



Some properties of white and yellow plantain (*Musa paradisiaca*, Normalis) starches[☆]

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ABSTRACT

Starch obtained from yellow and white plantain varieties were subjected to proximate analysis, physico-chemical and rheological characterization in order to evaluate their properties. Yellow plantain variety gave higher yield of starch than the white variety. The two varieties differed in the purity of starch extract; white plantain starch contained: ash (1.09%), protein (0.640%) and fat (0.276%) while yellow plantain starch contained: ash (0.95%), protein (0.325%) and fat (0.403%). The amylose content of yellow plantain starch (24.36% (apparent), 26.13% (total)) was similar to that of white plantain starch (24.24% (apparent), 26.01% (total)). Scanning electron microscopy revealed bimodal irregular shaped granules (3.74–7.00 and 10.00–33.00 μm) in white plantain starch and elliptical granules (11.22–41.00 μm) in yellow plantain starch. Both starches differed markedly in their physicochemical properties. Their differences in gelatinization temperature (yellow plantain, 64.99–73.90 $^{\circ}\text{C}$; white plantain, 68.08–77.15 $^{\circ}\text{C}$), swelling and solubility patterns, and pasting characteristics indicated that yellow plantain starch had weaker granule architecture compared with white plantain starch. Further evidence of differences in properties was obtained from flow and viscoelastic properties of the starch gels, paste clarity and freeze–thaw stability.

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1. Introduction

Plantain (*Musa paradisiaca normalis*) is extensively cultivated in the tropics and is a staple crop for over 70 million people of the sub-Saharan Africa. It is usually cultivated for its carbohydrate content and can be consumed as unripe fruit or when ripe (Ahenkora, Kyei, Marfo, & Banful, 1997). Traditional processing methods require boiling, roasting or frying. When processed into flour, it can be used as a component of baby food (Perez-Sira, 1997). Unripe dried plantain pulp consists of 83% starch (Ketiku, 1973), hence the rheological properties of plantain is to a great extent determined by the nature of the starch materials.

In Nigeria, two varieties are easily identifiable- the white variety (ogede fufun) and yellow variety (ogede pupa). These two varieties have different shapes of fruits and ripening characteristics. The white plantain fruit is fairly tender and longer while the yellow plantain fruit is bigger. When the pulp is blended in water, the supernatant of the yellow plantain pulp is orange while that of the white plantain is greyish. Although

there have been some reports on properties of plantain starches (Eggleton, Swennen, & Akoni, 1992; Nunez-Santiago, Bello-Perez, & Tecante, 2004) there has not been any report on properties of starches of these two local varieties of plantain. This work was aimed at studying the physicochemical properties of starches from white and yellow plantain varieties to see if the differences in the fruit characteristics are expressed in the starch physicochemical properties.

2. Materials and methods

2.1. Isolation of starch

The starch was isolated by a method similar to that of Perez-Sira (1997) except that the pulp cuttings (5–6 cm cubes) were rinsed in sodium sulphite solution and wet milled using a domestic blender. Five times its volume of water was added, the homogenate was sieved and the residue was washed with water until the wash water was clean. The dirty starch milk was centrifuged at 5000 rpm for 30 min. The supernatant was decanted. The resulting starch sediment contained a brown mucous layer. This was dispersed in a solution of 0.3% sodium hydroxide and washed repeatedly with the same until a clean white starch resulted on centrifuging. The clean starch was dispersed in distilled water

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and washed repeatedly until the wash water was neutral to litmus. The recovered starch was sun dried and stored in an airtight container. Fig. 1 shows the flow chart of the isolation procedure.

2.2. Chemical and physicochemical analyses

The moisture, ash, fat, crude protein and amylose contents were determined by standard procedures (International Institute of Tropical Agriculture, 1995).

Granule micrographs were obtained with a JSM 35 Genie Scanning Electron Microscope (SEM). The starch was sprinkled onto a double-backed adhesive carbon tab stuck to a circular aluminum stub. The aluminum 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.

The gelatinization enthalpy of starch was determined using differential scanning calorimetry (Micro DSC III, Setaram Instruments). 10% 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 25 to 90 °C at a scanning rate of 0.5 °C/min.

