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Comparative study of physicochemical properties of breadfruit (*Artocarpus altilis*) and white yam starches

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ABSTRACT

Starch from seedless breadfruit (*Artocarpus altilis*) was isolated and its granule characteristics, structural, physicochemical and rheological properties compared with white yam starch. Both starches exhibited a B-type diffraction patterns with a crystallinity of 36.2% for breadfruit starch and 37.3% for white yam. The two starches differed in granule size distribution and morphology; while breadfruit starch consisted of small, irregular shaped and aggregated granules (2.3–8.4 μm), white yam starch granules were large (19.2–30.8 μm), smooth and uniformly polyhedral. The amylose content and peak gelatinization temperature were different for breadfruit starch (20.0%; 69.3 °C) and white yam starch (22. 8%; 70.2 °C). The gelatinization temperature increased while the enthalpy decreased with increase in sodium chloride concentration for both starches. The starch molecules of breadfruit have a lower weight average M_w (1.72×10^7 g/mol) compared with white yam starch ($M_w = 2.32 \times 10^7$ g/mol). The swelling power (SP), amylose leaching (AML) at 95 °C, and paste clarity (PC) at 1% (w/w) of breadfruit starch (SP, 39.4 g/g; AML, 5.23%; PC, 2.25%) were lower than those of white yam starch (SP, 49.8 g/g; AML, 10.9%; PC, 12.79%). Its shear viscosity was lower but its ability to withstand viscosity breakdown was higher than white yam starch. The properties of breadfruit starch indicate it would require modification to improve water binding capacity and clarity of the paste, and reduce retrogradation. However, the small granule size of breadfruit starch makes it a candidate for application as a dusting starch.

1. Introduction

The seedless breadfruit (*Artocarpus altilis*, Forst) is native to Malaysia from where it has spread through the South Pacific and Caribbean, and was introduced into South Western Nigeria from the Caribbean (Adewusi, Udio, & Osuntogun, 1995). The fruits are usually harvested and used as a source of carbohydrate. Breadfruit is consumed in the same way as yam; it can be boiled, pounded or processed into flour. Adewusi et al. (1995) has described breadfruit as a poor man's substitute for yam. Breadfruit consists of about 53–76% starch (Beyer, 2007). Several workers have reported starch yields of 14.26–18.5% and amylose contents of 18.2%–27.68% for breadfruit (Akanbi, Nazamid, & Adebowale, 2009; Loos, Hood, & Graham, 1981; Rincon & Padilla, 2004). Tumaalii and Wootton (2006) reported on the starch particle size distribution, X-ray diffraction pattern, amylose content and gelatinization behavior of breadfruit starch. Current research efforts seem focused on diversifying the utilization of breadfruit starch as an industrial product. Beyer (2007) who studied its industrial potential reported it is well suited as a base for a range of consumer food and pharmaceutical products because of its pale colour and bland taste. Adebowale, Olu-Owolabi, Olawunmi, and Lawal (2005) and Daramola and Adegoke (2007) have studied the influence of modification on starch physicochemical properties. Its suitability as a binder in tablets in comparison with other starches has also been investigated (Adebayo & Itiola, 2003; Adebayo, Brown-Myrie, & Itiola, 2008).

Information on breadfruit starch is scanty especially in comparison to common food starches. Now that breadfruit has become a subject of major conferences (ISHS, 2007), more work is needed for a better understanding of the starch characteristics. In this work we examined the properties of breadfruit starch and related it to white yam starch.

2. Materials and methods

2.1. Starch extraction

Breadfruit starch was isolated from mature fruits harvested from a tree at Ijokodo in Ibadan while the yam tuber was bought from a local market in Ibadan, Nigeria. Both the fruits and the tuber were peeled separately, washed and wet milled with about five times its volume of distilled water using a local grinder. The

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resulting slurry was mixed with excess water and sieved using a muslin cloth. The starch milk was left to settle and the supernatant decanted. The brown sludge which settled with the starch was washed away by treating with 0.3% (w/v) sodium hydroxide solution (Schoch & Maywald, 1968). The resulting white starch was dispersed in distilled water and washed with the same until the wash water was neutral to litmus. The starch was sun dried for two days and stored in an air tight container.

2.2. Microscopy

Granule micrographs were obtained with a JSM 35 Genie Scanning Electron Microscope (Jeol Ltd., Tokyo, Japan). The starch was sprinkled onto a double-backed adhesive carbon tab stuck to a circular aluminium stub. The aluminium stub with the starch sample on it was placed in the vacuum chamber of a Polaron PS 3 sputter coater. After attaining a vacuum of 0.1–0.2 Torr and plasma current of 42 mA, the gold coating process was carried out for 140 s. The stub with gold coated starch was then placed in the SEM chamber which was evacuated before the electron beam was turned on. A 10 kV/2.05 A setting was used for the subsequent imaging work on starch, the aperture size being fixed at 3.

