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Structure and properties of *Treculia africana*, (Decne) seed starch

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ABSTRACT

Starch isolated from seed flours of four *Treculia africana* (African breadfruit) trees ranged from 36.0 to 41.7% (w/w, flour). Digital microscopy and image particle size analysis showed smooth, small to medium elliptical granules of sizes 3.56–13.60 μm with over 80% of the granules in the size range of 5.50–9.49 μm. *T. africana* starch displayed an A-type X-ray diffraction pattern with crystallinities in the range of 40.21–43.14%. The apparent amylose content ranged from 21.2 to 23.1% while the absolute amylose content was 13.7–21.7%. The gelatinization characteristics, swelling power and amylose leaching, paste clarity, freeze thaw stability and rheological properties were studied. The gelatinization onset temperatures ranged from 71.5 to 75.1 °C, and the peak gelatinization temperatures and endothermic enthalpies were 74.5–78.8 °C and 12.22–13.99 J/g, respectively. Rheological examination of 5% starch paste over the range of shear rate 0.1–1000/s gave shear viscosities of 3.357–8.285 Pa s and rate indices of 0.44–0.53 and the mechanical spectra indicated that the gels were formed with $G' > G''$ over the frequency range studied. *T. africana* starch exhibited low level of syneresis after six freeze thaw cycles (32–38%); however, it would require modification to enhance its application in processed foods.

1. Introduction

Starch continues to play a special role in the food industry. In addition to its nutritive value, starch is employed in many applications as a thickener, binder and gelling agent. Most regular starch pastes do not possess the application properties desirable in food processing, that is, they are subject to loss of viscosity when subjected to processing conditions and syneresis when applied in frozen foods. There is, therefore, the need to screen starches from new carbohydrate sources for novel properties.

Treculia africana, Decne (African breadfruit) is an important food crop in sub-Saharan Africa. It is a major source of calories for over 60 million people of Southern Nigeria and the Central African Republic. The seeds which are about 8.5 mm in length are used in many traditional food preparations. When the seeds are to be reduced to flour, dehulling is employed to remove the seed coat and improve the appeal of the product. Foods prepared from African breadfruit seeds are known to have good textural characteristic, which is attributable to the nature of the starch constituents. Several papers have examined the nutritive value of this important food material and research is being carried out to expand its application in processed foods (Akubor, 1997; Ejiofor, Obiagulu, & Okafor, 1988; Fasasi, Eleyinmi, Fasasi, & Karim, 2004; Nwokocha & Ugbomoiko, 2008). However the starch has remained unexplored possibly because of lack of information on the starch properties. In a preliminary study, we isolated the starch at a yield of 13.9% from fresh seeds. The starch exhibited a high pasting temperature (81 °C). An 8% (w/v) paste gave a high paste viscosity (780 BU), and showed considerable shear thinning and setback similar to cassava starch (Nwokocha & Ogunmola, 2005). In this work we collected seeds from four different *T. africana* trees grown in the city of Ibadan with the aim to further investigate the starch structure and properties.

2. Materials and methods

2.1. Starch isolation

T. africana seeds were obtained from matured and ripened fruits from four different trees and air dried. The seeds were dehulled and separately dry-milled to flour using a domestic milling machine (CORONA®, LANDERS and CIA, S.A.). The flours were sieved with a Muslin cloth (75 μm mess) and stored in sealed containers.

A known weight of flour was dispersed in about five times its weight of 0.3% aqueous sodium hydroxide solution, stirred and the suspension allowed to stand for 2 h. It was sieved with a 63 μm mesh. The chaff was rinsed several times and discarded while the resulting starch milk was allowed to settle and the supernatant decanted. The starch was purified by washing it several times with distilled water. The resultant starch was air dried and stored in

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sealed containers. The isolated starches from the four tree sources were labelled as TASS1, TASS2, TASS3 and TASS4.

2.2. Microscopy and image particle size analysis

The granule micrographs were obtained with a Keyence Digital Microscope (VH-Z500, Osaka, Japan). The starch granules were stained with a dye (Direct Red 80, Aldrich Chemical Company Inc., Milwaukee 53233, USA) and viewed on a microscope slide. Image particle size analysis was obtained using BT-1600 Image particle size analyzer (Bettersize Instruments Ltd, Dandong, China). The starch powder on a microscope slide was focused with a light microscope (objective magnification 40×) (Meiji Techno Co Ltd, Saitama 354-0043, Japan). The computer acquired video was processed and the granule characteristics determined for at least 130 granules.