The swelling power and solubility were determined according to the methods of Konik, Kiskelly, and Gras (1993), and Gudmundsson and Aliasson (1991) with modification. Approximately 0.5 g starch (d,b) in weighed centrifuge tubes were taken and 25 ml distilled water added. The tubes were immersed in a thermostatic Clifton water bath and heated from 50 to 90 °C at 5° intervals for 30 min and thoroughly stirred with a glass rod all through the heating period. The tubes were removed, cooled to room temperature and centrifuged at 5000 rpm for 15 min. The supernatant was carefully sucked into a pre-weighed crucible, evaporated over a steam bath and dried in the oven at 120 °C to constant weight. The weight of the pastes was determined and used to calculate the swelling power as weight of sedimented paste per gram of dry starch. The difference in weight

after drying the supernatant gave the weight of the soluble material. Percentage solubility was calculated as weight of solubles per weight of dry starch.

The pasting characteristics were determined in a Brabender Viscoamylograph (Brabender type 801203, Duisburg, West Germany). An 8% starch (d,b) slurry was heated from 30 to 95 °C at a spindle speed of 75 rpm and kept at this temperature for 30 min and then cooled to 50 °C. The heating and cooling rate was 1.5 °C per minute.

The rheological properties of 8% starch pastes were measured. The pastes were prepared by heating aqueous starch dispersions (8%, w/v) in a water bath maintained at 99 °C for 30 min. The starch dispersion was stirred within the first minute of immersion during which pasting occurred. The stirring was stopped and the sample left for 30 min. The paste was 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.) with cone and plate geometry (40 mm, 2° cone and 52 µm gap). Measurements were carried out at 25 °C at shear rates of 10⁻² to 120 s⁻¹. The TA Data Analysis software was used to fit the various shear stress-shear rate models to the experimental data. The Herschel Bulkley model (Eq. (1)) gave the best fit and was used to describe the shear stress- shear rate profiles of the starch pastes.

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

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

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 viscoelastic region (strain, 0.05%). The linear viscoelastic region was obtained by performing a stress sweep within the range of 0.01 to 50 Pa at an angular frequency of 2.683 rad s⁻¹. The storage modulus (G') and loss modulus (G'') of the starch pastes were analyzed by the TA Data Analysis software.

The paste clarity was determined by measuring the light transmittance of different concentrations of starch paste at 660 nm. The freeze-thaw stability was determined by alternate freezing and thawing (18 h, 3 h, respectively) according to the methods of Singhal and Kulkarni (1990).

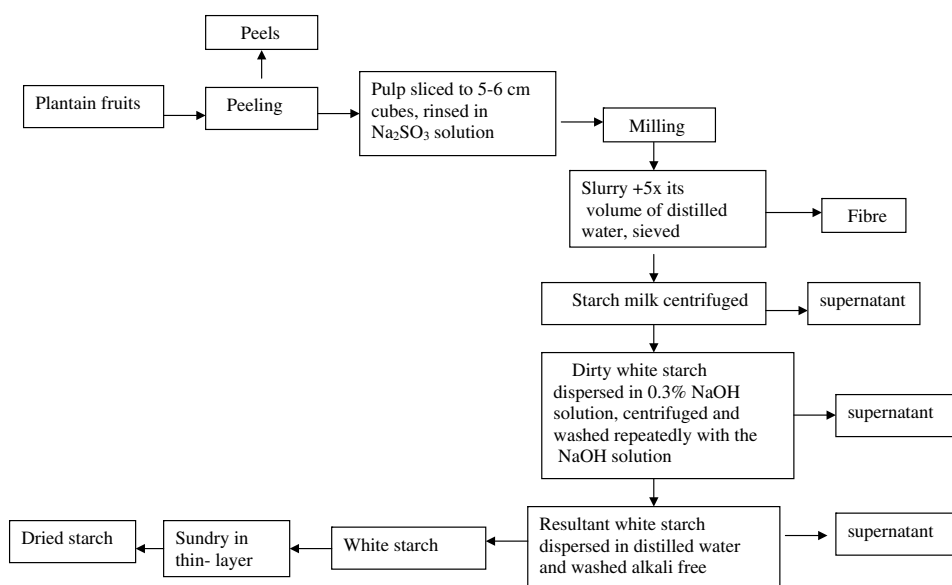


Fig. 1. Flow sheet for starch isolation from plantain fruits.

