data at various moisture levels, measured at

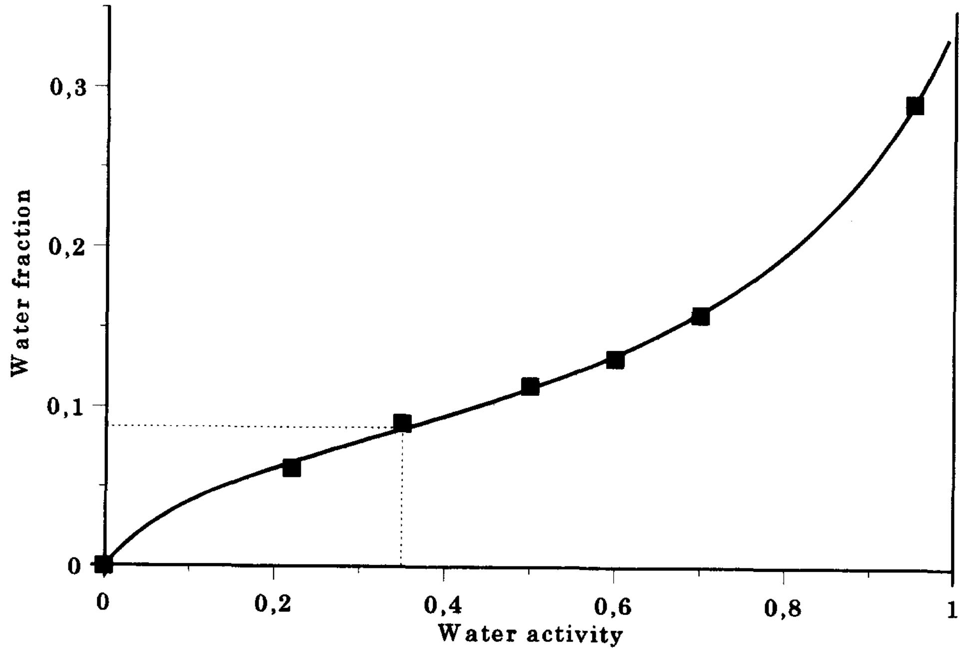

Fig. 5. Sorption isotherm of pregelatinized potato starch. The solid line represents the least square fit with the equation of Guggenheim, Anderson and De Boer, the dotted line gives the equivalent monolayer adsorption.

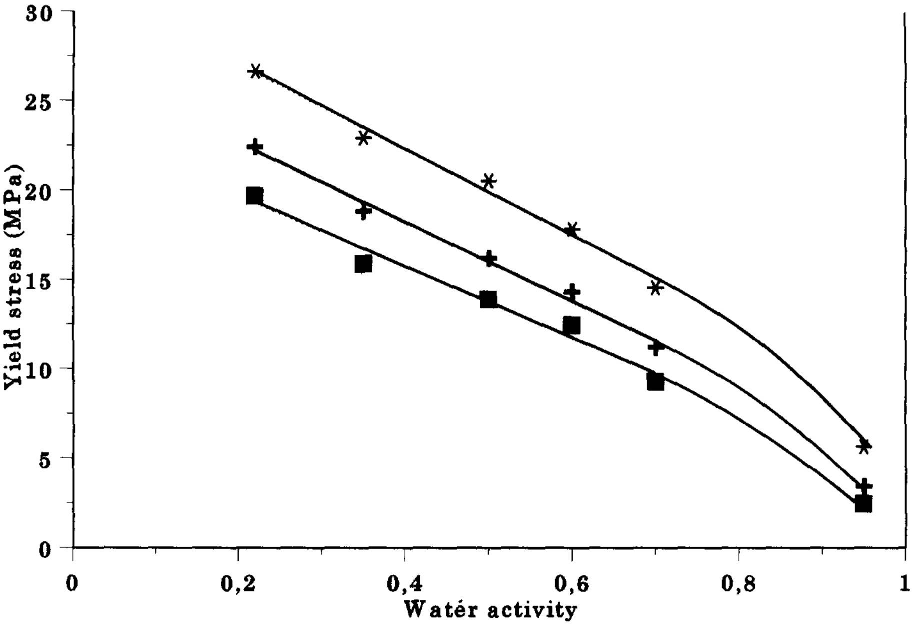

Fig. 6. Yield stress of pregelatinized starch at different water activities and three compaction speeds. Symbols as in Fig. 3.

three compaction speeds. The results show that the yield stress decreases with increasing water activity, and increases with compaction speed. The effect of compaction speed on yield stress was explained by Van der Voort Maarschalk et al. [11]. Fig. 6 shows a linear relationship between water activity and yield stress, as long as the material is in the glassy state, i.e. below a water activity of 0.80. When the material is in the rubbery state ($a_w = 0.95$), the yield stress is lower and deviates from linearity. The effect of water is a direct result of the sorption and associated molecular interaction of starch and water molecules. It would appear that, as a consequence, water acts as a plasticizer. This would explain how the presence of water causes a decrease in yield stress.