2.3. X-ray diffraction

The starch samples were oven dried at 50 °C overnight and then pulverized to a powder with a particle size of less than 63 μm mesh. The samples were placed in the cavity of a disc sample holder of the diffractometer. Diffraction diagrams were recorded using Inel X-ray equipment (INEL Diffractometer CSP120, 45410 Artenay, France) operating at 40 kV and generator current of 30 mA. Cu $K_{\alpha 1}$ radiation ($\lambda = 0.15405$ nm) was selected using a quartz monochromator and scanned between 3° 2θ and 30° 2θ. A curved position detector was used to monitor the intensities using 2 h exposure periods. PeakFit software (Systat Software Inc., Chicago, USA) was used to quantitatively estimate the degree of crystallinity using the Erfc Pk type in peak fitting and analysis of the amorphous area ($r^2 > 0.99$). The percentage crystalline area was obtained by difference.

2.4. Proximate analysis

The starch moisture was determined by oven drying at 105 °C for 15 h. The oven dried sample was used for ash determination by first igniting the sample on a hot plate in a fume chamber and completing the burning in a muffle furnace at 600 °C to a constant weight of ash. Nitrogen content was determined based on Total Kjeldahl Nitrogen (TKN) by the HACH method (1990) and protein content calculated as nitrogen × 6.25. Crude fat was obtained from hexane extraction and crude fibre determined with the defatted starch according to the method of Maynard (1970).

2.5. Determination of the blue value, apparent and absolute amylose contents

Dry starch (0.1 g) in a test tube was added ethanol (1 ml, 95%) to disperse it followed by NaOH solution (9 ml, 1 M) and heated in a water bath to gelatinize the starch. This was transferred quantitatively into a 100 ml standard volumetric flask and made up to mark with distilled water. 5 ml of the solution was taken into a 100 ml volumetric flask and acetic acid (1 ml, 1 M) added followed by 2 ml stock iodine (0.2 g I_2/2 g KI) and made up to mark with distilled water. This was left for 20 min for the colour to fully develop. The solution was put in a 1 cm cuvette and scanned in a Lambda 25 UV/Visible Spectrophotometer (Perkin Elmer, Massachusetts 02451, USA) (wavelength 350–950 nm, scan speed 480) using iodine solution of the same concentration, but without starch, in the reference cell. A calibration curve was prepared with potato amylose (Type III: from potato, Sigma–Aldrich Chemical Co., St Louis, MO) (10–50 mg) from which the amylose content of the starches was obtained by extrapolation from the absorbance–amylose concentration curve.

The blue value (Gilbert & Spragg, 1964) was calculated as:

$$\frac{\text{Maximum absorbance} \times 4}{\text{Starch concentration (mg/dL)}}$$

Absolute amylose content was determined as discussed above except that the starch sample was purified by dissolving in 90% dimethyl sulphoxide (DMSO) solution (Stevenson, Doorenbos, Jane, & Inglett, 2006) overnight, centrifuged and the starch solution precipitation with isopropanol.

2.6. Gelatinization properties

The gelatinization properties of starch were determined using differential scanning calorimetry (Micro DSC III, Setaram Instruments, 69300 Caluire, France). 10% (w/v) starch dispersions were placed in the sample cell and an equal mass of water was placed in the reference cell. The samples were heated from 30 °C to 100 °C at a scanning rate of 1 °C/min.

2.7. Swelling power and amylose leaching

Starch (0.1%, w/w, dry basis) was dispersed in distilled water by means of a magnetic stirrer. Dispersion aliquots (10 g) containing 1 mg/ml starch were transferred into pre-weighed tubes, sealed and immersed in a thermostatic water bath equipped with a mechanical shaker for 30 min from 60 °C to 95 °C at 5° intervals. The samples were agitated throughout the heating period to maintain a starch suspension. The samples were centrifuged at 1500 rpm for 10 min and the supernatant was carefully drawn off. The weight of the paste was determined and used to calculate the swelling power as weight of paste divided by the original weight of dry starch. 5 ml of the supernatant was transferred into a 100 ml volumetric flask followed by the addition of 1 ml of acetic acid, 2 ml of stock iodine solution (0.2 g I_2/2 g KI made up to 100 ml) and the volume made up to mark. This was shaken and the absorbance measured after 20 min. The amylose concentration was extrapolated from a standard absorbance–amylose curve. The amylose content was expressed as mg amylose/100 mg starch.