3. Results and discussion

3.1. Chemical composition

The yield and chemical composition of white and yellow plantain starches is shown in Table 1. The starch yield of the white and yellow plantain varieties is 4.51% and 6.82%, respectively. These values are lower than the 10–12% reported for plantain by Perez-Sira (1997). This low yield may have been affected by the texture of the fruits and the method used for extraction. The moisture content of the starches is low and within the acceptable range for marketing and storage. The ash content of the two varieties is higher than that reported by Perez-Sira (1997). Yellow plantain starch is higher in fat content (0.403%) than white plantain starch (0.276%); however, white plantain starch is higher in protein content than yellow plantain starch.

The two plantain varieties have comparable apparent and total amylose compositions. The amylose compositions of these varieties are higher than 9.11–17.6% reported by Eggleton et al. (1992) for some plantain cultivars but lower than 40% reported for banana starches (Hernandez, Emaldi, & Tovar, 2008; Waliszewski, Aparicio, Bello, & Monroy, 2003).

3.2. Microscopy

Fig. 2a and b show the scanning electron micrographs of white and yellow plantain starch granules. The two starches differed in granule size distribution and morphology. White plantain starch contained smooth irregular shaped bimodal granules with smaller granule sizes 3.74–7.00 μm and larger granule sizes 10.00–33.00 μm . Yellow plantain starch contained elliptical smooth granules with granule sizes 11.22–41.00 μm . Waliszewski et al. (2003) reported banana starch with compact granules irregularly shaped with elongated and spheroid forms (14–88 μm in width and 21–108 μm in length). Similarly, Eggleton et al. (1992) reported a granule size range of 7.1–69.8 μm among various plantain cultivars and hybrids while Nunez-Santiago et al. (2004) reported a granule average of 24.31 μm for uncooked banana starch. Coulibaly, Nemlin, and Amani (2006) reported a granule size range of 3.33–56.66 μm for some banana and plantain species and observed three distinct homogeneous particle sizes.

3.3. Gelatinization

The DSC heating curves for 10% dispersions of the white and yellow plantain starches are given in Fig. 3 and the resulting data is presented in Table 2. The DSC curves both show an endothermic peak which is attributed to the gelatinization process. A higher gelatinization temperature was obtained for white plantain starch

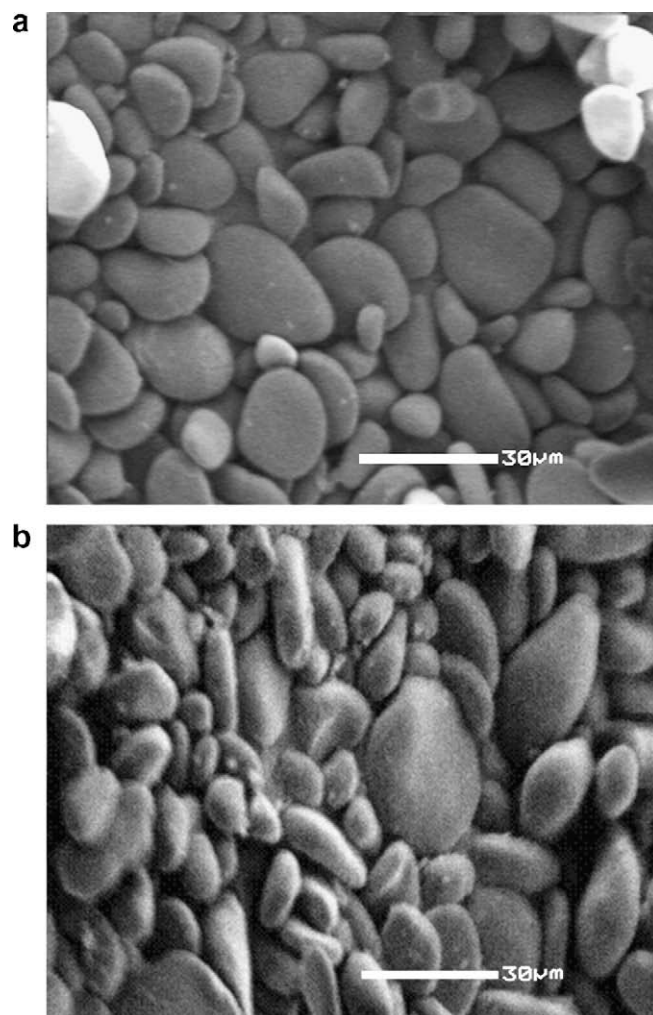


Fig. 2. (a) Scanning electron microscopy of white plantain starch (1600 \times). (b) Scanning electron microscopy of yellow plantain starch (1600 \times).

