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Physical, Thermal and Sorption Profile of Starch Obtained from *Tacca leontopetaloides*

The purpose of this study was to elucidate functional properties of starch granules obtained from tubers of *Tacca leontopetaloides* and compare them to a commercially available maize starch. Scanning electron microscopy (SEM), particle size analysis, X-ray powder diffraction (XRPD), gravimetric moisture sorption, and differential scanning calorimetry (DSC) were used to characterize the samples. Tacca starch exhibited a monomodal distribution of irregularly shaped granules with a mean particle size of 2.64 μm. The spherulites of both samples indicated an A-type pattern, with the degree of crystallinity estimated to be 35% for tacca starch and 38% for maize starch. The moisture sorption profile of both samples was analyzed according to the Guggenheim, Anderson and de Boer (GAB) equation. GAB analysis estimated the monolayer coverage for tacca and maize starch to be 0.0928 g/g and 0.0856 g/g, respectively. The gelatinization parameters of tacca starch were found to be 65.57 – 68.56 – 73.10°C while that of maize starch were 67.30 – 70.97 – 76.25°C. The results of DSC studies indicate that the associative forces that stabilize the granule structure in tacca starch are weaker than those in maize starch. The results obtained in this study establish the fundamental characteristics of tacca starch and suggest that further exploration of its potential for use in a variety of fields is warranted.

Keywords: Tacca starch; SEM; X-ray diffraction; Moisture sorption; Thermal analysis

1 Introduction

The versatility of starch applications is unparalleled as compared to other biomaterials. Starch has found use in industries as diverse as food, textiles, cosmetics, plastics, adhesives, paper, and pharmaceuticals. The food industry uses starch as a thickening agent in snacks, meat products, fruit juices, etc. [1]. Utilization of starch in the manufacture of disposable items like fast food utensils and containers is gaining increased attention [2]. Modified and unmodified starches are commonly used in products for personal care and cosmetic appeal [3]. From a pharmaceutical standpoint, starch finds its value in solid-oral dosage forms, where it has been used as a binder, diluent, and disintegrant [4]. Research in the area of bio-based desiccants has been vigorously pursued since *Ladisch* and *Dyck* demonstrated the potential of starch for the drying and separation of organic vapors [5]. However, such diversified applicability demands specific functional characteristics, that a single source is unlikely to be able to supply. Therefore, in order to provide market growth, the starch industry has been looking at alternatives that could satisfy particular demands.

Tuber crops form an essential part of the human diet and can serve as a good source of carbohydrate polymers. An appraisal by *Moorthy* indicates that, except for cassava and sweet potato, other tuber crops have not been exploited for their industrial potential [6]. The two main reasons cited were the difficulties during extraction and the dearth of information regarding the physicochemical properties. *Moorthy* further alludes to the fact that the properties demonstrated by certain tuber starches could replace some of the chemically modified starches. Hence research in the area of tuber starches should be encouraged to provide novel samples with unique characteristics. Nigeria has many native species whose potential remains fairly untapped. *Tacca leontopetaloides* (L), Taccacea, an annual herb, which grows upright to a height of 30 cm, is widespread in middle belt of Nigeria. The low cost and ready availability of tacca tubers served as an impetus for exploratory research of this species.

Since the functional properties of starch are clearly reflected by the physicochemical aspects, a thorough physical characterization of the sample is mandatory.

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The purpose of this study was to elucidate the physical, thermal and moisture sorption profile of tacca starch and compare it to a commercially available maize starch.

2 Materials and Methods

2.1 Materials

Tacca starch was isolated from the tubers of *T. leontopetaloides* collected from the middle belt of Nigeria. Starch granules were extracted as described by *Kunle* et al. [7].

2.2 Methods

2.2.1 Scanning electron microscopy (SEM)

Starch granule morphology was obtained using a Hitachi S5200 field emission scanning electron microscope (Hitachi High-Technologies Canada, Inc., Ontario, Canada). Images of uncoated samples were obtained at 1.0 kV accelerating voltage.