2.8. Determination of paste clarity

Paste clarity was determined by the method of Singhal and Kulkarni (1990) by measuring the percentage light transmitted by 1.0% (w/v) starch paste at 660 nm on a UV/Visible Spectrophotometer. Distilled water was used in the reference cell.

2.9. Freeze thaw stability

The freeze thaw stability was determined on 5% (w/v) starch pastes according to the method of Singhal and Kulkarni (1990), prepared by heating the starch dispersion in a water bath maintained at 95 °C for 30 min. The starch paste was stored at 4 °C (18 h) and thawed at 25 °C (3 h), and centrifuged at 2500 rpm for 10 min and the weight of exudates determined over a 6-day period. Freeze thaw stability was calculated as percentage weight of exudates per weight of paste.

2.10. Rheological properties

The rheological properties were investigated on 5.0% (w/v) starch pastes. The starch dispersions were heated in sealed tubes immersed in a water bath maintained at a temperature of 99 °C for 30 min. The samples were agitated during the first 3 min of immersion during which pasting occurred. The pastes were removed and left at 25 °C and the rheological properties

Table 1
Composition and granule size distribution of *Treculia africana* starches.

	TASS1	TASS2	TASS3	TASS4
Yield (%)[a]	36.0	41.7	39.1	40.1
Moisture (%)	6.51a	8.14a	7.66a	6.98a
Fat (%)	0.095a	0.040b	0.057b	0.131c
Protein (%)	1.63a	1.13b	1.25b	1.58a
Fibre %)	0.365a	0.338b	0.328b	0.318b
Ash (%)	1.12a	1.04b	1.11a	1.05b
Granule characteristics				
Particle number	130	154	162	150
Maximum diameter (μm)	11.64	10.11	13.60	11.59
Minimum diameter (μm)	4.33	3.5	4.49	5.15
Average granule size (μm)	7.93	7.02	7.77	7.79
Length/diameter, *L*/*D*	1.38	1.30	1.27	1.34
Roundness	0.56	0.66	0.69	0.60

Values with letters are means of two determinations. Different letters in a row are significantly different at 95% confidence interval ($p < 0.05$).
[a] Based on weight of flour.

examined after 1 hr. The flow properties were measured on a controlled stress Rheometer (AR 500, TA Instruments Ltd, Newcastle, UK) with cone and plate geometry (60 mm, 2° cone and 50 μm gap). Measurements were carried out at 25 °C at shear rates of 10^{-1} to 1000 s^{-1}. The storage modulus (G') and loss modulus (G'') of the starch pastes were determined by small deformation oscillatory measurements over the frequency 10^{-1} to 100 rad s^{-1} within the viscoelastic region (strain, 0.76%). The linear viscoelastic region was obtained by performing a strain sweep within the range of 0.01–100 Pa at an angular frequency of 1 rad s^{-1}. The samples were pre-sheared at 0.1 Pa for 10 min followed by equilibration for 2 min before taking the measurements.

2.11. Statistical analysis

Analysis of variance (ANOVA) was used to compare sample means at 95% confidence level ($p < 0.05$) using Microsoft Excel 2003 software.