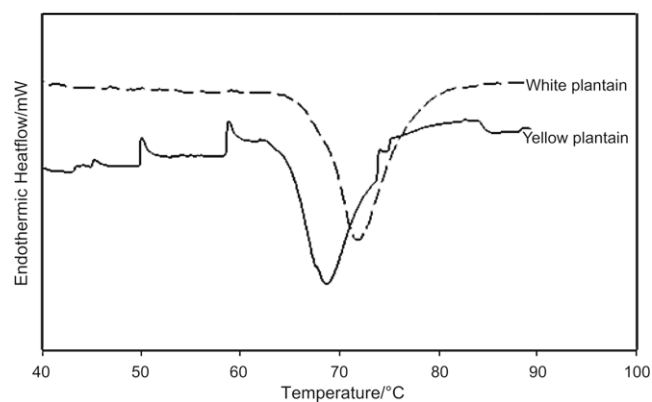


Fig. 3. DSC thermograms of white and yellow plantain starches.

Table 1

Composition of white and yellow plantain starches^a.

Parameters	White plantain	Yellow plantain
Yield (%)	4.51	6.82
Moisture (%)	8.44 \pm 0.014	8.62 \pm 0.014
Ash (%)	1.09 \pm 0.0001	0.95 \pm 0.0002
Protein (%)	0.640 \pm 0.0004	0.325 \pm 0.0001
Fat (%)	0.276 \pm 0.0001	0.403 \pm 0.0003
Amylose (apparent) (%)	24.24 \pm 0.014	24.36 \pm 0.014
Amylose (total) (%)	26.01 \pm 0.01	26.13 \pm 0.01
Granule size range (μm) ^b	10.00–33.00 (3.74–7.00) ^c	11.22–41.00

^a Mean of two determinations \pm standard deviation.

^b Major axis.

^c Smaller granules.

(71.88 $^{\circ}\text{C}$) compared to yellow plantain starch (68.68 $^{\circ}\text{C}$). The enthalpy of the gelatinization was significantly lower in yellow plantain starch (8.59 J/g) than for white plantain starch (15.02 J/g). These values are in the range reported by other authors (Nunez-Santiago et al., 2004; Zhang, Whistler, BeMiller, & Hamaker, 2005). The difference in gelatinization temperature among starches has been attributed to the interplay of three factors,

Table 2
Gelatinization properties of white and yellow plantain starches.

Gelatinization parameters	White plantain starch	Yellow plantain starch
Onset temperature, T_o (°C)	68.08	64.99
Peak temperature, T_p (°C)	71.88	68.68
Completion temperature, T_c (°C)	77.15	73.9
Gelatinization range, ($T_c - T_o$) (°C)	9.07	9.00
Endothermic enthalpy, ΔH (J/g)	15.02	8.59

namely, the starch composition, the molecular structure of the amylopectin and granule architecture. The gelatinization range is reported to depend on the difference in the degree of heterogeneity of the crystallites within the starch granules (Gunaratne & Hoover, 2002). The lower gelatinization temperature and enthalpy of yellow plantain starch are indicative of its weaker granular structure. The melting properties of starch have been reported to be directly related to starch granule size (Peng, Gao, Abdel-Aal, Hucl, & Chibbar, 1999; Steeneken & Woortman, 2008).

3.4. Swelling and solubility

Swelling and solubility patterns provide information on the nature of the associative bonding within the starch granule (Beleia, Varriano-Marston, & Hosene, 1980; Leach, McCowen, & Schoch, 1959). The starch granules are discrete semi crystalline aggregates consisting of amylose and amylopectin as major components. The ratio of these fractions in the starch granule and the manner in which they are arranged inside the granule affect the swelling and solubility of the starch (Beleia et al., 1980). In Fig. 4, yellow plantain starch swelled differently from white plantain starch. Relaxation of intra-granular bonds occurred faster in yellow plantain starch as indicated by its higher rise in swelling power with increase in temperature compared with white plantain starch. At 70 °C the swelling power of yellow plantain starch was 5.9 g/g while in white plantain starch it was 3.29 g/g, however, the values became narrower until they became close at 90 °C. This suggests a difference in the internal organization of the starch granules (Walter, Troung, Wiesenborn, & Carvajal, 2000); the lower relaxation temperature of yellow plantain starch indicates a weaker granule structure. In contrast, white plantain starch exhibited slightly higher solubilization than yellow plantain starch under the same conditions (Fig. 5). At 70 °C, the solubility of white plantain starch was 1.45% while that of yellow plantain starch was 1.05%. Since the amylose content of the plantain starch varieties were similar, this difference is attributed to the difference in inter-

