

Full Length Research Paper

Effect of heat moisture treatment on the functional and tableting properties of corn starch

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The effect of heat moisture treatment on the functional and tableting properties of corn starch BP was investigated. Corn starch was hydrothermally modified by heat moisture treatment (HMT) at 100°C, 16 h; 20% moisture level (HIC – 20), 25% moisture level (HIC – 25), and 30% moisture level (HIC – 30). The tablet formation properties were investigated using Heckel and Kawakita equation, while its tableting properties were assessed using tensile strength, crushing strength, friability and disintegration time. The results reveal that HMT reduces the gelatinisation temperature and pasting properties of the corn starch. However, all the starches swell as the temperature is increased, HMT of the corn starch lowered the swelling power of the starch, while the solubility profile increased. The X-ray diffractometry study reveal that the native and HMT starches maintained the characteristic 'A' diffraction pattern of the cereal starch with strong peaks at 15.35, 17.15, 18.2 and 23.55 Å. The bulk density of the starch was in the order: HIC-30 ≈ HIC-25 > HIC-20 > NaIC, with reduction in the Carr's index, compressibility index, and Hausner's ratio after HMT treatment. The mean yield pressure, P_y , (from Heckel analysis) which is inversely related to the ability of the materials to deform plastically under pressure, was relatively high after HMT of the corn starch. Also, the P_k values (from Kawakita analysis), which is related to the deformability of the individual powder increased after HMT of the corn starch compacts in the following order: NaIC << HIC-20 < HIC-25 < HIC-30. The tableting properties studied reveal a reduction in the crushing strength and tensile strength after HMT of the corn starch compacts. However, the friability of the starches increased while there was reduction in the disintegration time of the corn starch compacts after HMT. Thus, HMT of corn starch could be useful when fast disintegration, lower swelling power, and lower crushing strength are desired in tablet.

Key words: Heat moisture treatment, corn starch, tableting properties, functional properties.

INTRODUCTION

Starch is one of the most important excipient used in the pharmaceutical industry. The International Joint Conference on Excipients rated starch among the top ten pharmaceutical ingredients (Shangraw, 1992). Starch is used mainly as binders, disintegrants, fillers, glidants, or lubricants in the pharmaceutical excipients. In addition to the native starch, a variety of chemical and physical modification can be used to modified the starch and impart certain properties to the starch. Such modified starches find wide applications not only in the

pharmaceutical industry, but also in textile, food, glue and paper industries. Due to their relative safety, most industries (especially pharmaceutical and food industries) prefer starches that have not been chemically altered, hence physically modified starches are gaining wider acceptance. Heat moisture treatment (HMT), an hydro-thermal modification of starch that does not destroy the granular nature of the starch is one of the common forms of physical modification of starch. HMT involves incubation of starch granules at low moisture level (< 35% water w/w), during a certain period of time, at a temperature above the glass transition temperature but below the gelatinisation temperature (Jacobs and Delcour, 1998). HMT treatment increases and broadened the gelatinisation range (Kobayashi, 1993; Radosta et al., 1992),

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but lowered the gelatinisation enthalpy (ΔH) (Eerlingen et al., 1996; Hoover and Vasanthan, 1994a). Studies of the effect of HMT on starch pasting characteristics reveal a higher onset temperature of viscosity development, a lower peak viscosity, and a higher or lower end viscosity, depending on the treatment conditions (Hoover and Manuel, 1996; Abraham, 1993; Stute, 1992).

Lots of research work has been done on the characterisation of different type of HMT starches and their relationship (Eeligen et al., 1997; Franco et al., 1995; Kawabata et al., 1994). To the best of our knowledge, no work has been done to evaluate the usefulness of HMT corn starch as directly compressible excipients in tablet formulation. Hence, the objective of this work was to investigate the functional, compaction and tableting properties of HMT corn starch. The tableting properties were assessed using Heckel and Kawakita equation, while the tablet properties of the starch tablets were evaluated using crushing force, disintegration test. The functional properties of the HMT starch were also investigated.

MATERIALS AND METHODS

Corn starch BP was obtained from Sigma-Aldrich Chemicals, USA. While lactose (Granulac, Germany), paracetamol (Sigma-Aldrich Chemical, Germany), magnesium stearate (Siegfried, Zofingen, Switzerland) were also used. The powders were all of pharmaceutical quality and representative of the grades typically used in the pharmaceutical industries.

Heat moisture treatment of the starch

The method of Sair (1964) was employed for the heat moisture treatment (HMT) with slight modification. Starch samples were weighed into different glass containers, the starch moisture content was brought to 20, 25, and 30%, respectively. The sealed samples (in glass jars) were heated in an air oven at 100°C for 16 h. After heat treatment, all starches were dried at 45°C to a uniform moisture level (~10%). The starches are referred herein as follow: native corn starch, NaIC; heat moisture treated corn starch at 20%, HIC-20; heat moisture treated corn starch at 25%, HIC-25; and heat moisture treated corn starch at 30%, HIC-30.

Pasting properties

A Rapid Visco-Analyser model 3D (Newport Scientific Pty. Ltd., Warriewood, Australia) was used to determine the pasting properties of the starch in 25 g of distilled water underwent a controlled heating-and-cooling cycle under constant shear where it was held at 50°C for 1 min, heated from 50 to 95°C at 6°C/min, held at 50°C for 5 min (AACC, 2003).

X-ray diffraction

X-ray diffractograms of starch powders were obtained with a Rigaku D-Max- 2200 X-ray diffractometer (Rigaku Denki Co. Tokyo, Japan). The scanning region of the diffraction angle was from 3 to 40°, with target voltage 40 kV, target current, 100 mA, and aging time 5 min.

Thermal analysis

The thermal properties of the starches were studied using a differential scanning calorimeter (DSC – Mettler TA 4000, Switzerland). The gelatinization parameters of the starch were evaluated by the methods proposed by Ratnayake et al. (2001).

Swelling power and starch solubility

The method of Adebowale et al. (2002) was employed for the determination of the effect of temperature on the starch solubility and swelling.

Bulk and tap density

A 100 ml glass measuring cylinder with an internal diameter of 2.50 cm³ was used. 20 g of starch powder were carefully passed through a glass funnel into the graduated cylinder bent at 45°C. The volume (v) occupied by the powder was determined from the height (h) of powder bed and the internal radius (r) of the cylinder using the equation:

$$v = \pi r^2 h$$

The loose bulk density was obtained in gcm⁻³. Tap density (gcm⁻³) was determined by subjecting the powder to 100 taps in a cylinder by standardised tapping procedure of 38 taps per minute. Determinations were done in triplicate. The relative density, D_o of each starch powder was obtained from the ratio of its loose bulk density to its particle density.

Flow properties

The flow ability of the starches was assessed using the Hausner ratio (Herman et al., 1989) and Carr-index (Carr, 1965).

