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Production and partial characterization of food grade breadfruit acetylated starch

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Abstract
The necessity to develop and enhance the value of alternative sources of starch in Nigeria in order to boost import substitution of specialty starches serve as impetus to this study. Starch was isolated from mature green breadfruit and acetylated using three types of alkalizing reagents at two temperature regimes. Extent of modification was appraised by evaluation of pasting properties and some physicochemical properties of the breadfruit (*Artocarpus communis*) acetylated starch in comparison to the native starch samples. Breadfruit acetylated starches were characterized with high (496.95–860.25 RVU) peak viscosities compared to low (495.75RVU) peak viscosity of the native starch. The modified starch showed higher positive set back viscosities (164.42–223.08 RVU) in comparison to the lower positive setback viscosity of the native starch (+147.75RVU), acetyl content (0.688–3.784%), degree of substitution (D.S.) (0.0261– 0.1480) and pH (4.18–4.88) of the modified starches being within the range stipulated by law. Correlation exists between physicochemical properties such as pH, acetyl content, D.S. and paste clarity, and regression equations were established within limits of investigation. The product may find application in food systems as functional starch additive.

Key words: Breadfruit, starch, alkaline pre-treatment, acetylation, pasting properties.

Introduction

Starch is an important resource for food and non-food products because of its low cost and abundant supply irrespective of ecological zone. Starch value is enhanced by modification. Processes and potential usefulness of modified starches are well expressed in literature [1-3].

The recent global development in starch industry is in the utilization of raw materials other than the imported maize and potato, especially substitutes in which home has comparative production advantage. One of the potential alternatives of starch sources in Western Nigeria is breadfruit. Carbohydrate profile with respect to morphological parts of breadfruit and starch properties have been reported [4, 5]. However, there is no information on modification of starch isolated from breadfruit grown in Nigeria.

The fact that quality attributes and other functional properties of starches can be enhanced by slight modification serves as drive to this study. Alkalization and other forms of pre-treatment of starch prior to addition of modifying agents are a pre-requisite for chemical modification of starch [6]. These cause carbon cations/ carbon anions in starch molecular structure which prepare site for substitution of functional groups of modification agents. Extent of modification is always influenced among other factors by nature of modification/alkalization reagents and reaction conditions.

In this communication, we report on production and characterization of food grade breadfruit acetylated starch using three types of alkalization reagents at dual temperature regimes with view to unravel its potentials as food grade specialty starch. Our literature survey revealed that this has not been published prior to this report.

Material and Methods

Materials: Mature green breadfruits obtained from residential compound in Ado–Ekiti, Ekiti State, Nigeria, were peeled, cored, sliced and dried at 55°C and milled into flour. Acetic anhydride, sodium hydrogen carbonate, sodium hydroxide, sodium ethanoate and other chemicals used were of reagent grade.

Isolation of starch and preparation of acetate-substituted starches: Starch was isolated essentially according to the method of Loos *et al.* [5] Isolated starch was acetylated following the procedures of Agboola *et al.* [6] with modification for utilization of alkalization reagents and temperature of reaction (Table 1). Schematic diagram of acetylation procedure is presented in Fig. 1.

Table 1. Preparatory plan for acetylation of breadfruit starch.

Alkalization reagent	Reaction temperature (°C)	Product code
NaOH	30	$B_NS - P_1T_1$
NaOH	40	$B_NS - P_1T_2$
CH_3COONa	30	$B_NS - P_2T_1$
CH_3COONa	40	$B_NS - P_2T_2$
$NaHCO_3$	30	$B_NS - P_3T_1$
$NaHCO_3$	40	$B_NS - P_3T_2$

B_NS Breadfruit native starch; Pre-treatment reagents: NaOH P_1; CH_3COONa P_2; $NaHCO_3$ - P_3; Conditioning temperature: T_1 30°C; T_2 = 40°C