2.3. X-ray diffraction

The starch samples were oven dried at 50 °C overnight and then pulverized to powdered particulate size of less than 63 μm mesh sieve. The samples were placed in the cavity of a disc sample holder of the diffractometer. Diffraction diagrams were recorded using Inel X-ray equipment 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° and 30° 2θ. A curved position detector (Inel CSP120, 45410 Artenay, France) 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 samples were used in further analysis. In ash determination the sample was first ignited on a hot plate in a fume chamber and the burning completed 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 by hexane extraction and crude fibre determined with the defatted starch according to the method of Maynard (1970). Phosphorus was determined colorimetrically by the method of Smith and Caruso (1964).

2.5. Determination of the blue value and amylose content

To 0.1 g starch in a test tube was added 1 ml of ethanol (95%) to disperse the starch followed by 9 ml of 1 M NaOH solution 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 1 ml of 1 M acetic acid 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 Perkin Elmer 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 pure potato amylose (Type III: from potato, Sigma) in the concentration range (10–50 mg) from which the amylose content of the starches was obtained by extrapolation from the absorbance–amylose concentration curve.

The blue value was calculated according to Gilbert and Spragg (1964):

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

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, followed by precipitation with hot isopropanol.

2.6. Determination of molecular weight of starch

Starch purified as described in Section 2.5 was used for molecular weight determination.

The samples were prepared by dispersing the starch (~0.2%, w/w) in 0.1 M KSCN solution for 12 h by a magnetic stirrer at room temperature and then heated in a thermostatic water bath at 90 °C for 10 min. 10 ml of the solution was placed in a Teflon cup and placed in a microwave bomb and heated in a microwave oven at full power (800 W) for 40 s, brought out and kept in an ice bath to cool. The solution was filtered through a 0.45 μm Whatman nylon filter and injected into a 200 μl loop through the rheodyne connected to a guard column and three suprema columns (100, 3000 and 30000 Å) (Polymer Standards Service GmbH, Mainz, Germany) in series to a multiangle laser light scattering coupled to a refractive index detector (MALLS/RI) (Optilab DSP, Wyatt Technology Corporation, Santa Barbara, CA 93103). The columns were kept in an oven maintained at 58 °C. The eluant was 0.1 M $NaNO_3$ solution containing 0.005% of sodium azide pumped (Waters: 515 HPLC Pump, Milford, MA 01757, USA) through a degasser (CSI 6150, Cambridge Scientific Instruments, England) at a flow rate of 0.5 ml/min with the detector temperature maintained at 40 °C. The chromatogram was analyzed with Astra software (Astra for Windows 4.90.08 QELSS 2.xx) using Berry second order polynomial and a refractive index increment (dn/dc) of 0.146 (White Jr, 1999).

2.7. Gelatinization properties

The gelatinization properties of starch were determined using differential scanning calorimetry (Micro DSC III, Setaram Instruments, 69300 Caluire, France). A known weight (~700 mg) of 10% starch dispersions was placed in the sample cell and an equal mass of water was placed in the reference cell. The samples were heated from 25 °C to 90 °C at a scanning rate of 0.5 °C/min. The enthalpy changes were expressed on starch dry weight basis. The effect of salt concentration was investigated by preparing 10% starch dispersions in different concentrations (0.1 M, 0.4 M and 1.0 M) of sodium chloride instead of water using a solution of the same salt concentration in the reference cell. The DSC was initially calibrated using naphthalene crystals wrapped with aluminium foil placed in the sample cell and an equal weight of aluminium foil in the reference cell.

2.8. Swelling power and amylose leaching

Starch (0.2%, w/w, dry starch) 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 fitted with a mechanical shaker for 30 min from 50 °C to 95 °C at 5° intervals. The samples were mechanically agitated throughout the heating period to maintain a starch suspension. The samples were centrifuged at 1500 rpm for 10 min. The supernatant was carefully drawn up using a syringe. The weight of the paste was determined and used to calculate 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 acetic acid (1 ml, 1 M), stock iodine solution (2 ml, 0.2 g I_2/2 g KI/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 prepared in Section 2.5.

2.9. Determination of paste clarity

Paste clarity was determined by the method of Singhal and Kulkarni (1990) by measuring the percentage light transmitted by different concentrations of starch (0.5–3.0%, w/w) at 660 nm on a UV/Visible Spectrophotometer. Distilled water was used in the reference cell.

2.10. Rheological properties

The rheological properties were investigated on 4.0% and 6.0% (w/w) 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 examined after 1 h. The flow properties were measured on a controlled stress Rheometer (AR 2000, TA Instruments Ltd., Newcastle, UK) with cone and plate geometry (40 mm, 2° cone and 53 μm gap). Measurements were carried out at 25 °C at shear rates of 10^{-3} to 1000 s^{-1}. The viscoelastic properties of the starch pastes were determined by carrying out a frequency sweep in the range of 10^{-1} to 120 rad s^{-1} within the linear viscoelastic region (strain, 0.05%). The linear viscoelastic region was obtained by performing a stress sweep within the range of 0.01–50 Pa at an angular frequency of 6.283 rad s^{-1}. The storage modulus (G') and loss modulus (G'') of the starch pastes were analyzed by the TA Data Analysis software.

2.11. Statistical analysis

Analysis of variance (ANOVA) was used to compare sample means at 95% confidence level ($p < 0.05$) using Microsoft Excel 2007 software.