Compressibility

The compressibility index (CI) (Carr, 1965) was estimated from the bulk and tap volumes (V_{bulk} and V_{tap}) measured according to the test for apparent volume (European Pharmacopoeia, 2005):

$$CI \% = \frac{V_{bulk} - V_{tap}}{V_{bulk}} \times 100$$

The volume (v) occupied by the powder was determined from the height (h) of powder bed and the internal radius (r) of the cylinder using the equation:

$$v = \pi r^2 h$$

Preparation of compacts of starch powders

500 mg samples of each starch powder was compressed for 1 min into tablets with predetermined load on a Caver hydraulic hand press Model C (Carver Inc., Wisconsin, USA), using a 1.05 cm diameter punches and die and flat-faced punches lubricated with 2% w/v dispersion of magnesium stearate in benzene before each compression. After ejection, the tablets were stored over silica gel

for 24 h to allow for elastic recovery and prevent falsely low yield pressure values. The weights (w) and dimensions of the tablets were then determined within ± 0.1 mg and 0.01 mm respectively. The relative densities of the starch tablets were calculated from using the equation:

$$\rho = \frac{W}{V_t \rho_t}$$

Where V_t is the volume (cm^3) of the tablets (including hole when present) and ρ_s is the particle density (gcm^{-3}) of the starch powder.

Compressional characteristic of starches

The Compressional characteristics of the starches were determined using the Heckel and Kawakita plots.

Heckel parameters

Heckel plots (Heckel, 1961a,b) allows for the interpretation of the mechanism of compression. Heckel equation:

$$\ln \frac{1}{1-D} = kP + A$$

Where D is the relative density of a powder compact at pressure P . Slope k is a measure of the plasticity of a compacted material. Constant A is related to the die filling and particle rearrangement before deformation and bonding of the discrete particles.

Thus, Heckel plots of $\ln [1/(1-D)]$ against the applied pressure (P) were plotted for the different starches. Values of K and A were obtained from the slope and intercept of the plots respectively. The relative density, D_A , which represents the total degree of densification, and the relative density, D_B , which describes that phase of rearrangement of particles during the initial stages of compression, were calculated from the following equations:

$$D_A = 1 - e^{-A}$$

$$D_B = D_A - D_0$$

Regression analyses were carried out over the pressure range that did not stray from linearity for each Heckel plot and the mean yield pressure (P_y) were determined for each batch of tablets produced.

Kawakita parameters

The volume of each sample at zero pressure, V_0 was determined using the equation:

$$V_0 = \pi r^2 h$$

Where r is the radius of the cylinder, and h is the height of the sample. The volume of the tablet at different compression pressures, V_p , was also calculated. The degree of volume reduction was calculated from the Kawakita equation:

$$C = \frac{V_0 - V_p}{V_0} = \frac{abP}{1 + bp}$$

The compression parameters, $1/b$ and a , were derived from the Kawakita equation (Kawakita and Ludde, 1971):

$$\frac{P}{C} = \frac{P}{a} + \frac{1}{ab}$$

Where C is the degree of compression (volume reduction) of the powder bed at applied pressure P . The compression parameter ' a ' reflects the total degree of compression at infinite pressure and the reciprocal of the compression parameter b , $1/b$, is considered as an indication of deformation or failure stress of the particles (Fichtner et al., 2007; Nicklasson and Alderborn, 2000; Adams and McKeown, 1996; Kawakita et al., 1977). The parameters a and $1/b$ were determined from the equation obtained by linear regression in the pressure interval 1 to 200 MPa.

After ejection, the tablets were stored over silica gel for 24 h to allow for elastic recovery and hardening, and prevent falsely low yield values. Their weights (w) and dimensions were then determined to within ± 1 mg and 0.01 mm respectively, and their relative densities, D , were calculated using the equation:

$$D = w / V_t \rho_s$$

Where V_t is the volume (cm^3) of the tablet including the hole when present and ρ_s , is the particle density (gcm^{-3}) of the solid material.

Crushing strength

Crushing strengths of the tablets were determined at room temperature by diametral compression using a hardness tester. The tablet was placed between the plate of the tester and the knob was screwed until contact was made after which there was enough pressure due to further screwing to cause breakage. The hardness was then read on the side scale of the tester. Results were taken only from tablets which split cleanly into two halves without any sign of lamination. All measurements were made in triplicate or more and the results given are the means of several determinations.

Tensile strength of the starch compacts

The force, F (MN) required to break each tablet diametrically into two halves was determined following the procedure of Fell and Newton (1970), using a Monsanto Hardness tester.

Friability test

The percent friability of the tablets was determined using a Roche Friabilator operated at 25 rpm for 4 min. 10 weighed tablets (w_1) were placed inside the drum and allowed to tumble for 4 min at a speed of 25 revolutions per minute. The tablets were then weighed (w_2) and the loss in weight expressed as a percentage of the initial weight. Determinations were done in triplicate.

$$\% \text{ Friability} = \frac{w_1 - w_2}{w_1}$$

Disintegration time

The disintegration times, DT , of the relevant tablets were determined in distilled water at $37 \pm 0.5^\circ\text{C}$ using a BP Manesty disintegration test unit (Manesty Machines Ltd., Liverpool, U.K.). Tablets were placed on the wire mesh just above the surface of the distilled water in the tube and the apparatus was started simultaneously with a stop clock. The time taken for each tablet to disintegrate and all the granules to go through the wire mesh was

Table 1. Gelatinisation parameters of native and physically modified Corn starches

| Starch ^a | Transition temperature (°C) ^b | | | | ΔH (J/g) |
|---------------------|--|---------------------|---------------------|---------------------------------|------------------|
| | T ₀ (°C) | T _p (°C) | T _c (°C) | T _c – T ₀ | |
| NaIC | 67.3 | 73.0 | 82.7 | 15.4 | 9.3 |
| HIC 20 | 65.4 | 71.4 | 82.1 | 16.7 | 9.8 |
| HIC 25 | 66.8 | 71 | 84.5 | 17.7 | 10.1 |
| HIC 30 | 66.6 | 76.7 | 82.5 | 15.9 | 7.5 |

Table 2. Pasting properties of native and physically modified Corn starches.

| Analysis // Starch ^a | NaIC | HIC 20 | HIC 25 | HIC 30 |
|---------------------------------|--------|--------|--------|--------|
| Peak viscosity, PV (RVU) | 213.17 | 135.00 | 117.42 | 105.92 |
| Trough viscosity, TV (RVU) | 173.08 | 131.17 | 113.25 | 104.17 |
| Breakdown (PV - TV), (RVU) | 40.08 | 3.83 | 4.17 | 1.75 |
| Final viscosity, FV, (RVU) | 211.67 | 155.33 | 132.42 | 119.50 |
| Setback (FV - TV), (RVU) | 38.58 | 24.17 | 19.17 | 15.33 |
| Peak time (min) | 5.80 | 6.80 | 6.93 | 6.27 |
| Pasting temperature (°C) | 85.75 | 86.86 | 85.55 | 88.45 |

recorded. Determinations were made in triplicate.