2.2.2 Particle size analysis

The particle size distribution of the samples was obtained using a Beckman Coulter LS 13 320 laser diffraction particle size analyzer (Beckman Coulter, Inc., Fullerton, CA). The LS 13 320 is equipped with an optical bench and a Universal Liquid Module to measure the size distribution of particles suspended in water at 20°C. All measurements were obtained in triplicate.

2.2.3 X-ray powder diffraction

Structural characterization was carried out using a Siemens D5000 X-ray diffractometer (Siemens, Munich, Germany). Powder samples, packed in rectangular aluminum cells, were illuminated using CuK_α radiation (λ = 1.54056 Å) at 45 kV and 40 mA. Samples were scanned between diffraction angles of 5° to 40° 2θ, which is sufficient to cover all significant diffraction peaks of starch crystallites. Scan steps of 0.1 were used and the dwell time was 15.0 s. A nickel filter was used to reduce the K_β contribution to the X-ray signal. The '*d*' spacings were computed according to Bragg's law of diffraction. Triplicate measurements were made at ambient temperature. The degree of crystallinity was estimated utilizing the technique described by *Nara* and *Komiya* [8, 9].

2.2.4 Gravimetric moisture sorption

Moisture sorption isotherms were generated at 25°C and ambient pressure using an SGA-100 Symmetric Vapor Sorption Analyzer (VTI Corp, Hialeah, FL). The SGA-100 is equipped with an electronic microbalance (CI Electronics, Wiltshire, UK) and a dew point analyzer (Edgetech, Milford, MA) for the accurate measurement of weight and relative humidity (RH), respectively. The instrument was calibrated using sodium chloride and PVP K30. Samples were dried at 60°C and 0% RH for a minimum of 6 h and exposed to relative humidity in steps of 10% between 10% to 90% RH. Equilibrium was assumed when the microbalance recorded a change of less than 0.01% over a period of 5 min.

2.2.5 Differential scanning calorimetry

Differential scanning calorimetry (DSC) thermograms were obtained using a 2920 Modulated DSC (TA Instruments, New Castle, DE). The temperature axis and cell constant of the DSC cell were calibrated with indium (10 mg, 99.999% pure, melting point 156.60°C, heat of fusion 28.40 J/g). Starch samples ($\sim$ 4.0 mg, dry weight basis) were weighed in aluminum pans on an analytical balance (Sartorius Corp, Edgewood, NY). Approximately 9 μL distilled water was added to each sample pan and the pans were hermetically sealed. To account for the enthalphic contribution of water, the reference pans also contained 9 μL of distilled water. The samples were allowed to equilibrate for a minimum of 2 h and scanned from 25°C to 110°C at a heating rate of 5°C/min under continuous nitrogen flow. Gelatinization parameters were characterized by onset temperature (T_o; °C), peak temperature (T_p; °C), conclusion temperature (T_c; °C), and gelatinization enthalpy (ΔH_{gel}; J/g). All parameters were calculated using the Universal Analysis software (TA Instruments, New Castle, DE). The gelatinization range (R_{gel}; °C) was computed as ($T_c - T_o$) and the Peak Height Index (PHI; J g^{-1} K^{-1}) was calculated as the ratio of (ΔH_{gel}/ $T_p - T_o$) [10–12]. Peak Height Index (PHI) is a ratio that helps compare quantitatively the variation in endotherm shape between samples. This ratio varies directly with enthalpy (ΔH) and inversely with the difference ($T_p - T_o$), and thus provides a numerical value that is descriptive of the relative shape of the endotherm. Statistical analysis was carried out on a sample size of $n = 5$.