The simplified stress–strain relation (Fig. 1) allows calculation of the amount of energy that is stored during compression. Fig. 7 shows that the amount of stored energy decreases with increasing water activity and increases with increasing compaction speed. Eq. (1) clearly shows the large influence of yield stress on the amount of stored energy. The increase in stored energy with compaction speed and decreasing water activity is hence primarily a result of an increase in yield stress with compaction speed.

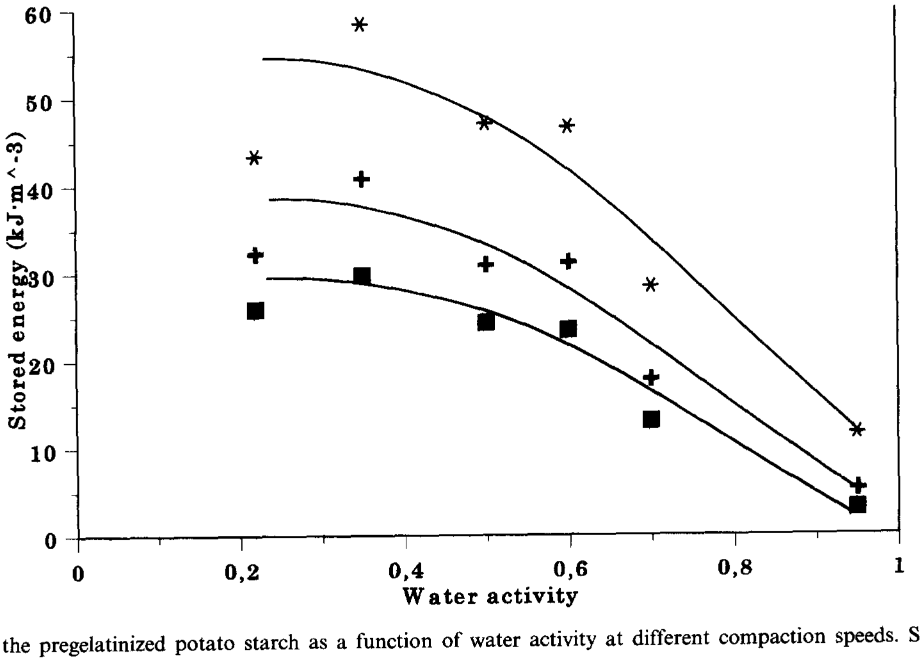

Fig. 7. Stored energy of the pregelatinized potato starch as a function of water activity at different compaction speeds. Symbols as in Fig. 3.