Statistical analysis

All determinations were done in triplicate, and the results were then averaged. Data were assessed by General Linearized Model (GLM) of Statistical Analysis System (SAS) to generate analysis of variance (ANOVA), means, standard error, and range. Correlation and regression analysis were also performed using procedure for correlation (Proc Corr) and procedure for regression (Proc Reg) procedures of SAS (SAS Institute Inc., 2000; Snedcor and Cochran, 1987).

RESULT AND DISCUSSION

Functional properties

The effect of heat moisture treatment on the gelatinisation of corn starch was presented in Table 1. The order for the gelatinisation range for the starches was: NaIC \approx HIC-30 < HIC-20 < HIC-25. This result is similar to that reported by Hoover and Vasanthan (1994b, c), Jacobs et al. (1998), and Eerlingen et al. (1996) who observed decreased in the gelatinisation range and enthalpies of pea, wheat, and potato starches studied. The HMT starches had lower gelatinisation temperatures while the gelatinisation range (T_c – T₀) increased compared to its native starch, NaIC (Table 1). Similar trend was observed for variety of maize (Hoover and Manuel, 1996), wheat and oat (Hoover and Vasanthan, 1994c). Eerlingen et al. (1997) observed that DSC gelatinisation of starch depend on moisture content. Decrease in the gelatinisation enthalpy was observed in HIC-30. Hoover and Vasanthan (1994a, b) also observed

similar decrease in swelling factor and amylose leaching for potato starch modified under similar condition. This effect was probably caused by changes in the packing arrangements of the starch crystallites and or interactions between starch components in the amorphous regions of the granule during hydrothermal treatment.

The pasting properties of the native and HMT corn starches were presented in Table 2 and their pasting profiles in Figure 1. There was decreased in the peak viscosity, trough viscosity, final viscosity, break down, set back after HMT, while the pasting temperature increased when compared with the native starch. However, the pasting profile of the starches did not changed significantly (Figure 1). Moisture treatment at 20% (HIC-20) results in higher peak viscosity, trough viscosity, set back, and pasting temperature, compared with moisture treatment HIC-25 and HIC-30. All the starches had the Type 'C' pattern characteristic of cereal based on Schoch and Maywald (1968) classification. These results indicated that heat moisture treatment had minimal effect on the granular arrangement of the starch with resultant lower swelling power when compared with their native starch. This observation concurred with that reported by Han and BeMiller (2007), Lim et al. (2002), and Sekine et al. (2000) for different starches. The reduction in the viscosity value as a result of HMT is a thinning effect which might be due to the weakening and breakdown of bonding forces within the granules and their breakdown (Rasper, 1980).

The effect of temperature on the swelling power of corn starches is presented in Figure 2. All the starches swelled as the temperature increased in the following order: NaIC > HIC -30 \approx HIC -25 \approx HIC -30. HMT lowered the swelling power of the corn starch after modification when

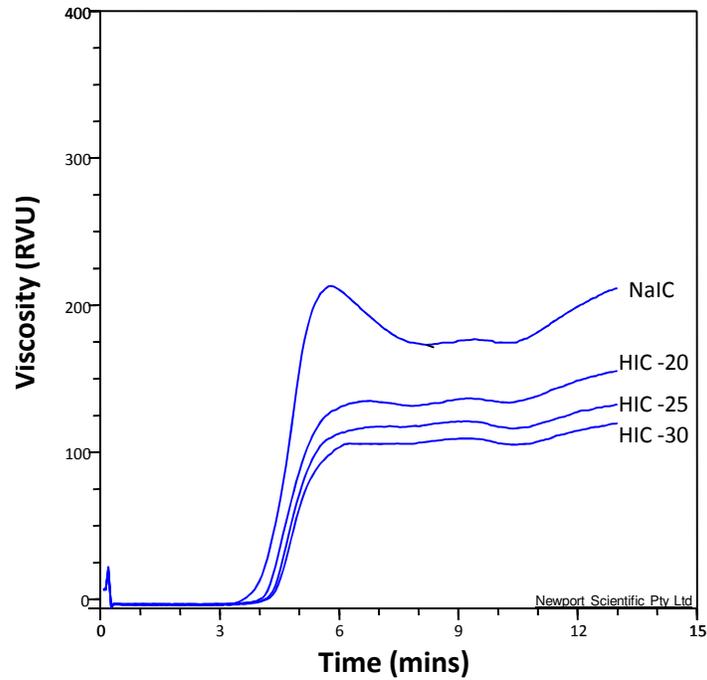


Figure 1. The RVA viscoamylogram of Heat-moisture treated at 20% (HIC-20), 25% (HIC-25), and 30% (HIC-30) Corn starches

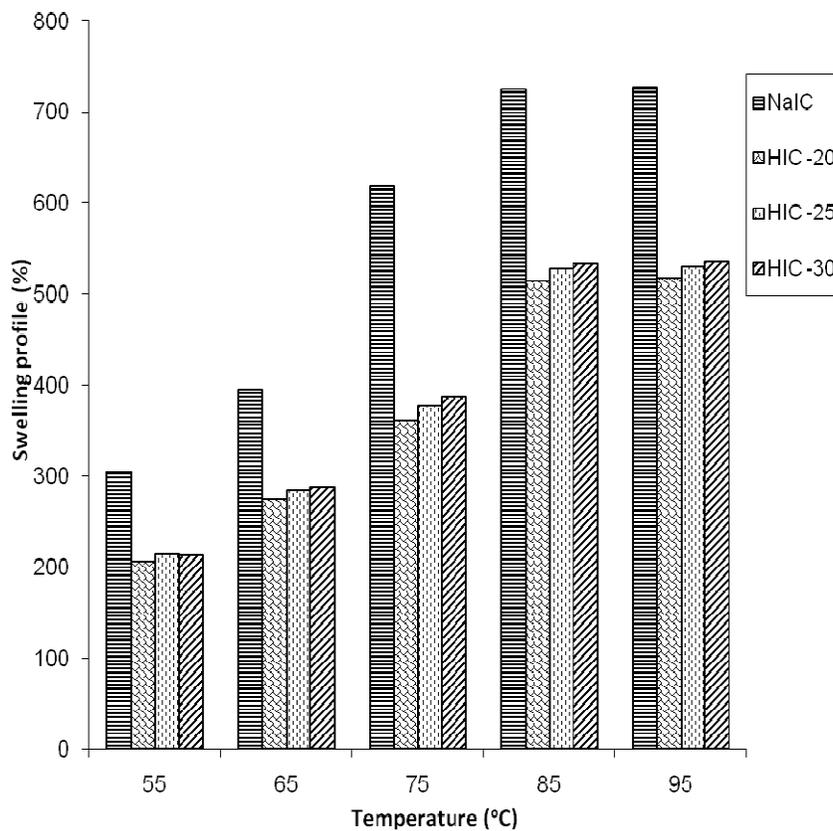


Figure 2. Swelling power of Heat-moisture treated at 20% (HIC-20), 25% (HIC-25), and 30% (HIC-30) Corn starches.