3 Results and Discussion

3.1 Morphology

The biological origin of starch serves as a determining factor in the granule shape, size and morphology. As a result, these characteristics not only help to differentiate

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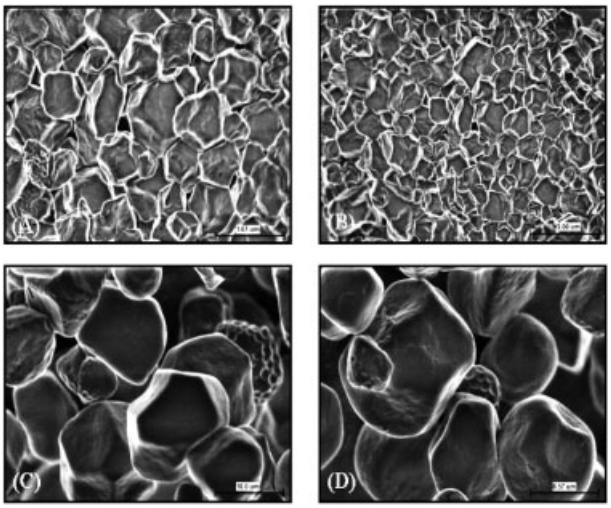

Fig. 1. Scanning electron micrographs of tacca (A and B) and maize (C and D) starch.

between various starches but also give an indication of the processing parameters. Starch granules obtained from tubers have been reported to be oval, spherical, polygonal or irregularly shaped [13, 14]. Scanning electron micrographs of maize and tacca starch are shown in Fig. 1. Tacca starch exhibits irregularly shaped, tiny granules with polyhedral edges while maize starch has round to oval granules with a relative lack of asperity. This observation is consistent with the difficulties encountered in the isolation of tacca starch [7]. The micrographs indicate uniformity of particle size, shape and morphology in tacca starch, compared to interparticulate variability for maize starch. This property of tacca starch could be of importance, especially when considering applications based on surface characteristics, e.g., use of granules as carrier particles.

3.2 Particle size distribution

In a recent review, *Lindeboom* et al. [15] noted that no precise categorization of granule size was found in the literature and hence classified starch granules in four categories: large ($>$ 25 μm), medium (10 – 25 μm), small (5 – 10 μm) and very small ($<$ 5 μm). Based on this classification, maize starch consists of medium granules with a mean particle size of 14.36 μm while tacca starch has very small granules with a mean particle size of 2.64 μm. It should be noted that the granule sizes obtained from the laser light scattering study are slightly smaller than those measured by image analysis [7]. This is attributed to the fact that most starch granules are not truly spherical [16]. The particle size distribution plot is shown in Fig. 2. Tacca starch exhibits a monomodal narrow distribution with most of the particles lying between 0.8 μm and 6.0 μm. Conversely, maize starch granules exhibit a broad size distribution ranging from about 8.0 μm to 32.0 μm. A review of the literature clearly indicates an increasing interest in starches, like tacca starch, with small granules and a narrow size distribution [15, 17, 18].

3.3 X-ray powder diffraction (XRPD)

Granular starches are usually found to give diffraction patterns, that have been classified as A, B or C depending upon the arrangement of the double helical amylopectin chains. The A-pattern is obtained as a result of a close-packed arrangement with a water molecule between each double helix, while a more open hexagonal packing, with water molecules in the central cavity, exhibits a B-pattern [19, 20]. Interplanar spacing and relative intensities of characteristic lines by which the three patterns can be differentiated are well documented in the literature [21]. Usually the diffraction pattern is dependent upon the

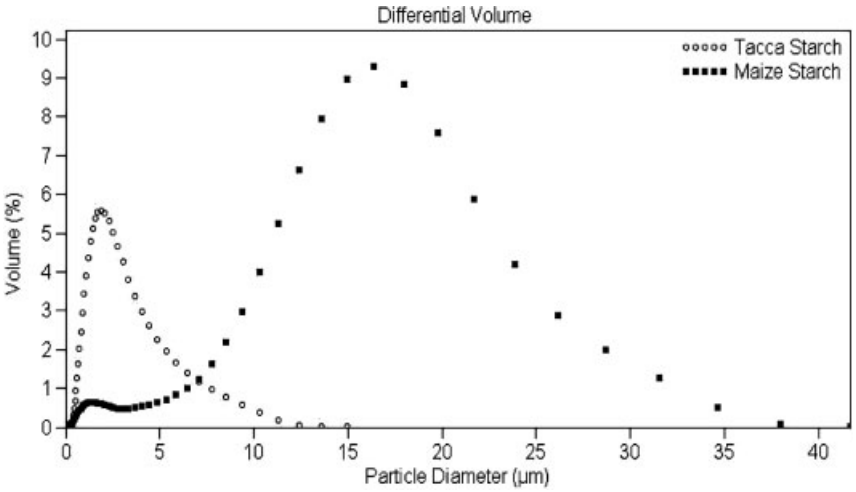

Fig. 2. Particle size distribution of tacca and maize starch.

