Compaction Properties of Starch Extracted from Seeds of Christ Thorn (Ziziphus spina-christi)

T. Izuagie, L. G. Hassan, A. Uba M. Achor, D. M. Sahabi and I. S. Sadiq

Abstract - The aim of this study was to compare the compaction property of starch extracted from seeds of Christ Thorn with that of standard commercial corn starch. Starch from Christ thorn seeds was extracted by hot water method whereas standard commercial corn starch was purchased from Hali Shuaibu Chemicals, Sokoto. The starches were initially characterized for particle size and shape using optical microscope. Compaction properties were then studied by determining Heckel and Kawakita parameters of the starch tablets formed by direct compression using an ACL hydraulic hand press (Model ACL, U.S.A). The results revealed that the starch from Christ thorn seeds had an oval granular shape, amylose content of 24.6%; bulk density of 0.97gcm⁻³ and particle diameter of 13.3μm. The results also revealed values of 0.53, 170.73 and 0.4906 for D₀, P₀ and D₀ respectively whereas P₀ and D₀ were 1.855 and 0.258 respectively. These showed that there were variations in the Heckel and Kawakita parameters of the compacts when compared with values of the standard commercial corn starch and standard values in literatures. Thus, as the packing properties of starch tablets is important in the production of tablets, capsules and other drug delivery systems containing these powders, the study concludes that Christ Thorn starch may not be a good raw material for producing tablets with desired properties by direct compression.

I. INTRODUCTION

Ziziphus spina-christi commonly called Christ thorn or Kurna in Hausa is a shrub or a tree belonging to the genus Ziziphus in the buckthorn family (Rhamnaceae) [1]. It is widely distributed in the tropical and subtropical regions of the world and is reported to be native to a vast area of Africa stretching from Mauritania through the Sahara and Sahelian zones of West Africa to the Red Sea [2]. It is drought hardy, very resistant to heat and can be found in desert areas with even 100 mm rainfall annually. The tree is frost tender, can withstand water logging for up to 2 months and 8-10 months of dry season. The plant has a height of 20 m and a diameter of 60 cm. It has a light-grey bark, which is very cracked, scaly and has a twisted trunk. It is also very branched, with crown thick; whitish and flexible shoots [2]. The plant is also characterized with thorns in pairs, one straight and the other curved. Its leaves are glabrous on the upper surface, finely pubescent below, with margins almost entirely ovatellanceolate or ellipsoid and conspicuous lateral veins. It has an average size of 50 g with a fruit of about 1 cm in diameter containing a single large seed [2].

Various parts of the plant are used for different purposes. For example, its wood is used as timber for spear shafts, posts, roofing beams, utensils and cabinet making while the leaves are used for animal feeds [3]. The leaves have also been reported to contain various alkaloids, including ziziphine, jubanine and amphibine, alpha terpinol, linalol and diverse saponins and as such can be used for medicine [3]. Its fruit is edible and could serve as food as it is generally regarded as save (GRAS). It is also used in making alcoholic drinks. A good yield of starch (43.2%) has recently been extracted from seeds of Christ thorn [4].

Today, world-wide demand for starch already has exceeded 500 million tonnes per annum and is predicted to increase as a result of growing daily demand of both food and non-food starch products [5]. The over dependence of many industries on food sources of starch like corn, wheat, cassava, yam, etc for raw materials has led to global increase in food prices, with its consequent effects on the global economy. Therefore, the importance of any work aimed at exploring discarded materials like seeds of Christ thorn as sources of starch for industrial application cannot be over emphasized. Among the numerous uses of starch, is its application as fillers, binders, disintegrants, lubricants, etc in the pharmaceutical industry. It is specifically used as binders in tablet formulations mostly by Direct Compression (DC) due to its suitable physicochemical properties and relative inertness [6].