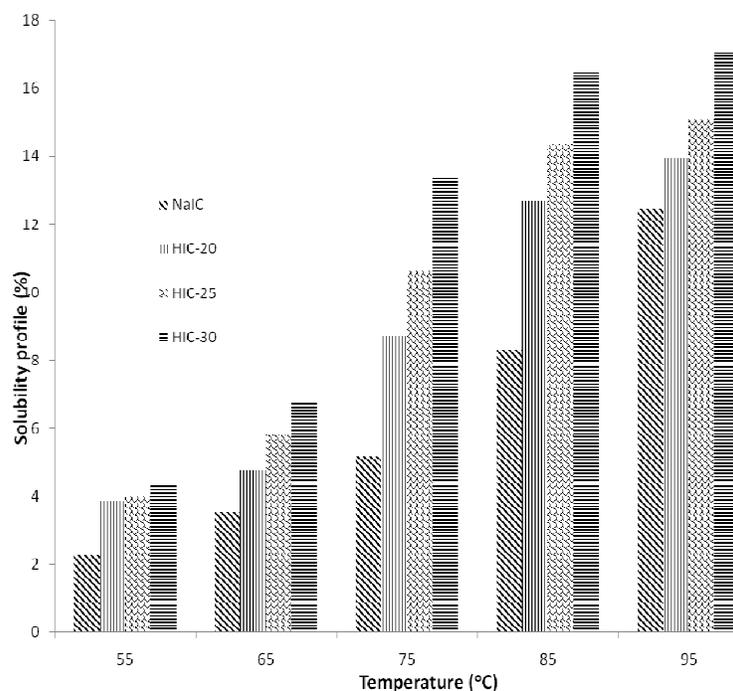


Figure 3. Solubility profile Heat-moisture treated at 20% (HIC-20), 25% (HIC-25), and 30% (HIC-30) Corn starches.

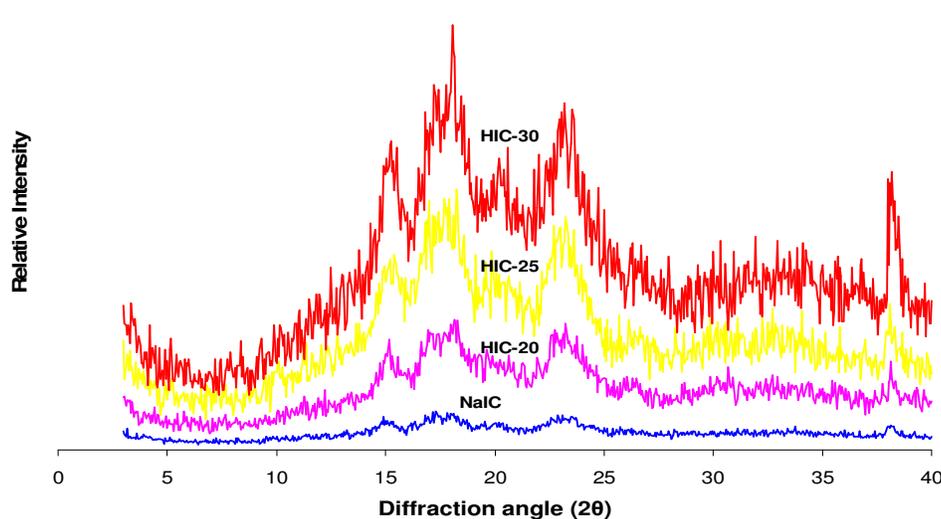


Figure 4. X-ray pattern of native (NaIC), and heat-moisture treated at 20% (HIC-20), 25% (HIC-25), and (HIC-30) corn starches.

compared with the native starch. There was rapid increase in the swelling power of all the starches studied between 65 and 75°C, and a slow or almost constant rate above 75-80°C. This type of behaviour was also observed by Barminas et al. (2007). Galliard and Bowler (1987) and Leach et al. (1950) attributed this type of behaviour to two sets of bonding forces which relax at different temperature. The effect of temperature on the solubility of native and modified Corn starches was

presented in Figure 3. The solubility increased for all the starches in the following order: HIC-30 > HIC-25 > HIC-20 > NaIC. This result is similar to that reported by Kulp and Lorenz (1981), and Radosta et al. (1992) who observed high solubility profile for the HMT wheat and rye starches respectively.

The X-ray diffraction pattern of native and HMT corn starch was presented in Figure 4. All the starches exhibited Type 'A' X-ray diffraction pattern common with

Table 3. Densities (gcm^{-3}) of native and heat moisture treated corn starches.

| Powder/starch | Particle density (gcm^{-3}) | Bulk density (gcm^{-3}) | Tapped Density (gcm^{-3}) | ¹ Relative density (D_0) | Carr's index (I) | Hausner's ratio (H.I.) |
|---------------|--|------------------------------------|--------------------------------------|---|------------------|------------------------|
| NaIC | 1.48 | 0.41 | 0.57 | 0.28 | 28.00 | 1.39 |
| HIC-20 | 1.50 | 0.44 | 0.57 | 0.29 | 22.71 | 1.29 |
| HIC-25 | 1.49 | 0.45 | 0.57 | 0.30 | 22.13 | 1.28 |
| HIC-30 | 1.50 | 0.45 | 0.58 | 0.30 | 22.63 | 1.29 |

¹Relative density at zero pressure. Results are means of triplicate determinations.

Table 4. The compressibility index (CI %) for the starch samples.

| Starch | V_{bulk} (cm^3) | V_{tap} (cm^3) | CI (%) |
|----------------------------------|-------------------------------------|------------------------------------|--------|
| Native corn starch (NIC) | 48.90 | 35.21 | 13.69 |
| HMT (20%) – corn starch (HIC-20) | 45.56 | 35.21 | 10.35 |
| HMT (25%) – corn starch (HIC-25) | 44.74 | 34.84 | 9.90 |
| HMT (30%) – corn starch (HIC-30) | 44.64 | 34.54 | 10.10 |

Results are means of triplicate determinations.

V_{bulk} = Bulk volume, V_{tap} = Tap volume.

the cereals. The native starch (NaIC) exhibited strong peaks at 15.35, 17.15, 18.2, and 23.55 Å. Heat moisture treated starches maintained the Type 'A' X-ray diffraction pattern of the native starch (Figure 4). HIC-20 had strong peak at 15.15 (5.84 Å), 17.1 (5.18 Å), 18.05 (4.91 Å), and 23.10° (3.85 Å). HIC-25 maintained the Type 'A' X-ray diffraction pattern with strong peaks at 15.25 (5.81 Å), 17.35 (5.11 Å), and 23.45° (Å), while HIC-30 had its strong peaks at 15.3 (5.79 Å), 17.05 (5.18 Å) and 20.3° (4.37 Å).

