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## The functional properties, pasting and baking behaviour of chemically modified sour cassava starches

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Starches obtained from three varieties of cassava (*Manihot palmata* Muell), (4(2)1425 (V1), NR84104 (V2) and NR84293 (V3)) were fermented and chemically modified. The functional and pasting properties of the starches were investigated and the possible contributions of these properties to the explanations of the baking potentials of the starches. The hydrophilic nature of the starches was found to improve strongly after fermentation, while the hydrophobic tendency decreased. The fermented acetylated starches gave the highest value for the swelling index (SWI) and these values were significantly different ( $p \le 0.05$ ) (with the exception of the acid-thinned starches). The pasting temperature for all the starches ranged from 71.9 to 77.6°C and the pasting time was higher in the fermented starches. The peak viscosity (PV) ranged from 151.58 to 317.75 RVU in V1, 154.08 to 249 RVU in V2 and 86 to 243.75 in V3. With the exception of unfermented acetylated starches (AcUFCS) all the modifications reduced the PV of the native starch. AcUFCS had the highest PV (317.75 RVU). Although, the different modification showed different effect on the sensory properties of the wheat/starch bread, highest score for the overall acceptability was associated with the unfermented acetylated starches.

Key words: Cassava, fermentation, modification, viscosity, specific volume.

## INTRODUCTION

In Nigeria, the major use of cassava is the traditional food processing in the house or in small-scale cottage operations. Apart from the traditional foods, there is great demand for cassava products which include raw materials like modified starches for the food, beverages, pharmaceutical and textile industries amongst others. Currently, increased production of cassava chips is been advocated for export and incorporation of 10% cassava flour into wheat flour as composite for bread baking (Bertolini et al., 2001). In Brazil, cassava can be processed into a sour form through fermentation. The sour starch is dried under the early morning sunlight (exposure to UV rays) and the final product is called *Polvilho azedo* and *Almidon agrio* in Colombia (Demiate et al., 2000; Lacerda et al., 2005). This predominantly lactic fermented and sun-dried cassava starch is in high demand in Brazil, for production of fried and baked goods. The sour starch gives dough that produce highly expanded bread-like products.

Different authors have tried to understand what kind of modification is responsible for the baking properties of the cassava sour starch, some attributed this property to the enzyme and the partial acid modifications of the starch as well as the presence of some bacterial exopolysaccharides produced during the fermentation (Camargo, et al., 1988; Lacerda et al., 2005). However, these factors have not been proved to be responsible for the baking behaviour. Others stated that the UV wavelengths as well as the lactic acid fermentation are essential for the baking expansion ability of the starch (Bertolini et al., 2001; Vatanasuchart, 2005). However, in their study with cassava starch samples using native, fermented sun-dried and oxidized starches, Demiate et al. (2000) were able to associate the high expansion of the baking characteristics to the carboxylate groups on

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the chemically treated starches. As the structural modification of the fermented and sun-dried starch were made detectable by the oxidation it may be possible to obtain other functional potentials of the fermented starch by some other form of modifications.

In this study, cassava starch samples; native and the fermented sun-dried were chemically treated (through acetylation, oxidation and acid-thinning). The functional properties, pasting characteristics and baking expansion were investigated. Three cassava varieties were used in this study, to investigate the effects of chemically (acetylation, oxidation and acid thinning) treated native and fermented sun-dried of three cassava varieties on the functional properties, pasting characteristics and baking expansion.

#### MATERIALS AND METHODS

Three improved cassava (*Manihot palmata* Muell.) varieties, (4(2)1425 (V1), NR84104 (V2) and NR84293 (V3)) were obtained from National Root Crop Research Institute (NRCRI) Umudike, Abia State Nigeria.

#### Starch extraction and fermentation

The cassava tuber varieties 4(2)1425 (V1), NR84104 (V2) and NR84293 (V3), were peeled, washed thoroughly, sliced and grated. The mash so obtained was washed extensively with water to remove the fibre and extract the starch. Subsequently, each of the extracted starch samples was fermented by submerging in water for 30 days making sure that the water level was 5 cm above the bed of the starch. After 30 days of fermentation, the moist starch was sun dried between 8.00 to 11.00 am daily for 3 days in other to expose the starch to the UV radiations of the sun (Vatanasuchart et al., 2005). The native unfermented cassava starch was referred to as native fermented cassava starch (NaFCS) for each of the varieties.

