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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