All the heat-moisture treated starches exhibit strong and sharp peaks at $2\theta = 17^\circ$. Kainuma and French (1971) suggested that cleavages of starch chains in the amorphous regions allows reordering of the chain segments to give a more crystalline structure with a sharper X-ray diffraction pattern. The Type 'A' X-ray pattern (shown mainly by cereal starches) and 'B' patterns represents the true crystalline forms of starch, but the Type 'C' patterns is believe to be a superposition of the 'A' and 'B' patterns (Buleon, 1998). This observation was further corroborated by Gidley (1987) who suggested that the Type 'C' pattern is not a true crystalline polymorph but rather a mixture of 'A' and 'B' polymorphs. A fourth pattern, the 'V' pattern, arises from complexes formed by amylose with a variety of polar organic molecules (Zobel, 1988a,b; Zobel, et al., 1988).

The functional properties of the starches showed that HMT probably caused depolymerisation of starch chains, oxidation of fats and also leads to denaturation of protein since cereal starch usually contain about 1% fat and protein. These parameters also have considerable influence on the crystallinity, viscosity, solubility and swelling power of the starch.

Flow ability of the starch powder

The density (particle, bulk, tapped, and relative density at zero pressure), Carr's index, and Hausner's ratio of the native and HMT corn starches were presented in Table 3. The particle density and bulk density of the starches increased after HMT.

The bulk density which is a measure of the flowability of the starch was in the order: HIC-30 \approx HIC-25 > HIC-20 > NaIC. This is an indication that HMT improve the potential of the starch to flow and rearrange under compression. The Carr's index and Hausner's ratio of NaIC was 27.99 and 1.39 respectively. There was reduction in the Carr's index (22.13 – 22.71) and Hausner's ratio (1.28 – 1.29) after HMT of the corn starch.

This shows that HMT may improve the flow properties of the starch since low Carr's index is indicative of excellent flow properties (Wells, 1997). Also, the relative density when the applied pressure is zero (D_0) also increased as a result of the HMT, which shows that the initial packing in the die during die filling increased after HMT of the corn starch (Alebiowu and Itiola, 2002a; Humbert-Droz et al., 1983). The compressibility index for the native and HMT starch was presented in Table 4. There was reduction in the bulk volume and compressibility index (CI) after HMT of the corn starch. The reduction in the CI after HMT may be an indication that the voids present among the native starch particle were easily filled during compression than that of the HMT starches, although volume reduction is also dependent on temperature, compaction rate and particle size.

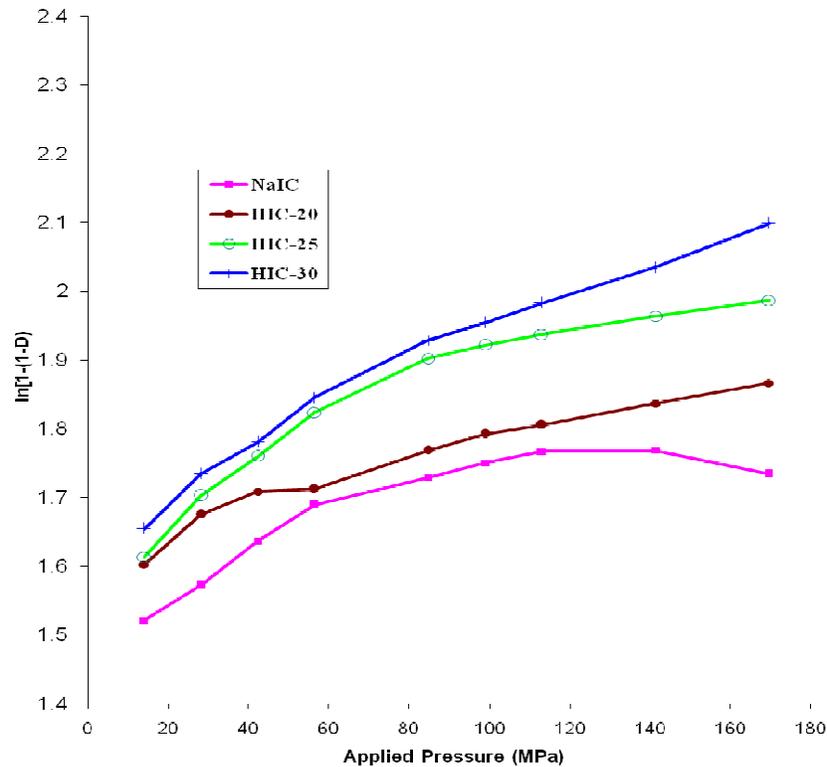


Figure 5. Heckel plots for native (NaIC) and heat moisture treated (HIC -20; HIC -25; HIC -30) corn starch compacts.

Table 5. Parameters from Heckel plots for the starches

| Starch | ¹ Applied pressure range (MPa) | P_y (MPa) | D_A | D_B | Correlation coefficient (R^2) |
|--------|---|-------------|-------|-------|-----------------------------------|
| NaIC | 14.14 – 56.57 | 248.97 | 0.77 | 0.49 | 0.999 |
| HIC-20 | 56.57 – 169.70 | 753.01 | 0.81 | 0.52 | 0.991 |
| HIC-25 | 84.85 – 169.70 | 938.44 | 0.84 | 0.54 | 0.997 |
| HIC-30 | 84.85 – 169.70 | 562.43 | 0.83 | 0.53 | 0.966 |

¹Applied Pressure range was used in the regression analysis to calculate P_y .

Heckel and Kawakita analysis

The Heckel plot (Figure 5) exhibited three distinct portions; an initial curve followed by linear region, and the regions above the peak pressure. The native and HMT corn starches exhibited Type B deformation (Hersey and Rees 1970; York and Pipel 1972). This shows that the starches consolidation precedes plastic flow. From the data (Table 5) obtained from Heckel analysis based on the regression analysis of the curves using its linear portion, there was an increment in the value of D_B after HMT in the following order: NaIC < HIC-20 < HIC-30 < HIC-25. D_B describes the phase rearrangement of particles during the initial stages of compression, that is, the extent of particle rearrangement during compaction. Hence HMT improve the phase rearrangement of

particles during the initial stages of compression by modifying the surface, structure, particle size and shape of the starch after HMT. Also, there was increase in the D_A values (Table 5) after HMT of the native corn starch. D_A represent the total degree of packing achieved at zero and low pressure as a result of rearrangement process before an appreciable amount of interparticulate bonding takes place. This shows that HMT also improve the degree packing due to rearrangement process before extensive interparticulate bonding takes place. There was relatively high P_y values (Table 5) after HMT of the corn starch. The mean yield pressure, P_y is inversely related to the ability of the materials to deform plastically under pressure. Hence, HMT of corn starch may slow down the onset of plastic deformation during compression and also resist consolidation.