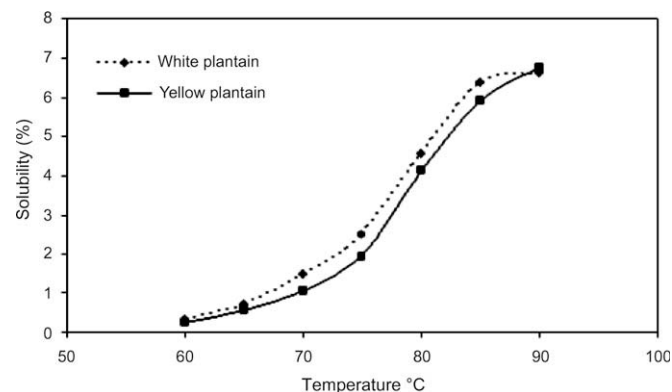


Fig. 5. Solubility patterns of white and yellow plantain starches.

nal granule organization or amylose molecular size (Walter et al., 2000). The swelling power and solubility of the banana and plantain starches reported by Coulibaly et al. (2006) were generally higher than those reported in this experiment.

3.5. Pasting characteristics

Fig. 6 and Table 3 show the Brabender viscoamylograph pasting curves and viscosity analysis of white and yellow plantain starches. Yellow plantain starch exhibited a lower pasting temperature, a higher viscosity peak, a lower stability ratio and a higher setback ratio compared with white plantain starch. These characteristics of yellow plantain starch are indicative of a weaker granular struc-

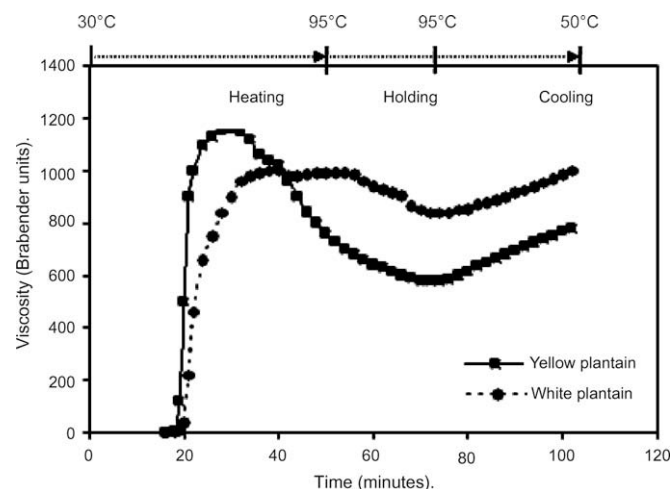


Fig. 6. Brabender amylograph pasting curves for 8% slurry of white and yellow plantain starches.

Table 3
Brabender paste characteristics of 8% slurry of white and yellow plantain starches.

Parameters	White plantain	Yellow plantain
Pasting temperature (°C)	68	61
Peak viscosity, P (BU)	1000	1160
Temperature at peak viscosity (°C)	95	77
Viscosity at 95 °C (BU)	1000	680
Viscosity, 30mins.at 95 °C, H (BU)	840	570
Viscosity at 50 °C, C (BU)	1000	770
Stability ratio = H/P	0.84	0.49
Setback ratio = C/H	1.19	1.35

BU, Brabender units.

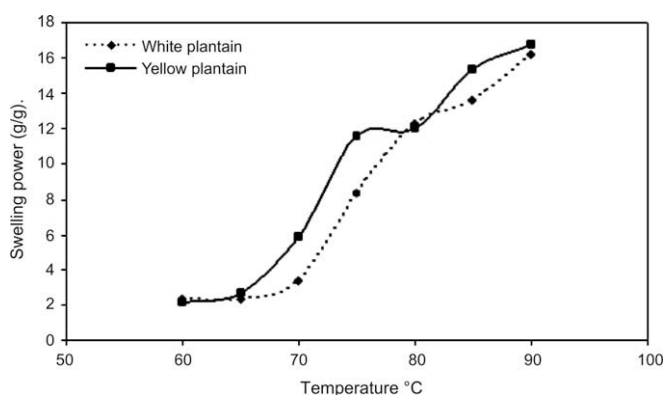


Fig. 4. Swelling patterns of white and yellow plantain starches.