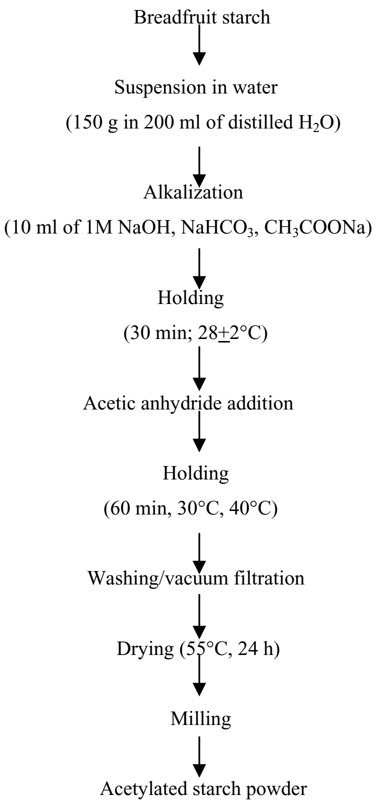

Figure 1. Flow diagram for the preparation of breadfruit acetylated starch.

Determination of pasting properties using rapid visco analyser (RVA): Pasting properties of acetylated starches and control samples were characterized using RVA as described by Delcour *et al.* [8].

Accurately weighed starch sample of 5 g was added into water at ratio of 1:2 (w/v). The sample slurry was heated from 28°C to 150°C at 4°C/min and all experiments were carried out in triplicate. The RVA -3d was operated with 250 g of 9.9% starch in water suspensions. The temperature profile included a 2 min isothermal step at 50°C, linear temperature increases to 95°C in 7 min, a holding step (8 min at 95°C), a cooling step (7 min) with a linear temperature decrease to 50°C and a final isothermal step at 50°C. Measurements agreed within 5RVU over the whole profile. Pasting peaks and associate parameters that are of paramount importance were identified and determined for technological interpretation.

Measurement of pH: The pH of the acetylated starch and control samples were determined using an omega H.HPX digital meter. Standardization of the pH-meter was carried out using buffer solutions of pH 9 and 4. A 5 g sample was dispersed in 25 ml of distilled water and the mixture was subjected to stirring until an equilibrium pH was obtained and the pH was measured [9].

Moisture content determination: Moisture content was determined in accordance with the method of A.O.A.C [10].

Determination of swelling power: This was determined in accordance with the method described by Leach *et al.* [11] with modification for small samples.

Paste clarity determination: This was determined from percent of light transmittance (%T) of starch paste as described by Craig *et al.* [12].

Determination of solubility: Solubility was evaluated by weighing 1 g of sample in 20 ml of distilled water in a test tube. This was subjected to heating in water bath at a temperature of 60°C for 30 min because there was no appreciable solubility at room temperature. At the end of heating, it was centrifuged at 1200 x g for 10 min and the absorbance of the supernatant was determined at 620 nm using distilled water as blank.

$$\text{Solubility} = \frac{\text{Absorbance of sample supernatant at test} - \text{Absorbance of sample supernatant at room temp}}{\text{Absorbance of sample supernatant at test}} \times \frac{100}{1}$$

Determination of acetyl content and degree of substitution (D.S.): Acetyl content and D.S. in modified starch were determined according to the method described by Smith [9].

Results and Discussion

Pasting properties of breadfruit acetylated starch: The pasting properties of native and acetylated starch prepared from mature green breadfruit using three alkalization reagents at two temperature regimes as extrapolated from pasting curves (Fig. 2) are presented in Table 2.