3. Results and discussion

3.1. Yield and composition

As shown in Table 1, the yield of starch from *T. africana* seed flours ranged from 35.95 to 41.70%. The starch content of *T. africana* is reasonably high for exploitation when compared with common sources of commercial starch: maize (45–63.8%; Ji, Seetharaman, & White, 2004) and potato (63–83.6%, dry weight of tubers; Leszczynski, 1989). Starch content reported for other seeds of forest origin varies with botanical source: *Araucaria araucana* seed (64%; Henriquez et al., 2008), *Ginkgo biloba* seed (22%; Spence & Jane, 1999), *Artocarpus heterophyllus* seed (18%; Tulyathan, Tananuwong, Songjinda, & Jaiboon, 2002). The moisture composition of the starches ranged from 6.51 to 8.14%. There was no significant difference in the moisture content of the starches ($p < 0.05$). Starch moisture is a function of drying and storage environment and is usually less than 20% in commercial starches (Soni, Sharma, Dun, & Gharia, 1993). The *T. africana* starches contained fairly high amounts of protein (1.13–1.65%) and ash (1.04–1.12%) but low fat content (0.040–0.131%). These values are lower than 6.7% (protein) and 4.2% (fat) reported for acorn starch (Stevenson, Jane, & Inglett, 2006). A significant difference ($p < 0.05$) was observed between the ash, protein, fat and fibre contents of the different *T. africana* starches.

3.2. Microscopy

Starch from different botanical sources presents characteristic shapes, sizes and morphologies (Jane, Kasemsuwan, Leas, Zobel, & Robyt, 1994; Lindeboom, Chang, & Tyler, 2004). In general, granule sizes may vary from less than 1 μm in amaranth and cow cockle starches to more than 100 μm in potato and canna starches. Lindeboom et al. (2004) in a review classified starch granule sizes as: large (>25 μm), medium (10–25 μm), small (5–10 μm) and very small (<5 μm). Fig. 1 shows the granules of African breadfruit seed starch obtained at a magnification of 2000×. The granules were smooth and elliptical in shape. Surface features became visible, indicating the presence of indented granules similar to an egg cut into two unequal parts, the hilum and growth rings. Similar indented granules are common in cassava starch granules (Nwokocha, Aviara, Senan, & Williams, 2009), and growth rings in the granules of potato starch (Pilling & Smith, 2003). The size distribution (Table 1) shows the starch granules were small to medium in size according to the classification of Lindeboom et al. (2004). The granule sizes ranged from 3.56 to 13.60 μm with over 80% of the granules in the size range 5.50–9.49 μm. The granule average diameter ranged from 7.02 μm in TASS2 to 7.93 μm in TASS1. The *L*/*D* ratio and roundness were 1.27–1.38 and 0.56–0.69, respectively. The largest granule was found in TASS3 (13.6 μm) while the smallest was in TASS2 (3.56 μm). TASS2 contained the highest number of small granules with about 12% in the size range 3.50–5.49 μm compared with 1.5–3% in the others. Granule sizes reported for other tree seed starches were: *G. biloba* seed starch (5–20 μm; Spence & Jane, 1999) and *Quercus palustris* (3–17 μm; Stevenson, Doorenbos, et al., 2006). Fractionation of starch into large and small granules has provided further interest on starch properties and several researchers have tried to correlated granule size with starch physicochemical properties. Goering and DeHaas (1972) reported lower pasting temperature for small granules of barley starch, but Lorenz (1990) report higher gelatinization temperatures for small granules of *Chenopodium quinoa* starch as compared to the large granules. Vasanthan and Bhatty (1996) did not observe any significant difference in the gelatinization temperature of the large and small granules of barley starch but noticed that the gelatinization range was consistently larger for the small granules than large ones in a study involving different barley varieties. This indicates that granule size could be one of the many factors affecting gelatinization temperature. Differences in amylopectin fine structure have been reported between small and large granules (Tang, Watanabe, & Mitsunaga, 2002). Greater swelling and enzyme susceptibility, and faster retrogradation have been associated with smaller granules (Fukai,

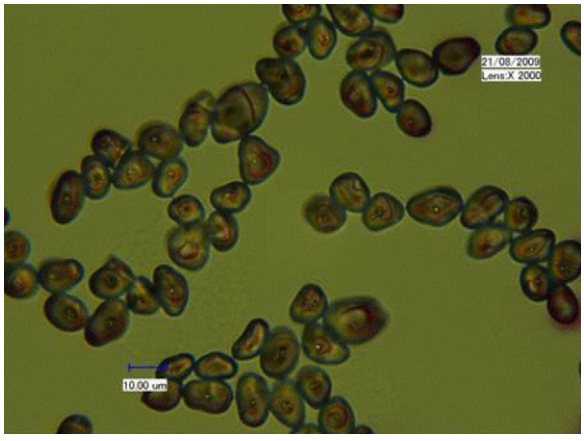

Fig. 1. *Treculia africana* starch granules.