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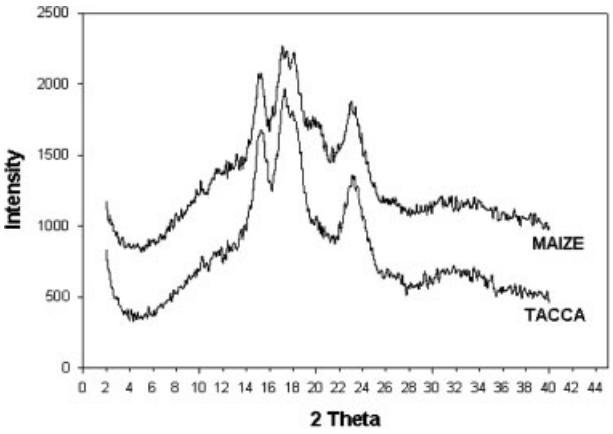

Fig. 3. X-ray powder diffraction pattern of tacca and maize starch.

biological origin, but is also affected by other factors like amylopectin chain length, amylose and moisture content [22, 23]. Powder X-ray diffractograms of maize and tacca starch are shown in Fig. 3. The Bragg reflection angle, 2θ, along with the interplanar spacing, *d*, and the relative intensity of the peaks is listed in Tab. 1. The interplanar spacing has been calculated using Bragg's equation given as $n\lambda = 2d \sin\theta$, where θ is one half the angle read from the diffractogram. As seen in Fig. 3 and Tab. 1, both samples show strong peaks at approximately 15°, 17° and 23° 2θ. Moreover the peak at 18° 2θ is unresolved and has been converted into a shoulder, characteristic of an A-type pattern. Although tuber starches usually give a B-type powder pattern, the characteristic peak for B-pattern at 5° 2θ is not seen for tacca starch. Thus it was concluded that both maize and tacca starch demonstrate A-type crystallinity. *Zobel* noted that powder patterns usually become weak at moisture contents below 10% and the discrete line pattern of B-type structure completely disappears below 1% moisture content [21]. Therefore, diffractograms of both samples were obtained at appropriate moisture content (~10%). Irrespective of the powder pattern, it is generally accepted that a starch granule involves alternating regions of amorphous and crystalline lamellae. Moreover, there is increasing evidence that the crystalline nature of starch is due to amylopectin, while amylose disrupts the order of the crystallites [24]. The degree of crystallinity was estimated to be 35% for tacca starch and 38% for maize starch. These results are consistent with the theory that higher amylose content corresponds to a lower crystalline order of the spherulites.

Tab. 1. X-ray powder diffraction data of maize and tacca starch.

Tacca starch			Maize starch		
2θ	*d*-spacing [Å]	Intensity	2θ	*d*-spacing [Å]	Intensity
10.2	8.67	weak	10.1	8.69	weak
11.8	7.51	weak	15.3	5.79	strong
15.3	5.79	strong	17.4	5.09	strong
17.3	5.12	strong	18.2	4.87	unresolved
18.0	4.93	unresolved	20.1	4.41	medium
23.2	3.85	strong	23.2	3.83	strong
31.3	2.86	weak	30.8	2.90	weak