3. Results and discussion

3.1. Proximate composition

From Table 1, breadfruit starch was higher in ash, protein and phosphorus but lower in fat compared to white yam starch. The two starches differed in their composition at $p < 0.05$. The breadfruit starch in this report is higher in protein and ash but lower in fat than that isolated by Rincon and Padilla (2004), with the composition: protein (0.61%), fat (0.06%) and ash (0.47%). The ash (0.19–0.51%) and fat (0.50–0.73%) contents reported for eight varieties of *Dioscorea alata* starches (Riley, Wheatley, & Asemota, 2006) are higher than obtained for white yam starch in this work. The phosphorus contents of breadfruit and yam starches were lower than reported for potato starch (Banks & Greenwood, 1959). Ash reflects the trace amount of minerals present in starch. The inorganic minerals are present as contaminants probably incorporated through processing water or as part of natural occurring phosphate in starch (Hizukuri, Tabata, & Nikuni, 1970). Starch phosphates exert different types of influence on physicochemical properties depending on the form. Phosphate ester in potato starch has been associated with its low gelatinization temperature, high paste viscosity, high clarity, and reduced retrogradation (Karim et al., 2007); while phospholipids in wheat starch reduced its paste viscosity and clarity (Swinkels, 1985). The high protein content of the isolated breadfruit starch indicated the low purity of the starch extract (Raeker, Gaines, Finney, & Donelson, 1998). Protein in starch is from the remains of cell wall or residues of enzyme. High protein content may affect surface charge, rate of hydration and thus interfere with starch swelling and gelatinization (Galliard & Bowler, 1987). Lipids can influence starch functionality by forming helical inclusion complexes with amylose and thus inhibit swelling and lower paste clarity (Bello-Perez, Ortiz-Maldonado, Villagomez-Mendez, & Toro-Vazquez, 1998; Bello-Perez, Roger, Baud, & Colonna, 1998).

Table 1
Proximate composition and some properties of breadfruit and white yam starches.

	Breadfruit starch	White yam starch
Moisture (%)	10.91	11.41
Ash (%)	$0.99^a \pm 0.01$	$0.15^b \pm 0.01$
Protein (%)	$1.39^a \pm 0.07$	$0.69^b \pm 0.02$
Fat (%)	$0.04^a \pm 0.01$	$0.29^b \pm 0.01$
Phosphorus (%)	$0.047^a \pm 0.001$	$0.02^b \pm 0.001$
Granule characteristics		
Granule size range (μm)	2.25–8.42	19.21–30.75
Average (μm)	4.34	23.33
Length/diameter	1.21	1.41
Roundness	0.76	0.52
Molecular weight characteristics		
M_w ($\times 10^{-7}$ g/mol)	1.718	2.316
M_w/M_n	1.842 ± 0.008 (0.5%)	1.618 ± 0.011 (0.7%)
R_w (nm)	88.6 (0.4%)	99.1 (0.4%)
Recovery (%)	46.3	96.3

Paste clarity (light transmittance at 660 nm)

Starch (% w/w)	1.0	1.5	2.0	2.5	3.0
1st day					
Breadfruit	2.253	1.263	1.017	0.821	0.825
White yam	13.603	10.386	9.177	20.637	25.333
4th day					
Breadfruit	1.999	1.164	0.95	0.714	0.721
White yam	10.116	6.826	6.152	10.044	9.393

Mean of three determinations ± SD. Values in a row with different superscripts are significantly different ($p < 0.05$).

3.2. Granule size and morphology

The scanning electron micrographs of breadfruit and white yam starches obtained at two different magnifications are presented in Fig. 1. Granule characteristics (Table 1) obtained with image particle size analysis indicated breadfruit starch granules were small and mostly indented and similar to those reported by Rincon and Padilla (2004). Granule sizes ranged from 2.25 to 8.42 μm with average size of 4.34 μm. On another hand, white yam starch granules were large, polyhedral and smooth with sizes in the range of 19.21–30.75 μm and granule average of 23.33 μm. White yam starch granules were about 8 times larger than breadfruit starch granules. The roundness and length/diameter (L/D) ratio were 0.76 and 1.21 for breadfruit, and 0.52 and 1.41 for white yam starch granules, respectively. Potato starch contains large granules as well as exhibits a wide range of granule sizes (1–110 μm) (Hoover, 2001). Breadfruit starch granules reported by Loos et al. (1981) were spherical and segmented (evidence of compound granules) with diameters of 10–20 μm while granule sizes 22.89–28.01 μm were reported for eight varieties of *D. alata* starches (Riley et al., 2006). Starch granule size has been reported to affect starch