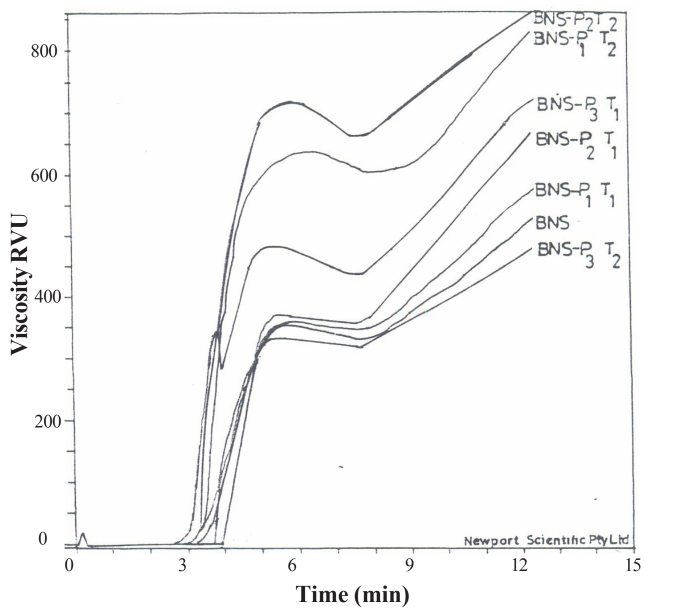

Figure 2. Rapid visco analyser pasting curves of acetylated and native starch from breadfruit (see Table 1 for interpretation of sample codes).

There was a general increase (332 – 74.08 RVU) in peak viscosities of acetic acid modified starches compared to low viscosity (348.00 RVU) of the native starch. Similar to this finding, Agboola *et al.* [7] reported increase in peak viscosity of acetylated cassava starch in comparison to low viscosity of the native starch.

High peak viscosity spectrum of acetylated breadfruit starch emanated from water absorption capacity, swelling power, solubility and weakened granule integrity [13] caused by the substitution of acetyl groups in starch polymers. Breakdown viscosities of the treated samples showed that preparation

Table 2. Pasting properties of acetylated and native starch from breadfruit.

Sample	PV (RVU)	TV (RVU)	BDV (RVU)	FV (RVU)	SV_{F-T} (RVU)	PT (min)	Pt (°C)	SV_{F-P} (RVU)
B_NS	348.00	327.83	20.17	495.75	167.92	5.47	80.80	+ 147.75
$B_NS - P_1 T_1$	352.42	167.00	185.42	223.75	56.75	4.53	77.55	– 128.67
$B_NS - P_1 T_2$	644.67	603.42	41.25	859.17	255.75	5.47	79.95	+ 214.50
$B_NS - P_2 T_1$	357.71	349.42	7.75	580.25	230.83	5.80	87.85	+ 222.08
$B_NS - P_2 T_2$	721.08	661.42	59.67	860.25	198.83	5.73	77.47	+ 139.17
$B_NS - P_3 T_1$	491.08	455.42	35.67	696.25	240.83	5.13	75.10	+ 205.17
$B_NS - P_3 T_2$	332.50	318.08	14.42	496.92	178.82	5.40	77.50	+ 164.42

See Table 1 for interpretation of sample codes. PV = Peak viscosity, TV = Trough viscosity, BDV= Breakdown viscosity (Peak – Trough), FV= Final viscosity, SV_{F-T}= Set back viscosity from trough (Final viscosity – trough viscosity), PT= Pasting time, Pt= Pasting temperature, SV_{F-P}= Setback viscosity from peak (Final viscosity – Peak viscosity), RVU= Rapid visco analyser unit.

initiated using Na-ethanoate appeared to give lowest breakdown viscosity (4.25, 7.25RVU) compared to other treatments (14.00 – 185.42RVU) and native starch (20.17RVU). The low breakdown viscosity implied that the starch–acetate produced using Na–ethanoate for alkalization will show resistant to mechanical fragmentation due to shear – thinning and heating.

Breadfruit acetylated starch appeared to be stable at cooking as revealed by the high final viscosities (496.95 – 860.25 RVU) of the paste compared to low final viscosity (495.75RVU) of native starch irrespective of alkalization agents and temperature of acetylation.

Generally, there was a positive setback from the peak viscosities for native and breadfruit aceylated starches. Acetylation appeared to enhance the magnitude of the setback viscosity. According to Mazurs *et al*. [14], low setback viscosity from peak reflects the stability of the cooked paste which implies reduced tendency to retrograde. Retrogradation has been attributed to the linear fraction of molecular starch (amylose) and the introduction of subsistent groups such as acetyl interferes with re–alignment of the linear fractions and consequently results to reduction in manifestation of retrogradation.