3.4 Moisture sorption analysis

Numerous treatments have been proposed for the analysis of moisture sorption by starch. The most prominent amongst them being the BET equation, developed by *Brunauer*, *Emmett* and *Teller*. However, the BET model suffers from the limitation that it is only valid at low relative humidity, and does not accurately predict the moisture sorption at the upper end of the relative humidity scale. As a result various modifications of this model have been proposed which improve the fit at high humidity. *Guggenheim*, *Anderson* and *de Boer* (GAB) proposed one such model that, to a first degree of approximation, involves realistic parameters and provides a good fit to moisture sorption data over the entire range of humidity. The GAB equation is an extension of the BET model, that accounts for the presence of an intermediate state between the tightly bound water 'monolayer' and the condensed molecules adsorbed at high RH. Molecules in the intermediate state can be considered to interact with the solid, but the interaction is weak compared to that of the 'monolayer'. Mathematically, the GAB equation is written as:

$$W = \frac{C_G K W_m (P/P_0)}{[1 - K(P/P_0)][1 - K(P/P_0) + C_G K(P/P_0)]}$$

where *W* represents the grams of water sorbed per gram of solid; W_m represents the grams of water in the form of a so-called "monolayer"; C_G and *K* are parameters related to the heat of sorption of the monolayer and intermediate layer, respectively; and P/P_o is the relative water vapor pressure. The moisture sorption profiles of tacca and maize starch are shown in Fig. 4. The GAB parameters from the moisture sorption analysis of the two samples are given in Tab. 2.

Moisture sorption by starch has been attributed to the interaction between the hydroxyl groups of the hexose moiety and water molecules [25]. Although water molecules form hydrogen bonds to both amylose and amylopectin, the amylopectin structure has been shown to physically trap water molecules. On this basis, it was hypothesized that starch granules high in amylopectin

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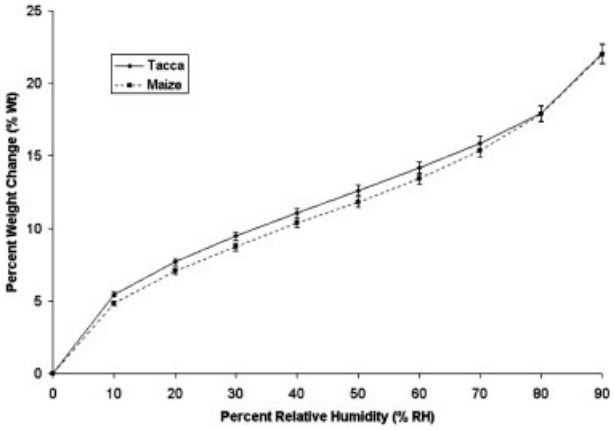

Fig. 4. Moisture sorption profile of tacca and maize starch.

would have a higher moisture sorption potential [26]. Contrary to this hypothesis, maize starch, with higher amylopectin content, exhibited less moisture uptake compared to tacca starch. The difference in moisture sorption by tacca and maize starch could be attributed to the difference in crystallinity. Crystalline polymers have been proposed to have extensive secondary intermolecular bonding. This secondary bonding causes the hydroxyl groups on adjacent glucose units to interact with each other and hence reduces the available sites for adsorption of water molecules [27]. As a result, the higher degree of crystallinity could reduce the moisture sorption, as seen in Fig. 4. The interaction parameter, C_G, and the amount of water sorbed as a 'monolayer', W_m, are both higher for tacca starch as compared to maize starch (Tab. 2), indicating an increased availability of active sites for moisture sorption. It is interesting to note that no significant difference is noted in the ability of both samples to sorb moisture at high relative humidity ($>$ 70% RH). This indicates that once the available sites are saturated at low relative humidity, the specific surface, which should be relatively higher for tacca starch, does not contribute to moisture sorption. The sorption process at high humidity is reduced to condensation of water molecules over the already existing molecules, forming layers, that have decreased interaction with the surface.

Tab. 2. GAB parameters for maize and tacca starch obtained from moisture sorption analysis.