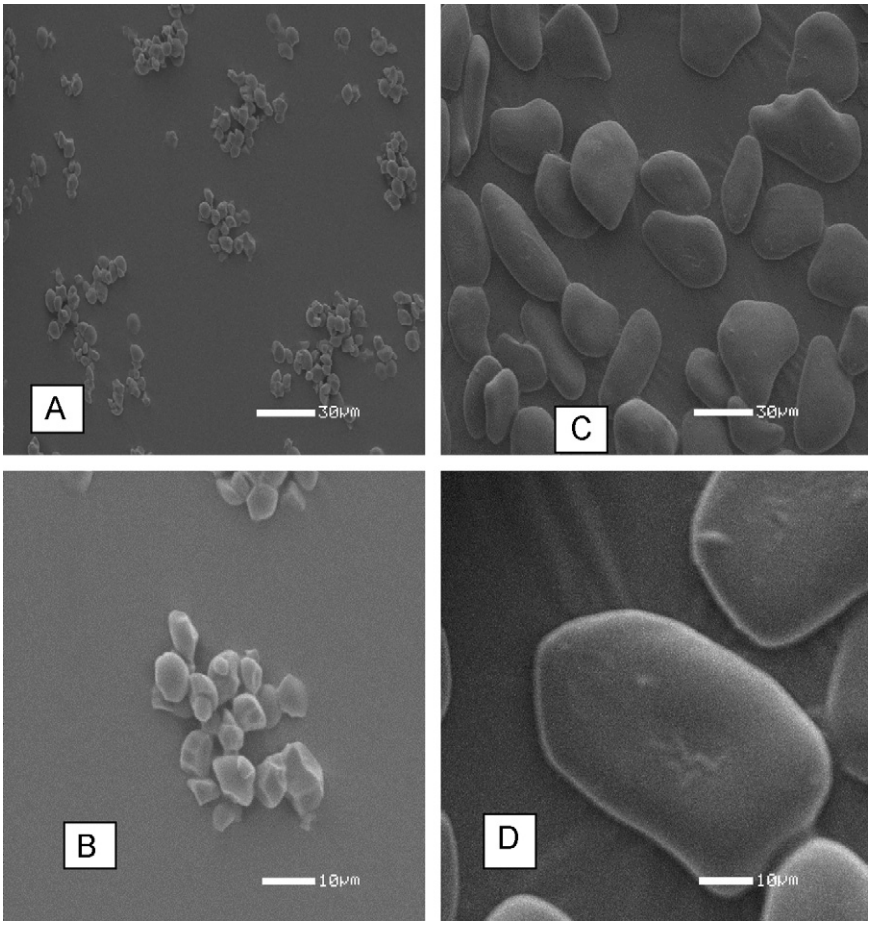

Fig. 1. Granule micrographs of breadfruit starch: (A) 1000× and (B) 3000× and white yam starch: (C) 1000× and (D) 3000×.

physicochemical properties. Zheng and Sosulski (1997) observed that at similar amylose content, smaller granules tend to have lower pasting temperature and more amylose leakage than larger granules.

3.3. X-ray diffraction

X-ray diffraction characteristics of breadfruit and white yam starches are presented in Fig. 2. Breadfruit starch gave strong diffraction peaks at 5.8, 14.76, 15.3, 17.32, 19.88, 22.92 and 23.88 while white yam starch gave strong peaks at 5.8, 15.52, 17.4, 19.88, 23.0 and 23.72. Native starches are known to display 3 characteristic diffraction patterns: A-type, B-type and C-type. An A-type diffraction pattern is common in cereal starches and has characteristic peaks at around 15, 17, 18 and 23 while the B-type pattern is common in tuber starches with peaks at around 5.8, 15 and a single peak at 17 (instead of a doublet at 17 and 18 as in A-type) and two small peaks at around 23 and 24. However, a C-type X-ray diffraction pattern which is common in pea starches is a mixture of A- and B-type patterns. The X-ray diffraction characteristics obtained for breadfruit (a fruit) and white yam (a tuber) starches indicated a typical B-type pattern similar to potato starch. The small diffraction peak at 19.88 2θ found in both breadfruit and yam starches has been attributed to the presence

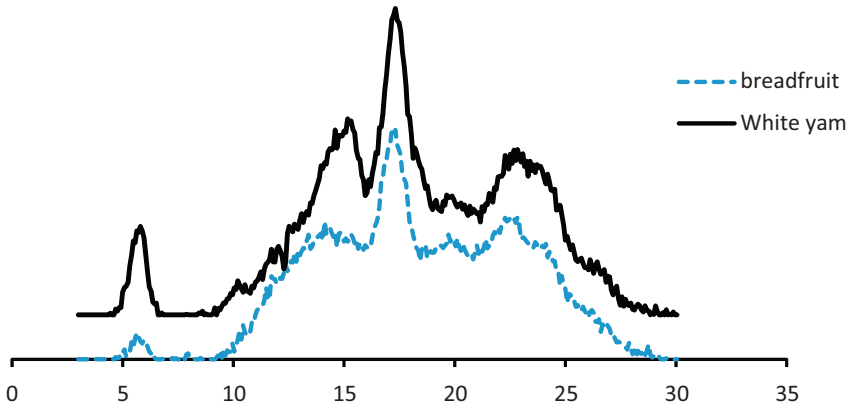

Fig. 2. X-ray diffraction characteristics of breadfruit and white yam starches.