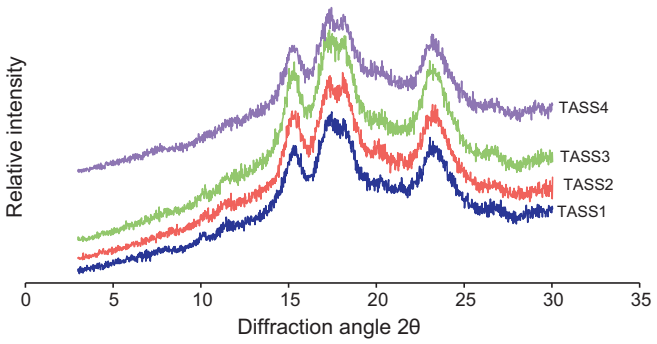

Fig. 2. X-ray diffraction patterns of *Treculia africana* starches.

Takaki, & Kobayashi, 1994; Tang et al., 2002; Vasanthan & Bhatty, 1996).

3.3. X-ray diffraction

The X-ray diffraction pattern of *T. africana* starches (Fig. 2) shows intense peaks at 2θ values of 15.3°, 17.4°, 18.4° and 23.4°. The absence of peaks at about 2θ 5.2° and lack of split at 22–24° shows that the diffraction pattern is characteristic of an A-type structure common in cereal starches like maize and barley. Also there was no prominent peak at 2θ 20° indicating little or absence of amylose–lipids complexes. A B-type diffraction pattern is common in certain tuber starches like potato, canna (Watcharatewinkul, Puttanlek, Rungsardthong, & Uttapap, 2009) and yam (Riley & Wheatley, 2006) while a C-type is common in the legume starches (Gernat, Radosta, Damaschun, & Schierbaum, 1990; Sandhu & Lim, 2008). The percentage crystallinities of *T. africana* starches were: TASS1 (43.14), TASS2 (40.96), TASS3 (40.21) and TASS4 (40.82). We have not found any report on the X-ray diffraction pattern of *T. africana* starch however an A type X-ray diffraction pattern has been reported for *Q. palustris* starch (Stevenson, Jane, et al., 2006) and both A- and C-type X-ray diffraction patterns for *G. biloba* starch (Spence & Jane, 1999), from seeds of trees of forest origin. The values of starch crystallinity vary from 15 to 45% (Liu, 2005) depending on starch source and method of calculating the crystallinity. Amylose content has little effect on the crystallinity of A-type starches; however, a higher amylose content results in lower crystallinity in B type starches but there is no trend in crystallinity in C-type starches (Liu, 2005). Acid hydrolysis has been reported to increase the crystallinity of starch granules; this is attributed to the preferential breakdown of the amorphous region of the granules (Wang, Gao, Yu, & Xiao, 2006).

3.4. Blue value and amylose content

The starch–iodine absorption characteristics and the apparent (amylose$_{(app)}$) and absolute amylose (amylose$_{(abs)}$) contents of *T. africana* starches are shown in Table 2. The wavelength of maximum absorption (λ_{max}) and blue value (BV) were not the same for all the starches. This could be due to the difference in the starch composition and structural characteristics. The $\lambda_{max\,(app)}$ was generally higher than the $\lambda_{max\,(abs)}$ except for TASS4. Generally, the BV$_{(app)}$ was higher than the BV$_{(abs)}$. The amylose$_{(app)}$ ranged from 17.1 to 23.1% while the amylose$_{(abs)}$ was 13.7–21.8%. Overestimation of absolute amylose could occur as long chain of amylopectin molecules could contribute to higher iodine binding. The amylose$_{(abs)}$ was lower than the amylose$_{(app)}$ for all the starches except for TASS4. Both amylose$_{(app)}$ and amylose$_{(abs)}$ showed statistically significant differences between them ($p < 0.05$). Some other workers have reported similar lower values of amylose$_{(abs)}$ to amylose$_{(app)}$ in other starches (Spence & Jane, 1999; Stevenson et al., 2006; Thitipraphunkul, Uttapap, Piyachomkwan, & Takeda, 2003). Mweta, Labuschagne, Koen, Benesi, and Saka (2008) reported the following values of λ_{max}, BV and amylose content for cocoyam starch (614.5 nm, 0.329, 16.27%) and some cultivars of cassava starch (596.5 nm, 0.234–0.289, 16.96–28.25%), respectively. Amylose composition influences the physicochemical and rheological properties of starch (Noosuk, Hill, Farhat, Mitchell, & Pradipasena, 2005). Schoch and Maywald (1968) in their study observed that increase in amylose content resulted in restricted swelling and stabilization of the hot paste viscosity in legume starches. Amylose interacts with lipids to form amylose–lipid complexes and higher amounts of amylose–lipid complexes inhibit swelling and gelatinization of starch (Lindeboom et al., 2004).