Sample	C_G	K	W_m [g/g]	Crystallinity	Amylose:amylopectin
Maize	15.6635	0.6908	0.0856	38%	11.5:88.5
Tacca	17.9807	0.6538	0.0928	35%	22.5:77.5

3.5 Thermal analysis

Starch gelatinization is commonly described as a series of thermally associated events that convert an aqueous dispersion of starch into a paste. This conversion has been related to various irreversible changes such as granule swelling, loss of birefringence, leaching of amylose, and increased viscosity and solubility. From a thermodynamic standpoint, gelatinization refers to the enthalpic transitions involving the starch granule treated as a semi-crystalline entity (spherulite). Collapse of the crystalline structure leads to a gain in entropy that tends to dislodge the hydrogen bonding network occurring in the spherulites. *Biliaderis* et al. have proposed a comprehensive thermodynamic explanation of gelatinization based on the theory of polymer spherulites [12]. Water is essential for gelatinization of starch as it acts as a plasticizer and moderates the glass transition temperature of the polymer. Various studies, discussing the effect of water on the gelatinization of starch, have been published [28–30].

Every starch sample gelatinizes over a specific range of temperature and hence the elucidation of gelatinization parameters is an integral part of starch characterization. Differential scanning calorimetry, because of its sensitivity and accuracy, has been extensively used to study the phase transitions of this process [11, 31]. The thermograms for tacca and maize starch are shown in Fig. 5 and the corresponding parameters are tabulated in Tab. 3. As expected, only a single endothermic peak is exhibited by both samples at high water content (volume fraction of water $>$ 0.70). This continuous endothermic transition is indicative of granule swelling and crystallite melting occurring over the gelatinization range [32]. The onset, peak, and conclusion temperatures of gelatinization of tacca starch were observed to be lower than that of maize starch. The results obtained from the X-ray diffraction studies indicate that the degree of crystallinity of tacca

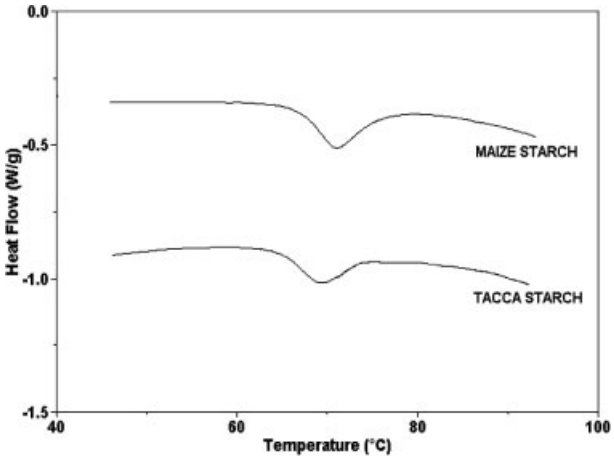

Fig. 5. Gelatinization behavior of tacca and maize starch.

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Tab. 3. Gelatinization parameters for tacca and maize starch (± SD for $n = 5$).

T_o [°C]	T_p [°C]	T_c [°C]	ΔH_{gel} [J/g]	R_{gel} [°C]	PHI [J g^{-1} K^{-1}]
Maize					
67.30 ± 0.41	70.97 ± 0.16	76.25 ± 1.78	7.01 ± 1.73	8.95 ± 2.19	1.89 ± 0.48
Tacca					
65.57 ± 0.77	68.56 ± 0.46	73.10 ± 1.15	3.49 ± 1.55	7.53 ± 1.66	1.14 ± 0.46

starch is lower than that of maize starch. Moreover, the enthalpy of gelatinization for tacca starch is considerably lower than that of maize starch. Thus it was concluded that maize starch has more crystalline regions, that are thermally and structurally stable as compared to tacca starch. These results are accord with a previous study [7], where it was shown that the swelling power of tacca starch is significantly higher than that of maize starch. The results from XRPD and DSC studies substantiate the fact that the associative forces, that stabilize the granule structure in tacca starch, are weaker than those in maize starch.

4 Conclusions

The results obtained in this study establish the fundamental characteristics of tacca starch and recommend further exploration of its potential for use in a variety of fields. The small particle size, along with a monomodal distribution, indicates its usefulness in the area of textiles for fabric stiffening [33]. The lower gelatinization temperature and the narrow gelatinization range demonstrate an energy efficient cooking process and have implications for the food industry. The weak associative forces stabilizing the tacca starch granules could be explored for its potential use as a disintegrant in the pharmaceutical sector. Further work will continue to develop insights to the various applications of tacca starch.

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