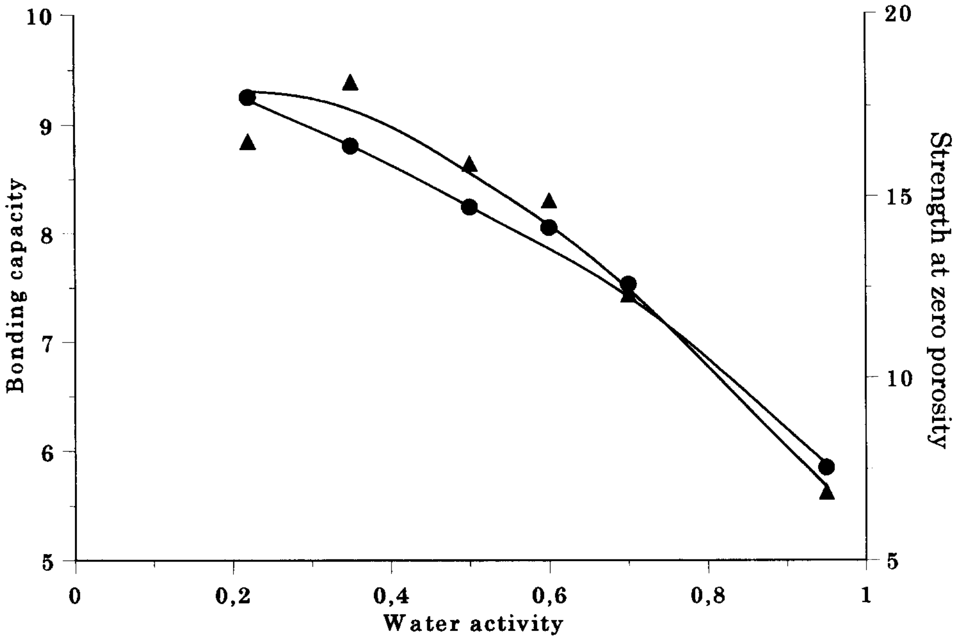

Fig. 8. Fit constants from Ryshkewitch–Duckworth relation at different water activities. Symbols: (●), bonding capacity; (▲), strength at zero porosity.

Analogous to what has been presented in a previous paper [5]—the energy storage may be considered as a tablet expansion factor, whereas particle bonding should be regarded as the counteracting parameter, responsible for the coherence of the compact. Particle attraction was quantified by fitting the data to the Ryshkewitch–Duckworth relation (Eq. (2)) at different water activities. Fig. 8 shows the bonding capacity ($k$) and the calculated values of tablet strength at zero porosity ($S_0$) as a function of water activity. This figure indicates that the material exhibits a lower bonding affinity at higher moisture content. Interestingly, bonding capacity and tablet strength at zero porosity follow the same relation. This can be understood if it is assumed that the inter-particle strength (i.e. strength of attraction between two particles) is less than the intra-particle strength (strength of one particle). As a result, tablet failure occurs by disruption of inter-particle bondings and not by fragmentation of the particles. Bonding capacity ($k$) then completely determines tablet strength ($S_0$). Moreover, particle bonding is directly determined by adsorbed water, which is analogous to the effect of water content on elastic modulus.

The effects of particle bonding and stored energy on maximum attainable tablet strength are summarized schematically in Fig. 9. According to Fig. 8 bonding capacity decreases with water activity. Large bonding capacity values indicate strong tablets. This is represented in Fig. 9 by the line with negative slope, indicating decreasing bonding with increasing water activity. In contrast, Fig. 7 shows decreasing stored energy with increasing water activity, this would lead to stronger tablets, if the bonding capacity was independent of water activity. The effect of stored energy on strength is shown in Fig. 9 by the line with positive slope (it is possible to consider this line as the reciprocal value of stored energy: the higher the reciprocal value of stored energy, the stronger the tablet). The final tablet strength is the overall result of these two phenomena, as indicated by the hatched lines in Fig. 9 which have maximum values at a water activity of about 0.70, which is close to the water activity where the glass transition temperature equals room temperature.

Compaction speed only affects stored energy (Fig. 7), and Fig. 9 presents the increase in compaction speed by a translation of the line representing reciprocal stored energy to lower values (an increase in stored energy gives a decrease in its reciprocal value). The product of reciprocal stored energy and bonding capacity then yields lower values of tablet strength at higher compaction speeds.

In conclusion, this study indicates that it is necessary to take into consideration inter-particle bonding when studying viscoelasticity of particles and their resulting compacts, because bonding affects viscoelasticity measurements. This work also shows that strong bonding prevents a tablet from extensive relaxation, which indicates that both viscoelasticity and bonding have an important effect on the final tablet strength. This interrelation between bonding and stored energy explains the maximum values in tablet strength at a relatively high water activity, which has also been observed by the maximum values in tablet strength at a relatively high water activity, which has also been observed by maximum values in tablet strength at a relatively high water activity, which has also been observed by both Rees and Tsardaka [4] and Bos et al. [3]. It is interesting