Table 2
Starch–iodine absorption characteristics of *Treculia africana* starches.

Starch source	TASS1	TASS2	TASS3	TASS4
$\lambda_{max\,(app)}$ (nm)	598–600	602–604	599–600	596–599
$\lambda_{max\,(abs)}$ (nm)	570	553–554	596	605
Blue value$_{(app)}$	0.4532^{a}	0.4530^{a}	0.4874^{b}	0.4596^{a}
Blue value$_{(abs)}$	0.3834^{a}	0.3592^{b}	0.4142^{c}	0.4525^{d}
Amylose$_{(app)}$ (%)	17.2^{a}	21.7^{b}	23.1^{c}	17.1^{d}
Amylose$_{(abs)}$ (%)	16.3^{a}	13.7^{b}	19.4^{c}	21.7^{d}

Values with superscripts are means of two determinations. Different superscripts on the same row are significantly different at 95% confidence interval ($p < 0.05$).

Table 3
Gelatinization characteristics of *Treculia africana* starches.

Gelatinization parameters	TASS1	TASS2	TASS3	TASS4
Onset temperature, T_o (°C)	71.53	75.11	72.61	71.98
Peak temperature, T_p (°C)	74.50	78.78	75.75	74.98
Completion temperature, T_c (°C)	78.70	82.59	79.13	79.31
Gelatinization range, ($T_c - T_o$) (°C)	7.17	7.48	6.52	7.33
Endothermic enthalpy, ΔH (J/g)	13.99	13.45	13.65	12.22

3.5. Gelatinization properties

Starch gelatinization is an order–disorder phase transition of starch granules in presence of water and heat resulting in loss of the crystalline order, swelling of the granules and solubilization of starch molecules. The transition is endothermic and the heat change is called the gelatinization enthalpy. Table 3 shows the gelatinization parameters of the different *T. africana* starch materials. The gelatinization onset temperature (T_o) varied with starch source and were: TASS1 (71.53 °C), TASS2 (75.11 °C), TASS3 (72.61 °C) and TASS4 (71.98 °C). T_o was highest in TASS2 and least TASS1. The starches had low gelatinization range (ΔT) 6.52–7.48 °C and enthalpy change 12.22–13.99 J/g. The low gelatinization range could be due to the fairly uniform granule sizes. Similar low gelatinization ranges were reported for starches from kiwifruit (7.4 °C; Sugimoto, Yamamoto, Abe, & Fuwa, 1988), water yam (5.4 °C; Farhat, Oguntona, & Neale, 1999) and winter squash (6.3 °C; Stevenson, Yoo, Hurst, & Jane, 2005). This very low gelatinization range would enable *T. africana* starch to be desirable for food processing as it will form viscous pastes with smooth texture and absence of lumps.

The gelatinization temperature of *T. africana* is comparable to 73.7 °C reported for *Q. palustris* starch (Stevenson et al., 2006) but lower than 80–85 °C reported for *Quercus leucotrichophora* starch (Soni et al., 1993), all from forest tree seeds. The ΔT for *T. africana* was smaller than 17.9 °C for *G. biloba*, another forest tree seed starch (Spence & Jane, 1999). Gelatinization temperature showed a general negative correlation with average granule size of the starches,

Table 4
Swelling power and amylose leaching patterns of *Treculia africana* starches.