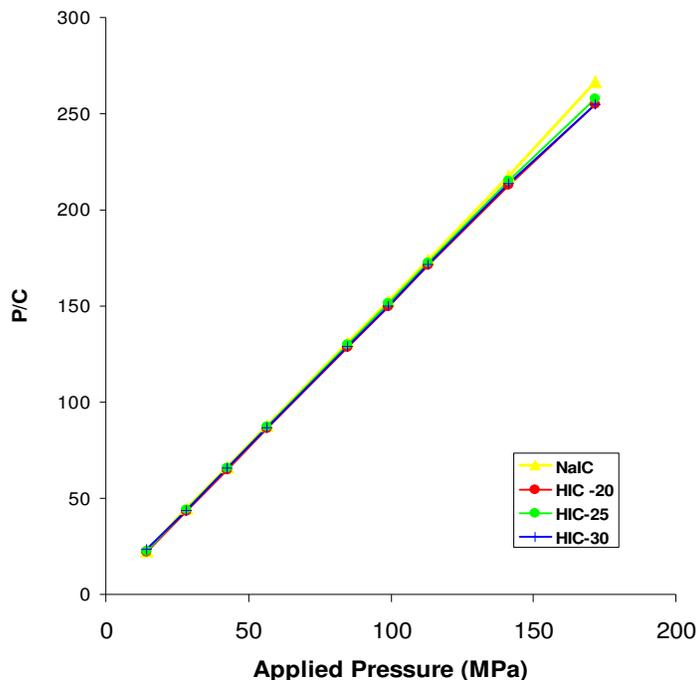


Figure 6. Kawakita plots for native (NaIC) and HMT (HIC -20; HIC -25; HIC -30) corn starch compacts.

Table 6. Parameters from Kawakita plots for the starch compacts.

| Starch | $D_i(1 - a)$ | P_k | Correlation coefficient (R^2) |
|----------------------------------|--------------|-------|-----------------------------------|
| Native corn starch (NaIC) | 0.35 | 0.36 | 0.999 |
| HMT (20%) – corn starch (HIC-20) | 0.33 | 1.22 | 0.999 |
| HMT (25%) – corn starch (HIC-25) | 0.33 | 1.42 | 0.999 |
| HMT (30%) – corn starch (HIC-30) | 0.33 | 1.97 | 0.999 |

The data obtained from the Kawakita analysis (Figure 6) of the corn starch compacts was presented in Table 6. The initial relative density of the starch with little pressure or tapping, D_i (Table 6), was generally higher than the corresponding values of the loose relative density D_o (Table 3). This result is at par with that reported by Alebiowu and Itiola (2000b) for the starches of sorghum, plantain, and corn starches. The P_k values which is related to the deformability of the individual powder increased after HMT of the corn starch in the following order: NaIC \ll HIC-20 < HIC-25 < HIC-30. This shows that the native corn starch which is soft and readily deform plastically under pressure is highly enhanced after HMT.

Tablet properties of the starch compacts

The crushing strength of the native and HMT corn starch compacts at different compression pressure was presented

in Figure 7. The crushing force of the HMT corn starch was generally lower than that of the native starch. The crushing force of all the starch compacts was generally lower than 50 N indicating that all compacts were weak. The tensile strength of the corn starches (Figure 8) also revealed reduction after HMT. The reduction in the crushing force and subsequently tensile strength after HMT can be considered as reduction in interparticle bonding inside the tablets. The decreased in tensile strength caused by a reduction of interparticle bonding, is related to a larger relaxation of the tablets (Zhao et al., 2006). These also reveal that the adhesive forces between the granules of the corn starch after HMT was higher than its cohesive force. Generally, the tensile strength increased with increase in the applied pressure for all the starches. Tablet compressed at higher compaction pressure exhibit higher tensile strength. This is due to the fact that the mean contact area between the particles increases in proportion to the compaction pressure (Mohammed et al., 2005).

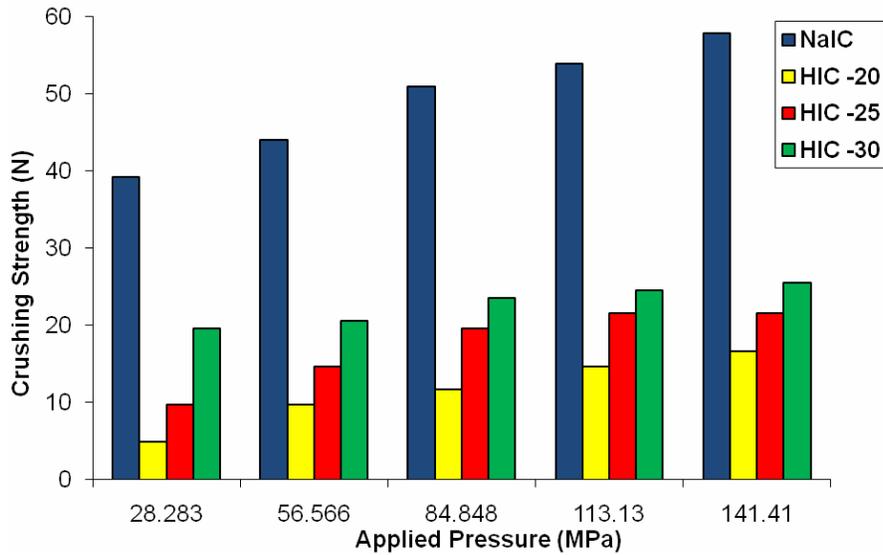


Figure 7. Crushing strength of native (NaIC) and HMT (HIC -20; HIC -25; HIC -30) corn starch compacts

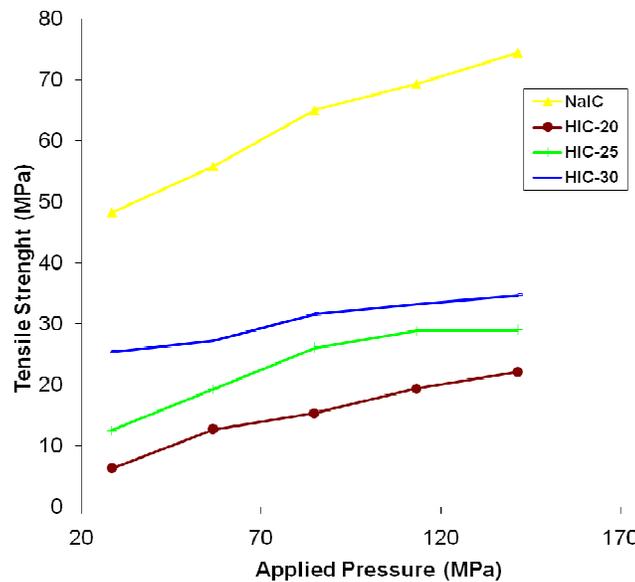


Figure 8. Tensile Strength of native (NaIC) and HMT (HIC -20; HIC -25; HIC -30) corn starch compacts.

The friability of the native and HMT corn starch was presented in Figure 9. The friability of the corn starch increased after HMT. This shows that the compacts were fragile. Also, the disintegration time of the HMT corn starch was lower than that of the native starch (Figure 10). The lower disintegration time of the HMT starch could be attributed to the fact that HMT of starch is hydrothermal treatment that has minimal effect on the granular nature of the starch (Jacobs and Delcour, 1998). This observation was collaborated by the gelatinisation

(Table 1) and swelling power (Figure 2) results which shows that HMT tightened the starch chains and restricts swelling of the starch granules, and also increased the gelatinisation temperature of the starch.