Direct compression is a process of applying pressure (via an upper and a lower punch) to materials held in a die cavity and tablets produced by this method have been reported to provide high efficiency over other tablet manufacturing processes like wet granulation [7]-[8]. Also, the compressibility of DC binders under pressure is extremely important in determining its functionality. This compressibility is predominantly determined by the material properties such as surface energy.
Materials from various sources have been used as binders but currently, only a few materials, such as starch, meet the criteria to allow their classification as DC binders [9]. Thus, a good understanding of the physico-chemical and compaction properties of starches is crucial to their use as DC binders. Therefore, this research work is aimed at studying the compaction properties of starch extracted from Christ thorn seeds with a view to determining their suitability for use as binders in the pharmaceutical industry.

II. MATERIALS AND METHODS

A. Materials

Seeds of Christ thorn were collected from waste sites around Sokoto metropolis and identified at the Botany Unit, Department of Biological Science, Usmanu Danfodiyo University, Sokoto. The seeds were washed thoroughly with distilled water, decorticated to remove skin, dried and ground into flour which was stored in an air-tight container before extraction of the starch. Standard commercial corn starch (M & B, England) was purchased from Hali Shuaibu Chemicals, Sokoto and was used as a positive control. All reagents used were of analytical grade. All analyses were done in triplicate.

B. Methods

Extraction of Starch

The starch was extracted using hot water extraction method. The starch was extracted using hot water method. The flour was soaked in 1000 cm$^3$ beakers in a thermostatic water bath at a constant temperature of 40°C for about 24hrs. One part of soaked flour and three parts of distilled water were blended for 3 min at medium and high speed. The resultant slurry was passed through double layer of muslin cloth and then centrifuged at 5000 rpm for 20 min. The supernatant was discarded and the sediment resuspended in excess 0.02% NaOH to remove any residual proteins and phenolic compounds. After standing for 4hr the supernatant was discarded. This procedure was repeated 6-8 times until the supernatant becomes colourless. The final sediment was suspended in distilled water and then subjected to filtration through 0.045 mm sieve, neutralized to pH 7.0, filtered on Buchner funnel and thoroughly washed with distilled water. The filtered cake was dried overnight at room temperature, ground to powder and stored in a tight glass bottle before further analysis [10]-[14].

Moisture Content Determination

This was determined by drying the starch sample at 110°C for at least 24 hours until the weight became constant [12], [15].

Amylose Content Determination

This was carried out as described in literature [16]. 5ml of 10% w/v aqueous slurry of starch and 55 cm$^3$ of 0.16M sodium hydroxide was introduced into a flask and swirled gently until the suspension clears. After 5minutes, 15ml of 5% v/v sodium hydroxide in 0.6M hydrochloric acid was added and mixed gently but thoroughly. The precipitate was harvested by centrifugation at 10, 000 rev. per min for 15 min, using (Hermle Z230) centrifuge. The supernatant was saved in a separate flask and the precipitate was washed by resuspending it with 1-butanol and letting it stand for a few hours and was collected by centrifugation at 5, 000 rev. per min for 15 minutes. The precipitate was then dried in a Gallenkamp oven at 40°C and weighed.

Particle Shape and Size

Particle shape and size were determined using an optical microscope equipped with ocular and calibrated stage micrometers. 5g of starch sample was suspended in glycerol to ensure uniformity of the test sample. One drop of the suspension was placed on a slide glass and used as the test specimen directly on the microscope to determine the granular size [17]. Each sample was measured 3 times.

Density

The bulk and true densities were determined using standard methods [7].

Compact Preparation and Evaluation

Compression

Compact compression was performed on a single-station manual tablet press (model ACL, London). Ten different compaction pressures (from 0.25 mT to 2.5 mT) were used for each starch sample. For each compact (n = 4), 500 mg of powder was weighed on an analytical balance, and then manually filled into the die. A flat-faced punch with a diameter of 12.5 mm was used. After subjecting the sample to a set pressure, a dwelling time of 30 seconds was allowed before ejection of compact. After ejection, the compacts were stored over silica gel for 24 hrs to allow for elastic recovery and hardening, and prevent falsely low yield values before weighing accurately. Its dimensions (diameter and thickness) were also measured with a digital slide caliper. This information was used for the calculation of relative density, porosity, and degree of volume reduction, which are essential parameters for Heckel and Kawakita analysis. These analyses and hardness properties were used in the study of the compaction properties as described in literatures [6].