Temperature (°C)	60	65	70	75	80	85	90	95
Swelling power (g gel/g dry starch)								
TASS1	4.999	6.596	11.990	24.195	25.969	31.613	32.232	33.287
TASS2	8.198	7.800	10.190	10.800	24.575	28.200	27.178	30.406
TASS3	6.797	7.203	7.591	23.191	24.815	27.011	29.776	31.406
TASS4	7.199	7.001	12.577	23.200	23.140	32.194	38.515	40.926
Amylose leached (%)								
TASS1	0.623	0.803	2.053	6.449	8.720	10.093	11.229	11.682
TASS2	0.631	0.771	0.991	3.331	9.500	10.006	10.922	12.208
TASS3	0.570	0.557	0.809	6.492	8.767	9.386	11.331	12.318
TASS4	0.553	0.593	1.134	4.078	5.862	9.117	11.640	11.640

with TASS2 having the highest gelatinization temperature. There was no clear relationship between amylose content and degree of crystallinity of the starches (Liu, 2005). Starch gelatinization temperature is a measure of the cooking quality of starch and an important parameter in food processing; starches with low gelatinization temperatures have good cooking quality (Waters, Henry, Reinke, & Fitzgerald, 2005).

3.6. Swelling power and amylose leaching

Immediately following gelatinization is granule swelling and solubilization. The swelling and amylose leaching patterns of the different *T. africana* starches are shown Table 4. No significant change in swelling and amylose leaching occurred in the starches below 70 °C. This is because there is a minimum energy required for the breakdown of the crystalline structure and permit water diffusion into the granules. TASS3 indicated the more pronounced granule structure as it was the last to show significant granule swelling at lower temperatures. All the starches exhibited restricted swelling except TASS4 which swelled freely. At 95 °C, the swelling power (g/g) and corresponding amylose leached (mg/100 mg starch) were TASS1 (33.3, 11.7), TASS2 (30.4, 12.2), TASS3 (31.4, 12.3), TASS4 (40.9, 11.6). The swelling power of the starches was inversely related with apparent amylose content and gelatinization temperature but the relationship with crystallinity was not well defined. Granule swelling has been reported to be mainly influenced by granule structure and composition and to some extent by granule size (Beleia, Varriano-Marston, & Hoseney, 1980; Lindeboom et al., 2004). Solubilized amylose contributes to both rheological and textural properties of cooked starch (Iturriaga, de Mishima, & Anon, 2006).

3.7. Paste clarity

The paste clarity of *T. africana* starch pastes at 1.0% (w/v) concentration was measured for the unpurified starch and for starch purified by solubilizing in 90% DMSO and re-precipitation with isopropanol. The unpurified starches exhibited very poor clarity (3.0–5.6%) compared with the purified samples (25.3–44.8%). The low paste transmittance of the unpurified starch could be due to the impurities present in the starch, like protein and lipids, which decrease light transmittance by absorption and refraction (Craig, Maningat, Seib, & Hoseney, 1989), which were removed during purification. Paste clarity was similar in the purified starches except TASS2, despite its lowest absolute amylose content. The low paste clarity might be due to the presence of small granules which were difficult to disperse (Amani, Buleon, Kamenan, & Colonna, 2004). Paste clarity has been reported to show negative correlation with amylose content (Visser, Suurs, Bruinenberg, Bleeker, & Jacobsen, 1997). In a previous paper we reported paste clarity of 5.2% for 1.0% (w/v) concentration of *T. africana* starch paste (Nwokocha and Ogunmola, 2005). The paste clarity is lower than reported for cassava starch but similar to cocoyam starch at the same concentration (Nwokocha et al., 2009).