#### Starch modification

#### Acetylation

One hundred grams of each of the starch samples (NaUFCS and NaFCS, for V1, V2, V3) was dispersed in 500 ml of distilled water and the pH of the slurry obtained was adjusted to 8.0 using 1.0 M NaOH and the slurry was acetylated using acetic anhydride (Sathe and Salunkhe, 1981). The acetylated slurry washed four times with distilled water, air dried at  $30 \pm 2^{\circ}$ C for 48 h. The samples were labelled AcUFCS and AcFCS (V1, V2 and V3) for the unfermented and fermented acetylated samples. Each sample was packaged and stored at  $28 \pm 2^{\circ}$ C for further analysis.

#### Oxidation

Slurry of each starch sample was prepared by dispersing 100 g of each in 500 ml of distilled water. The pH was adjusted to 9.5 with 2.0 M NaOH and the oxidation was carried out with 10 g of NaOCI (Forssel et al., 1995). The oxidized starch was filtered, washed, air dried and packaged as described earlier. Samples were labelled OxUFCS and OxFCS (V1, V2 and V3) packaged and stored as earlier.

#### Acid-thinning

The method described by Lawal (2004) was adopted, 100 g of each starch sample was slurried in 500 ml of 0.15 M HCl and the mixture was placed in water bath set at 50°C and stirred magnetically for 8 h. The acid modified starch was filtered. The residue obtained was treated as explained earlier and kept for further analysis. Samples were labelled AtUFCS and AtFCS (V1, V2 and V3) and packaged and stored as explained.

#### Water and oil absorption capacity

The measurement of the water/oil absorption capacity was as described by Abbey and Ibeh (1988). Ten millilitre of water/oil was added to 1 g of the starch sample in a centrifuge tube of known weight. The mixture was allowed to stand for 30 min, centrifuged (3500 g, 15 min) and the supernatant was discarded. The tube and the residue were weighed and the gain in weight was regarded as the water/oil absorption capacity.

#### Measurements of swelling index and total soluble solids

Three grams of each modified starch were transferred into a clean dry graduated 50 ml cylinder. The starch samples were gently levelled and the volume was noted. Distilled water (30 ml) was added; the cylinder was swirled and allowed to stand for 60 min while the change in volume (swelling) was recorded every 15 min. The swelling index (SWI) of each starch was calculated as a multiple of the original volume as reported by Ukpabi and Ndimele (1990). The total soluble solid measurement was as described by Udensi and Onuora (1999) using a 10 % starch dispersion.

#### Blue value index

The blue value index (BVI) for each of the starch samples was determined following the method of Kawabata et al. (1984). Each sample (3 g, db) was introduced into a 50 ml beaker and made up to 30 ml dispersion using distilled water. The dispersion was stirred occasionally within the first 30 min and then filtered through whatman filter paper No. 42. A 10 ml aliquot of the filtrate was pipetted into a conical flask, phenolphthalein (4 drops) was added and the filtrate titrated with 0.1 N I<sub>2</sub> solutions to a bluish-black end point. The BVI was calculated using the titre value and expressed in parts per million (ppm).

 $BVI (ppm) = (V_D/V_A)(V_T/M_S)(N_A/1000) \times 10^6$ 

Where  $V_D$  = Total volume of dispersion;  $V_A$  = Volume of aliquot used for titration;  $V_T$  = Titre Value;  $M_S$  = Mass of starch used and  $N_A$ = Normality of iodine solution used.

#### **Pasting characteristics**

The pasting profile was determined using Rapid Viscoanalyser (Model RVA – 4, Newport Scientific Pvt. Ltd., Australia) following the procedure given in the manual. The sample (3 g) was mixed with distilled water (25 ml) in aluminium sample holder can and

cooked by heating to 95°C in 3.7 min. It was held at this temperature for 2.5 min and cooled to 50°C where it was again held or 2 min. The parameters measured were peak viscosity (PV) which is the highest viscosity of the paste during the heating phase; hot paste or trough viscosity (TV) which is the viscosity of the paste at the end of the heating phase at 95°C, the cold paste viscosity or the final viscosity (FV) that is, the viscosity of the paste at the end of the heating phase at 50°C. The other parameters calculated were the breakdown (BD) viscosity, (PV – TV); and set back (SB) viscosity, (FV – TV).