An examination of the viscoamylograph pasting profile (Fig. 2) of breadfruit native and acetylated starches appeared to be characterized by absence of acute peak viscosities and one that remains constant or sometimes increase (Peak – Trough) during continued heating and shearing which indicates good hot stability and a cross–linked starch properties. This kind of starch is ideal for preparation of noodles [15].

The difference in pasting time (Table 1) of native and acetylated breadfruit starch appeared to be marginal. Breadfruit native starch has higher pasting temperature compared to other acetylated starches. Lower pasting temperature signified easy of cooking of acetylated starches. This observation is in agreement with the earlier report of Rutenberg and Solarek [2] that acetylated starches are characterized with lower gelatinization temperature, higher peak viscosity and reduced retrogradation upon cooling in comparison to native starch with higher gelatinization temperature, lower peak viscosity and marked retrogradation upon cooling.

All treatments at high temperature (40°C) appeared to be characterized with high peak viscosity when compared to the same treatments at low temperature (30°C). The observation demonstrated higher amount of water absorbed in starch at higher temperature. The observation can simply be explained in terms of solubility principle which states that solubility of solute (starch molecule) in a solvent (water) increases as temperature increases.

The difference in pasting time (Table 2) of breadfruit native and acetylated starch samples appeared to be marginal. Breadfruit native starch has higher (80.80°C) pasting temperature compared to acetylated starches. Schoch and Maywald [15] reported a reduction in gelatinization temperature of acetylated starches compared to native corn starch. Lower pasting temperature signified easy of cooking of acetylated starches which may have economic implication with respect to generation of energy.

Paste clarity: Acetylation improved paste clarity (%T) of modified breadfruit starch relative to native starch (Table 3). The observation can be explained in terms of the esterification of starch polymer with acetyl groups to form starch acetates. Acetyl groups distrupt interactions among outer chains of amylopectin, the branched form of starch and among amylose chain, the linear starch polymer [16]. Decreased interactions prevent cloudiness and syneresis in aqueous starch stored at low temperature [2] and consequently break structural network in the starch granule thereby offering better transmittance. There is a relationship (r = - 0.82) between paste clarity and pH of substituted starches.

Solubility: Solubility of breadfruit starch samples was evaluated spectrophotometrically relative to unmodified starch. Solubility appeared to be enhanced by acetylation (Table 3). This can be explained in terms of granule weakened by acetyl functional groups substituted in modified starches which enhanced dissolution of starch molecule.

Table 3. Physicochemical properties of breadfruit acetylated and native starches.

Sample	Transmittance (%)	pH	Moisture (%)	D.S.	Solubility	Acetyl (%)
B_NS	N.A.	5.24	9.00	N.A.	1.78	N.A.
$B_NS - P_1T_1$	11.74	4.19	9.00	0.1341	9.13	3.440
$B_NS - P_1T_2$	19.90	4.40	8.10	0.1200	0.60	3.090
$B_NS - P_2T_1$	28.80	4.18	9.32	0.1480	8.10	3.784
$B_NS - P_2T_2$	4.37	4.88	8.30	0.0261	8.85	0.688
$B_NS - P_3T_1$	6.25	4.72	8.70	0.0650	8.79	1.707
$B_NS - P_3T_2$	14.79	4.22	8.50	0.1232	0.30	3.164

N.A. = Not applicable (see Table 1 for interpretation of sample codes).

Acetyl content and D.S.: Smith [9] stated that low D.S. products are characterized with degree of substitution below 0.3. Since degree of substitution of the acetylated starches prepared under conditions employed in this study ranged between 0.0261 and 0.1480 (Table 3), the products are low D.S. acetylated starch. Starch acetate with D.S. not exceeding 0.2 is approved by FDA for application in food preparation [17]. D.S. is related (r = -0.98) to paste clarity.