3.8. Freeze thaw stability

Retrogradation is an important property when starch is employed to thicken sauces, pies and dips. Retrogradation is a process in which solubilized starch molecules reassociate through formation of junction zones leading to a gel network in the case of a concentrated solution or phase separation for a dilute solution. As retrogradation progresses, in the case of a gel, the entrapped water is pushed out, a process referred to as syneresis. This results in a poor product. The amount of water released is a measure of the stability of the paste. The suitability of a given starch to thicken sauces is assessed by subjecting the starch to freeze thaw cycles and measuring the amount of water released. A suitable starch will release little or no exudates when subjected to freeze thaw cycles. *T. africana* starch exhibited a low level of syneresis (3–5%) after the first freeze thaw cycle. The total exudates after six freeze thaw cycles ranged from 32 to 38%, with TASS2 releasing the highest and TASS4 the least. The amount of exudates increased with increase in the number of freeze thaw cycles. This indicates that intermolecular/intramolecular association increased with the length of storage at low temperatures. The percentage exudates were lower than 59.5% previously reported for *T. africana* starch (Nwokocha & Ogunmola, 2005). The freeze thaw stability of *T. africana* starch was close to 31.3% for cassava starch but lower than 47.4% for cocoyam starch (Nwokocha et al., 2009).

3.9. Rheological properties

The viscosity–shear rate profiles for 5% (w/v) concentration of *T. africana* starch pastes were fitted to different shear stress-shear rate models with the Herschel–Bulkley model (Eq. (1)) giving the best fit and therefore used to describe the flow characteristics:

$$\sigma = \sigma_Y + \eta(\dot{\gamma})^N \quad (1)$$

where σ is the shear stress (Pa), σ_y is the yield stress (Pa), η is the shear viscosity (Pa s), $\dot{\gamma}$ is the shear rate (1/s) and N is the rate index.

Table 5 shows the flow characteristics. All the starch pastes presented a positive yield stress indicating an initial resistance to flow. The shear viscosity was highest in TASS1 (8.285 Pa s) and least in TASS2 (3.357 Pa s). All the starches exhibited considerable shear

Table 5
Parameters of Herschel–Bulkley model fitted to flow curves of 5% *Treculia africana* starch pastes at 25 °C.

Starch	TASS1	TASS2	TASS3	TASS4
Yield stress (Pa)	3.651	6.158	6.136	3.103
Shear viscosity (Pa s)	8.285	3.357	5.372	5.423
Rate index	0.4424	0.5325	0.4737	0.4880
Standard error	12.90	6.634	6.248	7.404

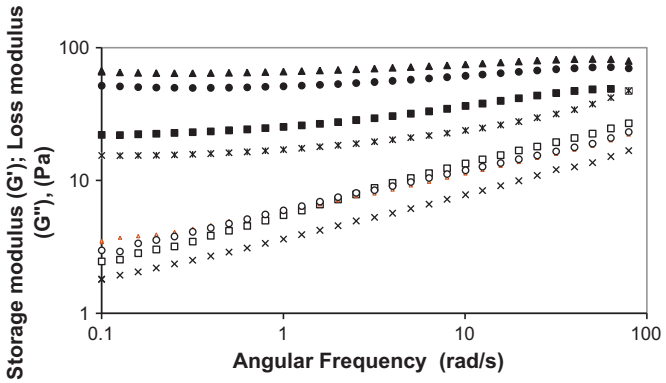

Fig. 3. Frequency sweep showing G' and G'' for 5% gels of *Treculia africana* starches. (■) TASS1 G', (□) G'', (▲) TASS2 G', (△) G'', (✱) TASS3 G', (×) G'', (●) TASS4 G' and (○) G''.

thinning with a rate index, $N \ll 1$. Fig. 3 shows the variation of storage modulus (G') and loss modulus (G'') with angular frequency. G' was higher than G'' at all the frequency range studied with the separation between them becoming narrower as angular frequency increased a characteristic of weak gels. G' was highest for TASS2 and least for TASS3.

4. Conclusions

The starch yield from *T. africana* seed flours ranged from 36.0 to 41.7%. The granule diameters were 3.56–13.60 μm. *T. africana* starch exhibited an A-type X-ray diffraction pattern with percentage crystallinities of 40.12–43.21%. The apparent and absolute amylose contents were 21.2–23.1% and 13.7–21.7%, respectively. The onset gelatinization temperatures ranged from 71.5 to 75.1 °C and the endothermic enthalpies were 12.2–14.0 J/g. The 5% starches paste exhibited a shear thinning property with shear viscosities ranging from 8.285 to 3.357 Pa s and the rate indices of 0.44–0.53. The mechanical properties were gel-like with G' much higher than G''. The freeze thaw stability of the paste was poor indicating it would need modification to enhance its application in processed foods.

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