## Baking properties and sensory evaluation of the starch samples

A 10 % cassava starch and 90 % wheat flour formulation was used. The method of Demiate et al. (2000) was adopted. Twelve grams of each blend of the starch/wheat sample was partially cooked by addition of 10 ml of boiled de-ionized water over the mass. The blend was homogenized to produce dough that were moulded and baked in an electric oven (200°C for 25 min). Each of the baked, dough was weighed, made impermeable by robbing paraffin prior to placing them into a graduated measuring cylinder containing water. The volume of the dough was determined on the graduated cylinders as the volume of water displaced. The expansion was calculated as the specific volume of the dough:

Specific volume (ml/g) = volume of the dough / weight of the dough.

A sensory evaluation was also conducted on the baked dough. The attributes evaluated were crust colour, aroma, taste, texture, mouth-feel and crumb colour. The values obtained for each attribute were averaged as the overall acceptability. Attributes were rated on a 9 point hedonic scale. The data obtained was statistically evaluated.

#### Statistical analysis

One-way analysis of variance (ANOVA) and the Pearson's correlation coefficient were performed where necessary (at 5% probability level) to assess the variation and possible association between the experimental data. XLSTAT-Pro version 2011.1.01 statistical software was used for the analyses.

## **RESULTS AND DISCUSSION**

## Water and oil absorption capacity

The results of the water and oil absorption capacity are presented in Figure 1. All the samples displayed stronger affinity for water than oil. The hydrophilic tendency of each starch was found to improve strongly after fermentation. In V1, the WAC for NaFCS was 1.27 > 1.06 ml/g for NaUFCS; 1.42 ml/g for OxFCS > 1.18 ml/g for OxUFCS; 1.51 ml/g for AcFCS > 1.29 ml/g for AcUFCS; 1.12 mg/ml for AtFCS > 1.02 ml/g for AtUFCS. Suggesting that fermentation enhanced the hydrophilic tendencies of the starches (Figure 1). Similar trend was observed for the V2 and V3. The hydrophobic tendency of the unfermented starches was found to be higher as observed in V1 (0.88 ml/g for NaUFCS > 0.75 ml/g for NaFCS; 0.93 ml/g for OxUFCS > 0.81 ml/g for OxFCS;

1.02 ml/g for AcUFCS > 1.12 ml/g for AcFCS; 0.73 mg/ml AtUFCS > 0.64 ml/g for AtFCS). Similar decreased in the hydrophobic ability after fermentation was observed for the other two varieties. The chemically modified starches (except for the acid thinned starches) gave higher values (for the WAC and OAC) than the native starches. Acetylated and oxidized starches showed the strongest affinity for water and oil absorption (irrespective of the variety). This observation however contradicts the findings of Yusuf et al. (2007) and Akintayo et al. (2000). These workers reported that oxidation and acetylation decreased the water and oil absorption capacities of *M*. *Sloanei* starch and Lima beans starch.

On the other hand, Sathe and Salunkhe (1981) have previously shown that modification did not affect oil and water absorption capacities of Great Northern bean starch. The result of this study supports the findings of Lawal (2005), acetylation and oxidation had a more pronounced effect on both the water and oil absorption capacities of native cassava starches than acid thinning. According to Carioca et al. (1996), this effect may be due to the breakdown of the glycosidic bonds and formation of a large number of end aldehyde groups in the starch fraction. In this study, these effects were found to be further enhanced by fermentation of the cassava starches. The increased hydrophilic and hydrophobic tendencies of the acetylated and oxidized starches have been related to the attachment of functional groups on the starch molecule the decrease in acid thinned samples have been related to the erosion of the amorphous region by the acid. However, while the hydrophilic nature was further improved by fermentation, the unfermented starches had greater hydrophobic tendencies. This may suggest that the erosion of the amorphous region was enhanced by fermentation.