ture compared with white plantain starch and are in line with the observed swelling pattern. The white plantain starch did not exhibit a well defined pasting peak and the viscosity remained fairly constant during the cooking period and increased during cooling. This property of white plantain starch indicates high heat and shear stability of the starch paste. The pasting profile of white plantain starch followed the Type C amylographic curve according to the classification of Schoch and Maywald (1968) which has been applied to other starches (Kasemsuwan, Bailey, & Jane, 1998; Wang, Sun, Zeng, & Lu, 2000). Starch paste behaviour in aqueous systems has been reported to be dependent on the physical and chemical characteristics of the starch granules, such as mean granule size, granule size distribution, amylose-amylopectin ratio and mineral constituents (Madsen & Christensen, 1996). For white plantain starch the pasting temperature (68 °C) obtained by the Brabender viscoamylograph is similar to the onset of gelatinization temperature (68.08 °C) obtained by DSC. The pasting profile of white plantain starch resembles the profile of the plantain starch reported by Perez-Sira (1997).

3.6. Rheological properties

Fig. 7 shows the shear stress-shear rate profiles for 8% gels of white and yellow plantain starches. White plantain starch had higher yield stress and cold paste viscosity than yellow plantain starch (Table 4). This suggests white plantain starch has superior cold paste viscosity and its gel is better structured to withstand shearing forces than yellow plantain starch paste. The rate index for the two starch pastes were less than 1 indicating their pseudo-plastic behaviour. Similar results were reported for other starch pastes (Mohd. Nuru, Mohd. Azemi and Manan, 1999; Zhao, Qiu, Xiong, & Liu, 2007). From Fig. 8, the viscoelastic characteristics of white and yellow plantain starch pastes indicate storage modulus (G') of the starches is significantly greater than the loss modulus (G'') over the measured frequency range and G' did not show strong dependence on the frequency. This characteristic is typical

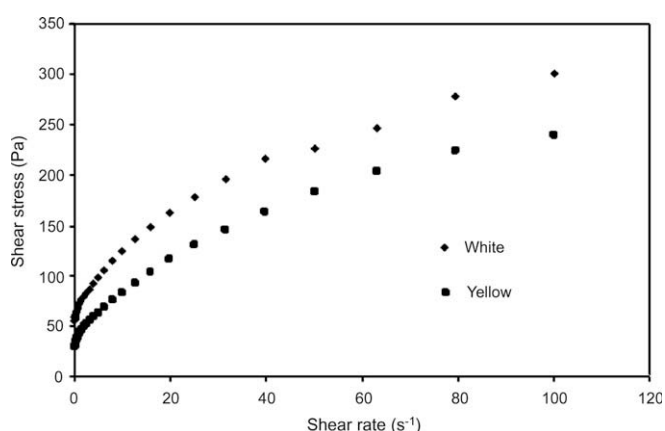


Fig. 7. Shear stress-shear rate profiles for 8% gels of white and yellow plantain starches.

Table 4
Parameters of Herschel Bulkley model fitted to flow curves of 8% gels of white and yellow plantain starch pastes at 25 °C.

Parameters	White plantain starch	Yellow plantain starch
Yield stress, σ (Pa)	48.84	25.45
Viscosity, η (Pa.s)	23.11	16.54
Rate index, N	0.5230	0.5667
Standard error, SE	10.36	12.77

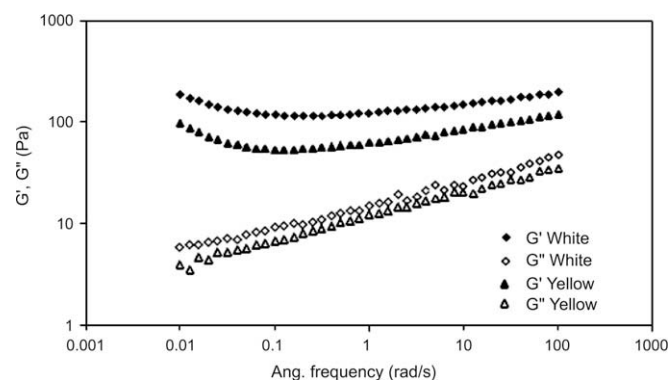


Fig. 8. Frequency sweep showing G' and G'' for 8% gels of white and yellow plantain starches.