Conclusion

The result obtained from the HMT corn starch at different moisture level showed that HMT enhanced the flow ability

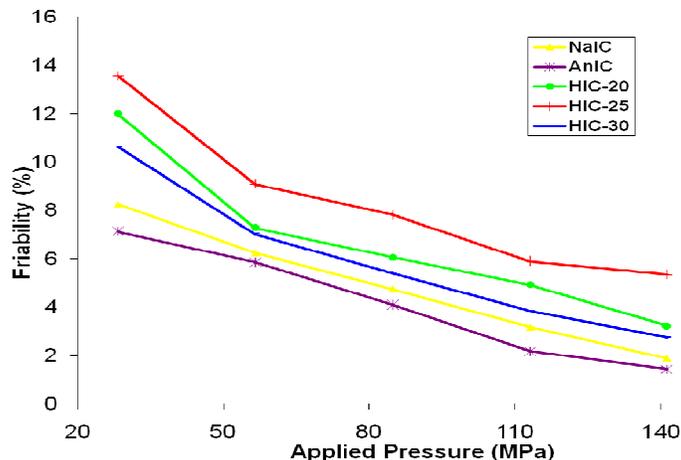


Figure 9. Friability native (NaIC) and HMT (HIC -20; HIC -25; HIC -30) corn starch compacts.

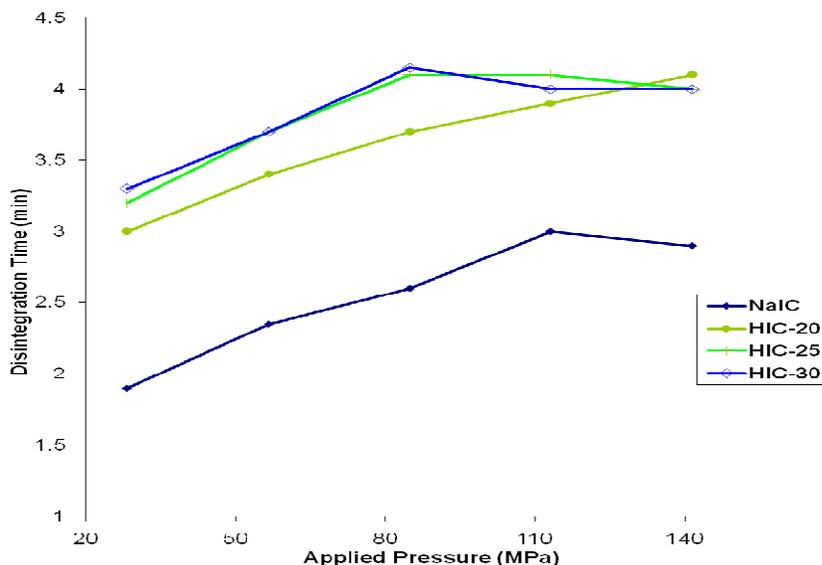


Figure 10. Disintegration time native (NaIC) and HMT (HIC -20; HIC -25; HIC -30) corn starch compacts.

and disintegration profile of the starch. The improved flowability of the corn starch after HMT could enhance corn starch uses as fillers in capsule formulation. On the other hand, the crushing strength and tensile strength of the starch compacts were reduced while its friability increased after HMT of the corn starch. Consequently, HMT of corn starch may be a suitable way to produce tablet with lower crushing force, lower swelling power and higher friability.