# Swelling index, total soluble solids and blue value index

The results of the swelling index (SWI), the total soluble solids (TSS), and blue value index (BVI) of the starches are presented in Table 1. The SWI and BVI of the fermented starches irrespective of the type of chemical modification were found to be lower than that of the unfermented starches (Table 1). The swelling index shows the degree of the water absorption of the starch granules (Carcea and Acquistucci, 1997). In this study, SWI obtained for acetylated samples > native starches > oxidized starches > acid-thinned for the unfermented and fermented starches irrespective of the variety. With the exception of the acid-thinned starches these values were significantly different ( $p \le 0.05$ ). The fermented-acidthinned starches recorded lowest SWI and this appeared to be same trend for all three varieties (V1, 0.510; V2, 0.503 and V3, 0.503 cm<sup>3</sup>/cm<sup>3</sup>). Similar reduction in



**Figure 1.** Water and oil absorption capacities of the three cassava varieties V1 ((4(2)1425); V2, (NR84104); and V3 (NR84293).

swelling power of the native cocoyam starches after acidthinning and oxidization was reported by Lawal (2005) and Deshpande et al. (1982). Acid-thinning diminishes the molar mass of the starch while it increases the free aldehyde group content. According to Atichokudomchai et al. (2000), this effect results in an increase in the crystallinity of the starch with the subsequent decrease in the amylose content. Wang and Wang (2001) studied the functional properties of acid-thinned corn, potato and rice starches and found that the modification changed the functional properties but the granular structure was not destroyed and the change in the properties differ according to the starch origin.

The values obtained for the total soluble solids for the unfermented native starches were 2.68, (NaUFCS V1); 2.25 (NaUFCS V2) and 2.58%, (NaUFCS V3) and fermented starches were 1.16%, (NaFCS V1); 0.98%, (NaFCS V2 and NaFCS V3). Indicating that fermentation

Samples	SWI (v/v)	TSS (%)	BVI (ppm)
NaUFCS, V1	$1.080 \pm 0.02^{kl}$	$2.676 \pm 0.01^{\circ}$	20.047 <sup>u</sup>
NaUFCS, V2	$1.030 \pm 0.02^{ij}$	$2.25 \pm 0.02^{\circ}$	22.137 <sup>×</sup>
NaUFCS, V3	1.050 ± 0.01 <sup>jk</sup>	2.573 ± 0.01 <sup>p</sup>	20.647 <sup>v</sup>
NaFCS, V1	$0.863 \pm 0.01^{e}$	$1.163 \pm 0.01^{j}$	19.937 <sup>s</sup>
NaFCS, V2	$0.787 \pm 0.01^{d}$	$0.98 \pm 0.00$ <sup>g</sup>	21.95 <sup>w</sup>
NaFCS, V3	0.857 ± 0.01 <sup>e</sup>	$1.08 \pm 0.00^{i}$	20.023 <sup>t</sup>
OxUFCS, V1	1.050 ± 0.01 <sup>jk</sup>	$1.97 \pm 0.00^{m}$	17.287 <sup>°</sup>
OxUFCS, V2	$1.013 \pm 0.01^{hij}$	$1.263 \pm 0.01^{k}$	18.12 <sup>r</sup>
OxUFCS, V3	$1.023 \pm 0.01^{ij}$	$1.693 \pm 0.01^{1}$	17.76 <sup>q</sup>
OxFCS, V1	$0.723 \pm 0.01^{\circ}$	$0.986 \pm 0.01^{g}$	17.073 <sup>m</sup>
OxFCS, V2	$0.633 \pm 0.02^{b}$	$0.613 \pm 0.01^{b}$	17.677 <sup>p</sup>
OxFCS, V3	$0.657 \pm 0.01^{b}$	$0.82 \pm 0.00^{d}$	17.183 <sup>n</sup>
AcUFCS, V1	$1.129 \pm 0.01^{m}$	$3.04 \pm 0.01^{t}$	15.77 <sup>i</sup>
AcUFCS, V2	$1.093 \pm 0.01^{klm}$	$2.883 \pm 0.01^{r}$	16.027 <sup>1</sup>
AcUFCS, V3	$1.113 \pm 0.01^{lm}$	$3 \pm 0.01^{\circ}$	15.863 <sup>j</sup>
AcFCS, V1	$0.973 \pm 0.01^{gh}$	$2.02 \pm 0.00^{n}$	15.603 <sup>g</sup>
AcFCS, V2	$0.837 \pm 0.01^{e}$	$1.963 \pm 0.01^{m}$	15.99 <sup>k</sup>
AcFCS, V3	$0.927 \pm 0.01^{f}$	$2.01 \pm 0.00^{n}$	15.74 <sup>h</sup>
AtUFCS, V1	$0.997 \pm 0.01^{ghi}$	$1.026 \pm 0.01^{h}$	14.247 <sup>b</sup>
AtUFCS, V2	$0.963 \pm 0.01^{fg}$	$0.843 \pm 0.01^{e}$	15.077 <sup>f</sup>
AtUFCS, V3	0.977 ± 0.01 <sup>gh</sup>	$0.936 \pm 0.01^{f}$	14.65 <sup>d</sup>
AtFCS, V1	$0.510 \pm 0.01^{a}$	$0.736 \pm 0.01^{\circ}$	14.16 <sup>a</sup>
AtFCS, V2	$0.503 \pm 0.01^{a}$	$0.526 \pm 0.01^{a}$	14.97 <sup>e</sup>
AtFCS, V3	$0.503 \pm 0.01^{a}$	$0.609 \pm 0.01^{b}$	14.503 <sup>c</sup>
(R <sup>2</sup> )	0.048	0.037	1