Moisture content: The moisture content of starch depends to a large extent on the method of drying and drying conditions [18]. The moisture content (%) of samples ranged between 8.10 and 9.30 which implied insignificant difference in total solid contents in samples used for subsequent analysis.

pH: The pH of the breadfruit acetylated starches (Table 3) ranged between 4.18 and 4.72 in comparison with high pH value (5.24) of breadfruit native starch. The low pH of the starch derivates could have been caused by carboxylic groups from hydrates of acetic anhydride that were substituted in the position of hydroxyl moiety of glucose units in the native starch polymer. This observation was similar to the one made by Agboola *et al.* [7] during acetylation of cassava starch.

Similar pH range of the starch derivatives suggest that any of the alkalization reagents can be used to effect this level of modification. The low pH of the modified starches means that they can be useful in modification of consistency of acid foods such as yoghurt (pH 4.5). There was a correlation (r = - 0.98) between pH and degree of substitution in acetylated starch samples. Correlation and regression equations showing relationship between selected physicochemical properties of breadfruit acetylated and native starch is summarily presented in Table 4.

Table 4. Correlation and regression equation between pH, %T, acetyl content and degree of substitution of breadfruit acetylated and native starches.

X	Y	R	R^2	Regression equation
pH	AC	- 0.98	0.969	Y = 18.3735 – 3.54X
pH	%T	- 0.815	0.66	Y = 102.19 – 19.77X
pH	D.S.	- 0.983	0.966	Y = 0.7183 – 0.1386X
%T	D.S.	0.875	0.767	Y = 0.02531 + 0.00512X
%T	AC	0.875	0.76	Y = 0.667 + 0.1305X

R = correlation coefficient, R^2 = coefficient of determination, %T = percent transmittance, AC = acetyl content, DS = degree of substitution.

Swelling power: The swelling power of breadfruit native and acetylated starches are shown in Fig. 3. Swelling power was determined by heating a weighed dry starch sample in water and defined as the swollen sediment weight (g) per gram of dry starch. Generally, swelling power of acetylated starches was higher than that of native starch irrespective of heating temperature. Swelling power is a measure of hydration capacity, because the determination is a weight measure of swollen starch granules and their occluded water [19]. Food eating quality is frequently connected with retention of water in the swollen starch granules.

Conclusions

Acetylation of starch isolated from mature green breadfruit under conditions used in this study results to improvement in pasting and functional property markers such as peak viscosity, setback viscosity, swelling power, solubility and paste clarity of the modified starches. Existence of relationship between physicochemical properties such as pH and transmittance of the product can be exploited to predict functional properties such as D.S. and paste clarity respectively. The acetylated starches of breadfruit produced under conditions employed in this investigation may be useful as alternative food grade starch additives that may serve to boost import substitution.

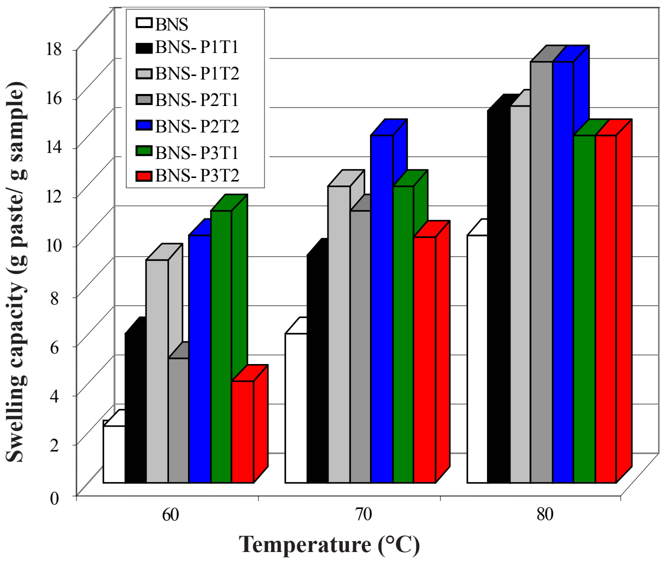

Figure 3. Swelling capacity of acetylated and native starch from breadfruit (see Table 1 for interpretation of legend).

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