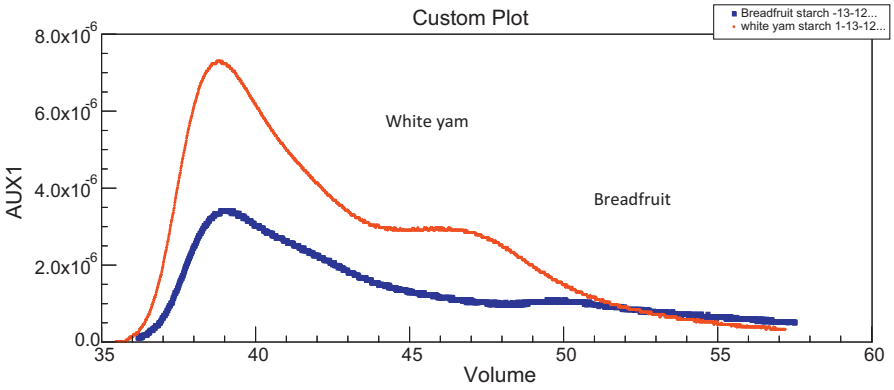

Fig. 3. GPC elution profiles of breadfruit and white yam starches.

of amylose–lipid complexes (Vasanthan & Bhatty, 1996; Yoo & Jane, 2002). The degree of crystallinity estimated for breadfruit was 36.2% and white yam 37.3%. A B-type diffraction pattern had been previously reported for breadfruit (Tumaalii & Wootton, 2006) and yam starches (Riley & Wheatley, 2006). Zuluaga, Baena, Mora, and Ponce D'leon (2007) have reported a degree of crystallinity of 34% for *D. cayenesis-rotundata* starch. Huijbrechts et al. (2008) reported degree of crystallinities of 41.9% for waxy maize starch and 38.9% for normal maize starch and observed a negative correlation with amylose content. However, our result showed that white yam starch with higher amylose content was more crystalline than breadfruit starch. Liu (2005) in a review observed that amylose content had little effect on the crystallinity of A-type starches but higher amylose content resulted in lower crystallinity in B-type starches while there was no trend in crystallinity in C-type starches. It is interesting to observe that breadfruit (a fruit) and yam (a tuber) both with similar food uses, despite belonging to different food classes, have their starch granules exhibit the same crystalline packing.

3.4. Blue value (BV) and amylose content (AC)

The starch–iodine absorption spectra showed the wavelength of maximum absorption (λ_{max}) was lower for untreated breadfruit starch (574 nm) than for treated (574–576 nm) and for untreated white yam starch (594–595 nm) than for treated (597–602 nm). The increase in λ_{max} indicates an increase in availability of amylose in aqueous solution to form an iodine-amylose complex (Singh, Kaur, Singh, & Singh, 2000). The absolute blue value (BV_{abs}) and amylose content (AC_{abs}) (breadfruit: 0.427, 18.58%) and white yam (0.437, 20.78%) were lower than the apparent (breadfruit: BV_{app}, 0.466; AC_{app}, 19.96%) (white yam: BV_{app}, 0.486; AC_{app}, 22.78%) and these were significantly different ($p < 0.05$). Overestimation of absolute amylose could occur as long chain of amylopectin molecules could contribute to higher iodine binding. Our result indicated a positive correlation between AC and the crystallinity of the starches. AC has been reported to show negative correlation with crystallinity (Atichokudomchai, Shobsngob, Chinachoti, & Varavinit, 2001; Huijbrechts et al., 2008; Zhang et al., 2007). Positive correlations have also been reported (Cheetham & Tao, 1998). It has been pointed out that apart from amylose, crystallinity is affected by amylopectin chain length (Cheetham & Tao, 1998). Some previous workers have reported amylose content of 18.2–27.68% for breadfruit starch (Loos et al., 1981; Rincon & Padilla, 2004) while values of 20.08–23.0% were reported for eight *D. alata* starches (Riley et al., 2006). The amylose contents of the breadfruit and white yam starches are in the range reported for potato starch (Banks & Greenwood, 1959; Sabiniano, Ishibashi, Hironaka, & Yamamoto, 1994).

3.5. Weight-average molecular weight

In Fig. 3, the chromatograms of breadfruit and white yam starches did not show separation of the higher molecular weight amylopectin and lower molecular weight amylose macromolecules thus making it difficult to estimate the characteristics of the amylopectin and amylose fractions of the starches, separately. Hence the weight average M_w of the whole starch was determined. The results are presented in Table 1. The molecular characteristics if breadfruit starch were: M_w 1.72×10^7 g/mol, radius of gyration, $R_w = 88.6$ nm, and polydispersity, $M_w/M_n = 1.842$ while for white yam starch: $M_w = 2.32 \times 10^7$ g/mol, $R_g = 99.1$ nm and $M_w/M_n = 1.62$. The mass recovery for breadfruit starch (46.3%) was very low compared with white yam starch (96.3%). The low mass recovery of breadfruit starch highlights some problems associated with accurate determination of M_w of starch and suggests complete dissolution of the breadfruit starch might not have been achieved. This could be associated with the very small granule fragments which were difficult to solubilize. We have not found any M_w data on breadfruit starch for comparison; however, values of 1.88×10^8 to 3.27×10^8 g/mol were reported for ten yam starches (Roland-Sabate, Amani, Dufour, Guilois, & Colonna, 2003). Starch M_w has been shown to be influenced by several factors including the technique used to determine the polymer M_w (Othman, Al-Assaf, & Hassan, 2010). Accurate determination requires the complete dissolution of starch without degradation or formation of molecular aggregates. Treatment of starch with DMSO, dissolution with KSCN, microwave treatment at $\leq$45 s and use of column-oven temperature of about 60 °C have been reported to enhance accurate determination (Ahmad, Williams, Doublier, Durand, & Buleon, 1999; Bello-Perez, Roger, et al., 1998; Othman et al., 2010). Bello-Perez, Roger, et al. (1998) have reported M_w ranging between $2.2 \pm 0.2 \times 10^8$ and $2.4 \pm 0.2 \times 10^7$ g/mol for starches with different amylose contents obtained from different botanical sources while Othman et al. (2010) obtained M_w of 2.91×10^7 g/mol for sago starch.