of strong gels. Similar observation has been reported on the rheological behaviour of banana starch paste (Nunez-Santiago et al., 2004). The G' of white plantain starch paste was significantly higher at all points than that the G' of yellow plantain starch paste, indicating increased gel characteristics. This observation is in agreement with the result in Brabender paste characteristics where white plantain starch exhibited higher stability to shear compared with yellow plantain starch. The G' of starch pastes has been reported to be affected by the rigidity of starch granules (Han, Campanella, Guan, Keeling, & Hamaker, 2002; Tsai, Li, & Lii, 1997). G' has also been reported to be positively correlated with amylose content and molecular mass (Case et al., 1998).

3.7. Paste clarity

From Fig. 9, yellow plantain starch had higher paste clarity than white plantain starch at all starch concentrations. This is in line with the observed swelling pattern of the starches and in agreement with the general observation that starches with high swelling power and low retrogradation have high paste clarity (Balagopalan, Padmaja, Nanda, & Moorthy, 1988).

3.8. Freeze-thaw stability

Both white and yellow plantain starch pastes did not survive the first freeze-thaw cycle indicating poor freeze-thaw stability (Fig. 10). At the first freeze-thaw cycle, yellow plantain starch exuded 14.41% of its paste water while white plantain starch

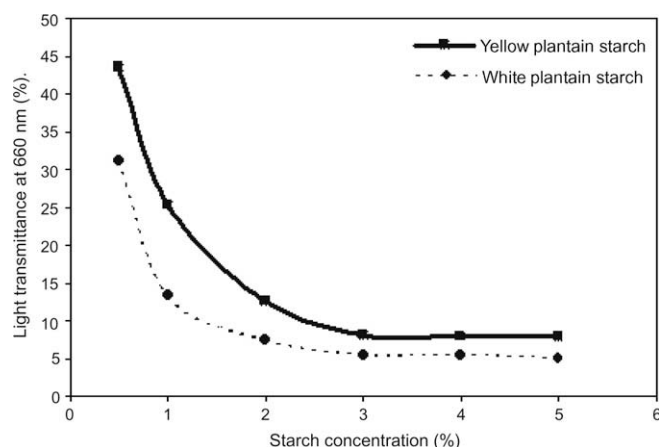


Fig. 9. Paste clarity of white and yellow plantain starches.

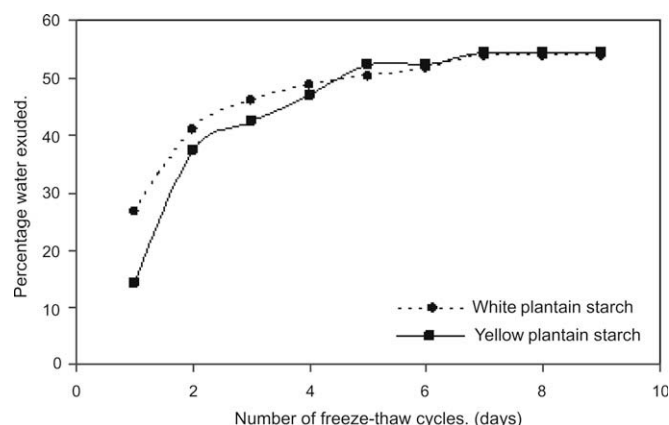


Fig. 10. Freeze–thaw stability of white and yellow plantain starches.

exuded 26.48%. It took four freeze–thaw cycles before the two starch pastes could achieve comparable amounts of paste exudates. Hence retrogradation of starch paste occurred more rapidly in white plantain starch than in yellow plantain starch indicating greater freeze thaw stability of yellow plantain starch paste. The lower freeze–thaw stability of white plantain starch could be attributed to its smaller starch granule size (Singhal & Kulkarni, 1990).

4. Conclusion

The granules of starch isolated from white and yellow plantain fruits differed in morphology and size, with white plantain starch being bimodal. The starches also differed physicochemically, with yellow plantain starch exhibiting lower gelatinization temperature, higher peak viscosity, higher breakdown and a slightly higher setback ratio. The rheological parameters show that white plantain starch has a higher yield stress and higher cold paste viscosity and is better structured to withstand shear forces.

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