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REFERENCES

AACC (2003). Approved Methods of the American Association of

- Cereal. Chemists (10th ed.). St. Paul, MN: The Association.
- Abraham TE (1993). Stabilisation of paste viscosity of cassava starch by heat-moisture treatment. *Starch/Starke*, 45: 131-135.
- Adams MJ, McKeown R (1996). Micromechanical analyses of the pressure volume relationship for powders under confined uniaxial compression, *Powder Technol.*, 88: 155-163.
- Adebayo AAS (2001). A study of breadfruit and cocoyam starch as excipients in paracetamol tablet formulations. Ph.D. Thesis, University of Ibadan, Ibadan, Nigeria. Adebowale KO, Afolabi TA, Lawal OS (2002). Isolation, chemical modification and physicochemical characterisation of Bambara groundnut (*Voandzeia subterranean*) starch and flour. *Food Chem.*, 78: 305-311.
- Alebiowu G Itiola OA (2002a). Compressional characteristics of native and pregelatinised forms of sorghum, plantain, and corn starches and the mechanical properties of their tablets. *Drug Dev. Industrial Pharmacy*, 28(6): 663-672.
- Alebiowu G, Itiola OA (2002b). Effects of pregelatinisation of starch binders on the interacting variables acting on the mechanical properties of a paracetamol tablet formulation. *S.T.P. Pharm. Sci.*, 12(6): 379-383.
- Barminas JT, Onen AI, Williams ET, Zaruwa MZ, Mamuru SA, Haggai D (2007). Studies on functional properties of borassus starch from fresh germinating nuts of giginya (*Borassus aethiopum*) palm, *Food Hydrocolloids*, doi:10.1016/j.foodhyd.2006.11.018.
- Buleon A, Colonna P, Planchot V, Ball S (1998). Starch granules: Structure and biosynthesis. *Int. J. Biol. Macromol.* 23: 85-112.
- Carr RL (1965). Evaluating flow properties of solids. *Chem. Eng.*, 72: 163-168.
- Eerlingen RC, Jacobs H, Block K, Delcour JA (1997). Effects of hydrothermal treatment on the rheological properties of potato starch. *Carbohydrate Res.*, 297: 347-256.
- Eerlingen RC, Jacobs H, Van Win H, Delcour JA (1996). Effect of hydrothermal treatment on the gelatinization properties of potato starch as measured by differential scanning calorimetry. *J. Thermal. Anal.*, 47: 1229-1246.
- Fell JT, Newton JM (1970). Determination of tablet strength by diametral compression test. *J. Pharmaceut. Sci.*, 59: 688-691.
- Fichtner F, Rasmuson AC, Alander EM, Alderborn G (2007). Effect of preparation method on compactability of paracetamol granules and agglomerates, *Int. J. Pharmaceut.*, 336: 148-158.
- Franco CML, Preto JDR, Ciacco CF, Campinas QT (1995). Effect of the heat-moisture treatment on the enzymatic susceptibility of corn starch granules. *Starch/Starke*, 47(6): 223-228.
- Galliard T, Bowler P (1987). Morphology and composition of starch. In T. Galliard (Ed.), *Starch: Properties and potentials. Critical reports on applied chemistry*, Great Britain: John Wiley & Sons, (4): 55-78.
- Gitley MJ (1987). Factors affecting the crystalline type ('A' - 'C') of native starches and model compounds; a rationalization of the observed effects in terms of polymorphic structure. *Carbohydrate Res.*, 161: 301-304.
- Han JA, BeMiller JN (2007). Preparation and physical characteristics of slowly digesting modified food starches, *Carbohydrate Polymers*, 67: 366-374.
- Heckel RW (1961a). Density-pressure relationships in powder compaction, *Trans. Metall. Soc. AIME*, 221: 671-675.
- Heckel RW (1961b). An analysis of powder compaction phenomena, *Trans. Metall. Soc. AIME*, 221: 1001-1008.
- Herman J, Remon JP, De Vilder J (1989). Modified starches as hydrophilic matrices for controlled oral delivery. I. Production and characterisation of thermal modified starches, *Int. J. Pharmaceut.*, 56: 51-63.
- Hersey JA, Rees JE (1970). Particle size analysis conference, Bradford, England.
- Hoover R, Mannuel H (1996). The effect of heat - moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, dull waxy maize and amylo maize V starches. *J. Cereal Sci.*, 23: 153-162.
- Hoover R, Vasanthan T (1994a). The effect of annealing on the physical properties of wheat, oat, potato and lentil starches. *J. Food Biochem.*, 17: 303-325.
- Hoover R, Vasanthan T (1994b). The flow of native, heat-moisture treated, and annealed starches from wheat, oat, potato and lentil. *J. Food Biochem.*, 18: 67-82.
- Hoover R, Vasanthan T (1994c). Effect of heat-moisture treatment on the structure on the structure and physicochemical properties of cereal, legume, and tuber starches. *Carbohydrate Res.*, 252: 33-53.
- Humber-Droz P, Gurny R, Mordier D, Doelker E (1983). Densification behavior of drugs presenting availability problems. *Int. J. Pharm. Tech. Prod. Mfr.*, 4: 29-35.
- Jacobs H, Delcour JA (1998). Hydrothermal modifications of granular starch, with retention of the granular structure: A review. *J. Agric. Food Chem.*, 46: 2895-2905.
- Jacobs H, Mischenko N, Koch MHJ, Eerlingen RC, Delcour JA, Reynaers H (1998). Evaluation of the impact of annealing on gelatinization at intermediate water content of wheat and potato starches: a differential scanning Calorimetry and small angle X-ray scattering study. *Carbohydrate Res.*, 306: 1-10.
- Kainuma K, French D (1971). Naegeli amyloextrin and its relationship to starch granule structure. I. Preparation and properties of amyloextrins from various starch types. *Biopolymers*, 10: 1673-1680.
- Kawabata A, Takase N, Miyoshi E, Sawayama S, Kimura T, Kudo K (1994). Microscopic observation and X-ray diffraction of heat-moisture treated starch granules. *Starch/Starke*, 46: 463-469.
- Kawakita K, Hattori I, Kishigami M (1977). Characteristic constants in Kawakita's powder compression equation, *J. Powder Bulk Solids Technol.*, 1: 3-8.
- Kawakita K, Ludde KH (1971). Some considerations on powder compression equations, *Powder Technol.*, 4: 61-68.
- Kobayashi T (1993). Susceptibility of heat-moisture-treated starches to pancreatic α -amylase, and the formation of resistant starch by heat-moisture treatment. *Depun Kagaku*, 40: 285-290.
- Kulp K, Lorenz K (1981). Heat - moisture treatment of starches. I. Physicochemical properties. *Cereal Chem.*, 58: 46-48.
- Leach HW, McCowen LD, Schoch TJ (1950). Structure of the starch granule. I : Swelling and solubility patterns of various starches. *Cereal Chem.*, 36: 534-544.
- Lim ST, Han JA, Lim HS, BeMiller JN (2002). Modification of starch by dry heating with ionic gums. *Cereal Chem.*, 79: 601-606.
- Mohammed H, Briscoe BJ, Pitt KG (2005). The interrelationship between the compaction behaviour and the mechanical strength of pure pharmaceutical tablets, *Chem. Eng. Sci.*, 60: 3941-3947.
- Nicklasson F, Alderborn G (2000). Analysis of the compression mechanics of pharmaceutical agglomerates of different porosity and composition using the Adams and Kawakita equations. *Pharm. Res.*, 17: 949-954.
- Radosta S, Kettlitz B, Schierbaum F, Gernat C (1992). Studies on rye starch properties and modification. Part II. Swelling and solubility behaviour of rye starch granules. *Starch/Starke*, 44: 8-14.
- Rasper V (1980). Theoretical aspects of amylography. In W. C. Shuey, & K. E. Triples (Eds.), *The amylograph handbook*. St Paul, MN: American Association of Cereal Chemists, pp. 1-6.
- Ratnayake WS, Hoover R, Shahidi F, Perera C, Jane J (2001). Composition, molecular structure, physicochemical properties of starches from four field pea (*pisum sativum* L.) cultivars. *Food Chem.*, 74: 189-202.
- Sair L (1964). Heat moisture treatment of starches. In: *Methods in carbohydrate chemistry*, ed. R.L. Whistler; Academic Press Inc., New - York. 4(283) 87-145
- SAS Institute Inc (2000). SAS software release 9.1. SAS Institute Inc., Cary, North Carolina, USA.
- Schoch TJ Maywald EC (1968); Preparation and properties of various legume starches. *Cereal Chem.*, 45: 564-573.
- Sekine M, Otobe K, Sugiyama J, Kawamura Y (2000). Effects of heating, vacuum drying and steeping on gelatinization properties and dynamic viscoelasticity of various starches. *Starch/Starke*, 52: 389-405.
- Shangraw RF (1992). International harmonization of compendia standards for pharmaceutical excipients, in: D.J.A. Crommelin, K. Midha (Eds.), *Topics in Pharmaceutical Sciences, MSP, Stuttgart, Germany*. pp. 205-223.
- Snedcor GW, Cochran WG (1987). *Statistical methods* (17th ed.). The Iowa state University Press, Ames., IA.
- Stute R (1992). Hydrothermal modification of starches: the difference

- between annealing and heat – moisture treatment. *Starch/Starke*, 44: 205-214.
- Wells JI (1997). In: *Tablet testing*, Swarbrick, J., Boylan, J.C. (Eds.), *Encyclopedia of Pharmaceutical Technology*, vol. 14. Marcel Dekker, New York. pp. 401-418.
- York P, Pipel N (1972). The effect of temperature on the mechanical properties of some pharmaceutical powders in relation to tableting. *J. Pharm. Pharmacol.*, 24: 47-56.
- Zhao J, Burt HM, Miller RA (2006). The Gurnham equation in characterizing the compressibility of pharmaceutical materials. *Int. J. Pharmaceut.*, 317: 109-113.
- Zobel HF (1988a). Starch crystal transformations and their industrial importance. *Starch/Starke*, 40: 1-7.
- Zobel HF (1988b). Molecules to granules: a comprehensive starch review. *Starch/Starke*, 40(2): 44-50.
- Zobel HF, Young SN, Rocca LA (1988). Starch gelatinization. An X-ray diffraction study. *Cereal Chem.*, 66: 443-446.