3.6. Gelatinization properties

The gelatinization of the starch granules was studied using a differential scanning calorimeter. The gelatinization properties obtained included the onset (T_o), peak (T_p) and completion temperatures (T_c) and the energy absorbed (ΔH) in melting the starch crystallites. The endothermic gelatinization properties are presented in Table 2. The gelatinization onset temperature of white yam starch (67.2 °C) in water was slightly higher than that of breadfruit starch (66.41 °C). However, the gelatinization range was similar for both starches while the endothermic enthalpy (16.51 J/g) of white yam starch was lower than that of breadfruit

Table 2
Gelatinization properties of breadfruit and white yam starches in different concentrations of NaCl solution.

	T_{o1} (°C)	T_{p1} (°C)	ΔT_1 (°C)	ΔH_1 (J/g)	T_{o2} (°C)	T_{p2} (°C)	ΔT_2 (°C)	ΔH_2 (J/g)	T_{o3} (°C)	T_{p3} (°C)	ΔT_3 (°C)	ΔH_3 (J/g)
A. Breadfruit												
Water	66.4135	69.3339	6.0733	19.271								
0.1 M NaCl	68.	5646	71.6493	5.7054	18.512							
0.4 M NaCl	70.1035	72.8962	5.2453	14.625								
1.0 M NaCl	71.3329	73.9540	4.8768	14.979								
B. White yam												
Water	67.2262	70.1666	6.0346	16.508	76.518	77.969	3.155	0.114				
0.1 M NaCl	69.9559	72.3229	5.3076	14.792	77.2577	80.4488	5.0174	0.409				
0.4 M NaCl	70.9132	73.2689	5.2704	9.580	79.5113	82.4765	5.4053	0.706				
1.0 M NaCl	71.4182	73.8691	5.5881	9.661	77.9832	79.2552	2.3446	0.208	80.7018	84.5646	7.1615	1.296
Deffated[a]	69.5365	72.4481	6.5365	6.860	81.1113	84.9128	6.4494	1.331				

T_{o1}, T_{p1}, T_{c1}; T_{o2}, T_{p2}, T_{c2}; T_{o3}, T_{p3}, T_{c3} and ΔH_1, ΔH_2, ΔH_3 are the onset, peak, completion temperatures and endothermic enthalpies for the gelatinization peaks 1, 2 and 3, respectively. Peaks 2 and 3 are attributed to the melting of amylose–lipid complexes.

[a] DSC using 1.0 M NaCl solution.

starch (19.27 J/g). White yam starch showed a weak endothermic peak at higher temperature (T_{p2}, 76.97 °C and ΔH_2, 0.0114 J/g) attributed to the melting of amylose–lipid complexes (Paredes-Lopez & Hernandez-Lopez, 1991); this was not obvious in breadfruit starch. Adewusi et al. (1995) have reported a gelatinization temperature of 67 °C for breadfruit starch while Riley et al. (2006) reported gelatinization onset temperatures and enthalpies of 71.4–74.2 °C and 4.80–12.75 J/g for eight *D. alata* starches. The gelatinization properties of starch have been reported to vary with the strength of the intra-granular bonds, starch botanical source and presence of electrolytes (Ahmad & Williams, 1999; Paredes-Lopez & Hernandez-Lopez, 1991). Sodium chloride concentration was found to have a marked influence on the gelatinization properties of both breadfruit and white yam starches. On the effect of sodium chloride concentration, T_{o1}, T_{p1}, T_{c1} increased while ΔT_1 and ΔH_1 decreased with increase in sodium chloride concentration. The intensity of the peak due to amylose–lipid complexes in white yam starch increased as NaCl concentration increased. At 1.0 M NaCl concentration, this peak was split into two unequal peaks – a smaller peak (T_{p2}, 79.26 °C; ΔH_2, 0.208 J/g) and a larger peak (T_{p3}, 84.56 °C; ΔH_3, 1.296 J/g). This is attributed to the existence of amylose–lipid complexes with different melting enthalpies. Soxhlet extraction with hot hexane for 10 h before gelatinization in 1.0 M NaCl removed one of the two peaks. This means defatting with hexane could only remove certain categories of bound lipids. It also means these two categories of lipids have slightly different melting enthalpies distinguishable at 1.0 M NaCl concentration. Defatting was found to degrade the granule structure as indicated by the lower T_{p1} and ΔH_1 observed in the defatted compared with the undefatted starch. Shahidi (2001) has reported that hexane extraction does not remove polar lipids; it could be that melting enthalpy for amylose–lipid complexes observed after hexane extraction was due to the presence of polar lipids.