Hardness

Hardness was evaluated by determining the crushing strength of compact by compressing the compact diametrically on a Phamatinon tablet tester. The radial tensile strength of the compact was calculated from the compact crushing strength and compact thickness using the equation...
$T = \frac{2F}{\pi \times d \times t}$

where $T$ is the tensile strength (MPa); $F$ is the force required to cause failure in tension (N); $d$ is the diameter of the compact (mm); and $t$ is the thickness of the compact (mm). The use of tensile strength allows the dimensions of the compact to be taken into account, which is in contrast to the use of crushing strength only [7].

**The Heckel and Kawakita Plots**

Heckel plots of $\ln(1/(1-D))$ versus applied pressure ($P$) [18], [19] and Kawakita plots of $P/C$ versus $P$ [20] were constructed for starch. The plots were obtained from the Heckel equation $\ln[1/(1-D)] = KP + A$ and the Kawakita equation $(C = (Vo - Vp) / Vo = abP / (1 + bP))$ or rearranged as: $P/C = P / (a + 1 / ab)$. Where $D = \text{relative density of powder during compression}$, $P = \text{Applied pressure}$, $K$ and $A$ are constants that were gotten from the plots and were used to calculate the mean yield pressure, $P_y$, and the relative densities, $D_A$ and $D_B$ as follows

$P_y = \frac{1}{K}$

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

$D_B = D_A - D_o$

Where, $P_y$ is the mean yield pressure, $D_o$ is the relative density of the starch at the point where applied pressure is zero and is used to describe the initial rearrangement phase of densification as a result of die filling. The relative density $D_B$, describes the phase of rearrangement at low pressures, whereas $D_A$ is the relative density at the intercept, $A$ [18], [19].

Also, $V_o = \text{initial bulk volume of the powder}$ and $V_p = \text{bulk volume after compression}$. The constant $a$ is equal to the minimum porosity of the material before compression whereas the constant $b$ is related to the plasticity of the material [20].

**III. RESULTS AND DISCUSSION**

**A. Physico-chemical properties**

**Moisture Content**

The moisture content of the starch extracted from Christ thorn seeds (Table 1) was within the range of values obtained for other starches in literature [15]. It also compared very well with that of the standard commercial corn starch.

**Amylose Content**

The amylose content of the starch (Table 1) was higher than values obtained for the commercial starch and those reported for oat [21], [22], [23] and corn starches [24] but was less than those reported for Horse Gram starch [13]. Also, the value was within the range of values reported for pulse starches (11.6 - 88.0%) [25]. The amylose content of starch determines crystallinity and thus affects the starch solubility [26].

**Particle Shape and Size**

Optical micrographs (Plates 1 and 2) show that the shape of the starch granule was oval as compared to the round shape of the commercial starch granule. Starches of oval shape have been reported [24]. The micrographs also showed that the particle size of the starch was 13.3μm which was smaller than the value obtained for the standard commercial starch (18.8μm). The smaller size however might not aid compaction as there would be greater mechanical and electrostatic forces to prevent packing [6].

**B. Compaction Properties**

**Hardness**

The result for hardness is shown in Fig.1. A linear relation between tensile strength and compression pressure was observed for both the Christ thorn and standard commercial starches. The result shows that as the compression force increases, tensile strength also increases for both starches. Starches from corn, yam and rice have earlier been reported to show a linear relation between compression force and tensile strength and as a result could be used as fillers for making tablets [6], [7]. However, the relationship between tensile strength and compression force was not a very linear relationship for the Christ thorn starch when compared to the commercial starch.