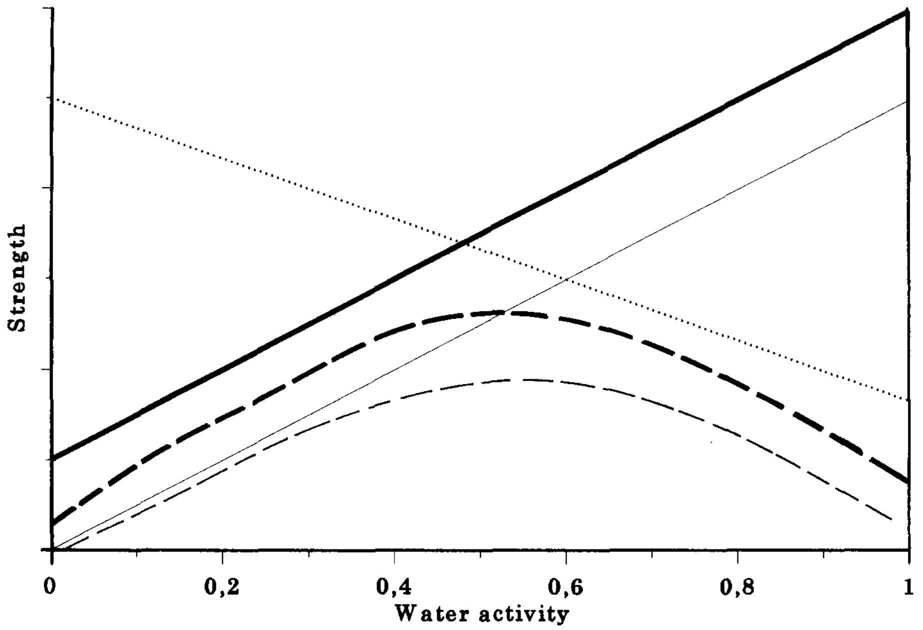

Fig. 9. The effect of bonding capacity (dotted line) and the effect of stored energy (solid line) on final tablet strength (dashed line) at low (thick lines) and high (thin lines) compaction speeds, respectively. Explanation in text.

to note that Rees and Tsardaka [4] came to the same conclusion. They applied creep experiments to discriminate between the different types of deformation and used another starch type.

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## Appendix A. Nomenclature

| | |
|---|---|
| $a_w$ | water activity |
| $A_{comp}$ | penetration depth |
| $C_g$ | constant |
| $E_0^*$ | complex modulus |
| $f$ | angular frequency |
| $k$ | constant |
| $K$ | constant |
| $S$ ($S_0$) | tensile strength (at zero porosity) |
| $v$ | compaction speed |
| $W_{rev}$ | stored energy |
| $\gamma_c$ | critical deformation |
| $\epsilon$ | porosity |
| $\sigma_c$ | yield stress |
| $\omega$ ($\omega_m$) | amount of adsorbed water (as a monolayer) |

## References

[1] R.J. Roberts, R.C. Rowe, The effect of punch velocity on the compaction of a variety of materials, J. Pharm. Pharmacol. 37 (1985) 377–384.

[2] L. Slade, H. Levine, Water relationships in starch transitions, Carbohydr. Polym. 21 (1993) 105–131.

[3] C.E. Bos, G.K. Bolhuis, H. Van Doorne, C.F. Lerk, Native starch in tablet formulations: properties on compaction, Pharm. Weekbl. Sci. Ed. 9 (1987) 274–282.

[4] J.E. Rees, K.D. Tsardaka, Some effects of moisture on the viscoelastic behaviour of modified starch during powder compaction, Eur. J. Pharm. Biopharm. 40 (1994) 193–197.

[5] K. Van der Voort Maarschalk, K. Zuurman, H. Vromans, G.K. Bolhuis, C.F. Lerk, Porosity expansion as a result of bonding and deformation of particulate solids, Int. J. Pharm. 140 (1996) 185–193.

[6] R.J. Crawford, Plastics Engineering, 2nd ed., Pergamon, Oxford, 1987, pp. 18–23.

[7] G.W. Radebaugh, S.R. Babu, J.N. Bondi, Characterisation of the viscoelastic properties of compacted pharmaceutical powders by a novel nondestructive technique, Int. J. Pharm. 57 (1989) 95–105.

[8] R.W. Heckel, Density pressure relationships in powder compaction, Trans. Metall. Soc. AIME. 221 (1961) 671–675.

[9] R.W. Heckel, An analysis of powder compaction phenomena, Trans. Metall. Soc. AIME. 221 (1961) 1001–1008.

[10] W.H. Duckworth, Discussion of Ryshkewitch paper by Winston Duckworth, J. Am. Ceram. Soc. 36 (1953) 68.

[11] K. Van der Voort Maarschalk, H. Vromans, G.K. Bolhuis, C.F. Lerk, The effect of viscoelasticity and tabletting speed on consolidation and relaxation of viscoelastic material, Eur. J. Pharm. Biopharm. 42 (1996) 49–55.

[12] J.T. Fell, J.M. Newton, The tensile strength of lactose tablets, J. Pharm. Pharmacol. 20 (1968) 657–658.

[13] C. Van den Berg, Vapour sorption equilibria and other water-starch interactions; a physico-chemical approach. Ph.D. thesis, Wageningen, (1981) 58–62.

[14] B.C. Hancock, G. Zografi, The relationship between glass transition temperature and the water content of amorphous pharmaceutical solids, Pharm. Res. 11 (1994) 471–477.