3.7. Swelling power and amylose leaching

The ability of the starch granules to loosen and imbibe water when heated in aqueous suspension was studied. From Fig. 4, the swelling power (A) could best be fitted to a 3-order polynomial equation ($R^2 = 0.99$). Both starches did not show any significant granule swelling at temperatures up to 60 °C. However at 65 °C, granule swelling was more pronounced in breadfruit starch than white yam starch. The lower relaxation temperature of breadfruit starch could be attributed to its smaller granules and overall higher specific surface area (Chiotelli & Le Meste, 2002). Above 70 °C granule swelling was more in white yam starch than breadfruit starch indicating its overall weaker granule structure. At 95 °C, the swelling power was breadfruit (39.4 g/g) and white yam (49.8 g/g). The amylose leaching patterns (Fig. 4B) of the starches could best be fitted to a 2-order polynomial equation ($R^2 \geq 0.97$). In breadfruit starch, 5.23 mg amylose/100 mg starch was leached out at 95 °C representing 26.5% of total starch amylose. However in yam starch, 10.9 mg amylose/100 mg starch was leached representing 47.8% of total starch amylose. The results indicate a higher association of the amylose in the breadfruit starch compared to yam starch. Banks and Greenwood (1959) reported the release of over 95% of the total amylose in potato when the starch was dispersed in water at 100 °C for 1 h. Atkin, Abeysekera, and Robards (1998) have remarked that when starch granules swell to the maximum size they attain a critical stress point when the swollen envelope ruptures releasing the internal starch molecules, while a majority of the starch polymers remain trapped by the collapsed envelope which is referred to as a ghost. Vasanthan and Bhatty (1996) reported that high degree of amylose association with other starch components decreased amylose leaching. A two stage swelling and solubility pattern had been reported for breadfruit starch (Loos et al., 1981). The amount of

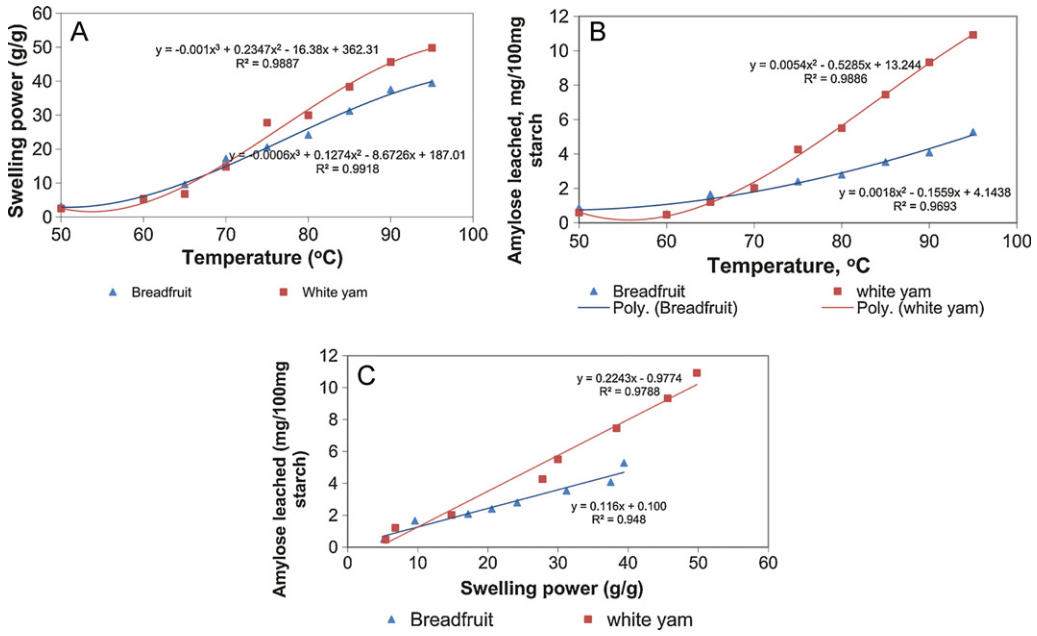

Fig. 4. Swelling power (A) and amylose leached (B) vs. temperature; amylose leached vs. swelling power (C) for breadfruit and white yam starches.

amylose leached for both starches varied linearly ($R^2 \geq 0.95$) with swelling power (Fig. 4C); with the slope for white yam starch being about twice that of breadfruit starch. Thus breadfruit starch which exhibited restricted swelling power also exhibited restricted amylose leaching and agrees with the observation of Vasanthan and Bhatty (1996). This is because the process of swelling loosens the granules permitting water uptake and diffusion of the amylose from the granule interior into the surrounding medium.