**Heckel Plot**

Fig. 2 displays the Heckel plot of the starches. It showed that Christ thorn starch followed a linear relationship, with a correlation coefficient < 0.990 indicating little deformation by plastic flow whereas the commercial starch showed a linear relationship with correlation coefficient ≥ 0.999, thus deforming readily by plastic flow. The constants $P_y$, $D_o$, $D_A$ and $D_B$ for the Heckel plot of the starches are also displayed in Table 2. The value of $D_o$ represents the degree of initial packing in the die as a result of die filling for the starches. The $D_o$ was directly related to the particle shape and size as the small particle size of the starch gives more mechanical and electrostatic forces to prevent packing than in the commercial starch [6]. The value of $D_A$, which represents the total degree of packing at zero and low pressures and $D_B$ which represents the phase of rearrangement of the particles in the early stages of compression were lower for Christ thorn starch than the standard commercial starch. The values of $D_A$ and $D_B$ have been found to be directly related to the shape [6]. Thus the oval shape of the starch might be responsible for the small $D_A$. Decreased in $D_A$ values for yam, rice and corn starches as the particle shape deviated from spherical has also been reported in literatures [6]. The mean yield pressure $P_y$ is inversely related to the ability of the starch to deform plastically under pressure [27]. The result indicates that Christ thorn starch exhibited a slow rate of deformation when compared to the commercial starch.
Kawakita Plots

Fig. 3 shows the Kawakita plots for the starches. Also Christ thorn starch gave a linear relationship at all compression pressures employed, with the starch again having a correlation coefficient < 0.999 whereas the commercial starch had a correlation coefficient ≥ 0.999. Table 2 also displays P_k and D_1 values for the starches. The values of D_1, which is a measure of the packed initial relative density of the starch with the application of small pressures or tapping [6] was lower than values obtained for the commercial starch. It was also higher than values obtained for yam, rice and corn starches in literature [6]. The value of P_k, which is an inverse measure of the amount of plastic deformation occurring during the compression process was higher than that of the commercial starch, thus indicating a smaller plastic deformation during compression. Literature have showed that the lower the P_k value for rice, yam and corn starches, the more the total plastic deformation occurring during compression [6]. This indicates that the Christ thorn starch exhibited smaller plastic deformation during the compression process than the commercial starch.

IV. CONCLUSION

From the analyses performed and the results obtained, the study concludes that even though Christ Thorn starch possess some good physico-chemical properties, the starch has a poor compaction property and may not be a good raw material for making binders for the production of tablets with desired properties by direct compression.

REFERENCES

Table 1: Physico-chemical properties of starches

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Christ thorn starch</th>
<th>Standard Commercial Corn starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>7.8±0.4</td>
<td>8.4±0.2</td>
</tr>
<tr>
<td>Amylose content</td>
<td>24.6±1.7</td>
<td>21.6±0.5</td>
</tr>
<tr>
<td>Particle shape</td>
<td>Oval</td>
<td>Round</td>
</tr>
<tr>
<td>Particle Size (μm)</td>
<td>13.3±1.1</td>
<td>8.8±0.7</td>
</tr>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>0.97±0.11</td>
<td>1.45±0.12</td>
</tr>
<tr>
<td>True density (g cm⁻³)</td>
<td>0.63±0.02</td>
<td>0.81±0.01</td>
</tr>
<tr>
<td>Physical appearance</td>
<td>Off-White</td>
<td>White</td>
</tr>
</tbody>
</table>

Data were reported in means ± SD (n = 3)

Table 2: Parameters derived from density measurements, Heckel and Kawakita plots of the starches.

<table>
<thead>
<tr>
<th></th>
<th>Heckel</th>
<th>Kawakita</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R²</td>
<td>D₀</td>
</tr>
<tr>
<td>Christ thorn starch</td>
<td>0.9308</td>
<td>0.53</td>
</tr>
<tr>
<td>Standard Commercial Corn starch</td>
<td>0.999</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Fig. 1: Hardness properties of the Starch from Christ thorn seeds and Commercial Corn Starch.

Fig. 2: Heckel plot of Starch from Christ thorn seeds and Commercial Corn Starch.

Fig. 3: Kawakita plot of Starch from Christ thorn seeds and Commercial Corn Starch.

Plate 1: Optical micrographs of starch extracted from Christ Thorn Starch at x 1000 magnification.

Plate 2: Optical micrographs of standard commercial corn starch at x 1000 magnification.
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