3.8. Paste clarity and retrogradation

Paste clarity is an important starch property when considering starch for use as thickener in food products such as pies, gravies, sauces and soups. A high clarity paste implies a good aesthetic appeal while low clarity starch pastes will give starch-thickened foods a dull colour. Manufacturers of starch-thickened products will want the starch that will provide the desired appeal to consumers. From Table 1, breadfruit starch presented lower paste clarity at all the starch concentrations compared with white yam starch with clarity decreasing as starch concentration increased. The relative clarity at 1% starch concentration was breadfruit 2.25%, white yam 12.79% and at 3%, breadfruit 0.85% and white yam 27.42%. White yam starch exhibited a minimum clarity at 1.5% starch concentration and paste clarity rose rapidly as starch concentration increased to 3%. A similar low percentage light transmittance has been reported for breadfruit starch at neutral pH by Rincon and Padilla (2004). They attributed this to possible formation of amylose–lipid inclusion complexes. In our work, the breadfruit starch was isolated at low fat content hence the influence of amylose–lipid complexation on paste clarity will be minimal. The low light transmittance of the starch paste appeared to correlate with the very small granule size of the starch (Amani, Buleon, Kamenan, & Colonna, 2004) and therefore could be attributed to the poor aqueous dispersion of the cooked starch granules as they tend to have rigid structure and are hard to disperse. The high clarity of white yam is positively correlated with the large granule size. Similar high paste clarity reported for potato starch has been attributed to the large granules which when cooked disintegrate with less granule remnants in the starch paste, which allows the light to pass through instead of being refracted/scattered (Singh, Kaur, &

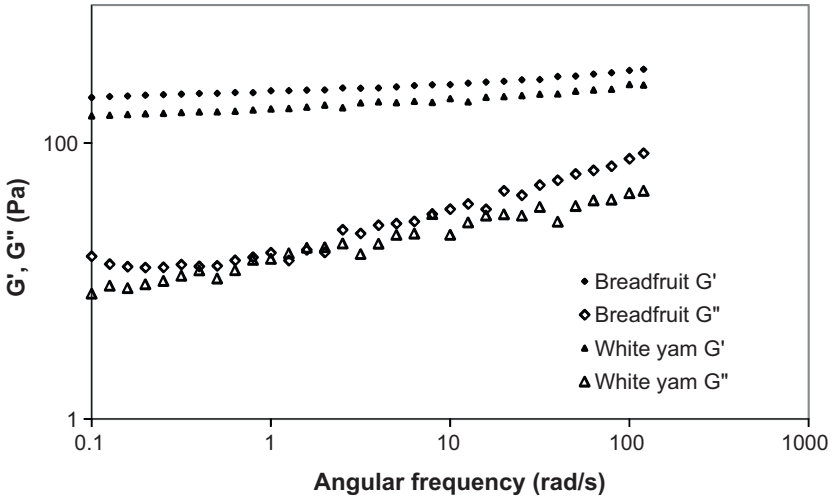

Fig. 5. Elastic (G') and loss (G'') moduli for 6% gels of breadfruit and white yam starch pastes.

Table 3
Parameters of Herschel–Bulckley model fitted to flow curves of 6% and 4% breadfruit and white yam starch pastes at 25 °C.

Parameters	Breadfruit starch		White yam starch	
Starch (w/v)	6%	4%	6%	4%
σ_y (Pa)	36.771	7.231	−16.300	0.648
η (Pa s)	11.15	2.415	72.51	9.349
N	0.529	0.604	0.270	0.456
S.E.	7.165	3.523	36.40	6.75

σ_y (Pa) is the yield stress, η (Pa s) is the shear viscosity, N is the rate index and S.E. is the standard error.

Singh, 2004). The high clarity of white yam starch paste at higher starch concentrations is an important property for application in jelly foods. The light transmittance of the starch pastes decreased after storage at room temperature for 4 days. Similar observations have been reported for corn and potato starches (Singh et al., 2004). This they attributed to the retrogradation involving the solubilized amylose and granule remnants. Retrogradation was more at higher starch concentrations because of increased amounts of leached out amylose in solution.

3.9. Rheological properties

Various shear stress–shear rate models were fitted to the flow curves of 4% and 6% starch pastes of breadfruit and white yam to determine the flow characteristics, Herschel–Bulckley model (Eq. (1)) gave the best fit with least standard error:

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

The result is presented in Table 3. At all the starch concentrations, breadfruit starch exhibited higher yield stress than yam starch. This indicates a greater resistance to flow of the breadfruit starch paste. The shear viscosities of white yam at 4% (9.349 Pa s) and 6% (72.51 Pa s) were higher than for breadfruit: 4% (2.415 Pa s) and 6% (11.15 Pa s). The rate index for breadfruit at 6% (0.529) and 4% (0.604) was higher than for white yam 6% (0.270) and 4% (0.456) indicating its higher resistance to shear thinning. The shear thinning properties of the starches showed concentration dependence; the rate index at 4% was more than at 6% indicating that shear thinning was more at higher starch concentration. Similar concentration dependence flow characteristics have been reported for other polysaccharides (Che et al., 2008).

Fig. 5 presents the mechanical spectra for the two starch gels. The storage modulus, G' and the loss modulus, G'' for both starches exhibited frequency dependence indicating weak gel characteristics. G' was significantly greater than G'' for both starches. The G' for breadfruit starch was higher than the G' for white yam starch possibly due to its small granules which tended to be elastic.

4. Conclusion

Starch isolated from breadfruit was characterized and compared with white yam starch. Breadfruit contained smaller starch granules compared to white yam and both starches exhibited a B-type X-ray diffraction pattern. The amylose content, gelatinization temperature, swelling power, amylose leached and the average M_w of breadfruit starch were lower than those of white yam starch. Breadfruit starch showed poor paste clarity and retrogradation properties.

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