Table 1. The swelling index, total soluble solids and the blue value index of the starches.

Values within the same column with different superscript are significantly different at p < 0.05 correlation coefficient ( $R^2$ ) was determined against BVI.

caused a decrease in the solubility of the native starch and the effect of acid-thinning was most remarkable. On the contrary, acetylation showed increased solubility (with slight decrease after fermentation) for all the three varieties (3.04 ± 0.01%, AcUFCS V1 > 2.02%, AcFCS V1; 2.883 ± 0.01%, AcUFCS V2 > 1.963 ± 0.01 AcFCS V2 and 3 ± 0.01%, AcUFCS V3 > 2.01%, AcFCS V3). The high values obtained for the swelling index and solubility of the acetylated starches was probably due to the bulky acetyl groups on its structure, the repulsion between the acetate groups of adjacent chains will increase hydration by weakening the extent of bonding within the amylopectin structure. Similar explanation for phosphate group on potato starch was given by Gallaird and Bowler (1987). Other workers associated the characteristic behaviour of starches with the amylose composition in the granular structure. During the acid modification the hydroxonium ion  $(H_3O^{+})$  attacks the glycosidic oxygen atom and the glycosidic bond is hydrolysed. The acid entering the starch granule preferentially attacks the amorphous region and the crystalline region consisting mainly of amylopectin is left intact. This therefore results in the increase of the crystallinity of starch granule after the acid thinning and these accounts for the reduction in swelling index and solubility (Cairns et al., 1990). As the starch granule is a complex structure it is possible that the processes that occurred during fermentation and sun drying are equally complex. Making the starch granules more vulnerable to the chemical agents, easy hydrolysis of the amorphous region and the depolymerisation of the crystalline region. Increased solubility after acid-thinning and oxidation has been attributed to depolymerisation of the starch granular structure, the oxidizing agent penetrate deeply into the granule and acts mainly on the amorphous region (Forssel et al., 1995).

The linear regions of the amylose when reacted with iodine form a dark blue complex in aqueous solution at room temperature. This interaction is used to define amylose as the starch that can bind 20% of its weight of iodine, under the same condition, amylopectin will normally bind less than 1%. The binding iodine allows a distinction to be made between amylose and amylopectin and permits an estimate of the amylase content of the

Pasting	Nat	ive	Oxic	lized	Acety	lated	Acid th	ninned
Properties	UFS	FS	UFS	FS	UFS	FS	UFS	FS
V1								
Peak viscosity	289.08	151.58	140.3	174.42	317.75	172.08	-4	-3.58
Trough viscosity	126.25	69.25	83	103.67	136.92	87.25	-4.58	-4
Final viscosity	170.25	107.08	143.5	161.5	181	126.17	-4	-3.58
Breakdown	162.83	82.33	57.33	70.75	180.53	84.83	0.58	0.42
Setback	44	37.83	60.5	57.83	44.08	38.92	0.58	0.42
Peak time	3.93	4.27	4	4.27	3.87	4.13	1.27	2.07
Pasting temperature	73.6	73.54	72.8	76.7	72.75	77.6	76.45	72.55
V2								
Peak viscosity	249.58	104.92	190.9	152.67	183.42	154.08	-3.25	-3.33
Trough viscosity	109.33	44.75	113.6	88.33	64.67	69.17	-3.67	-3.83
Final viscosity	149.25	67.92	188.8	143.17	105.42	97.83	-2.92	-3.42
Breakdown	140.25	60.17	77.33	64.33	118.75	84.92	0.42	0.5
Setback	39.92	23.01	75.17	54.83	40.75	28.67	0.75	0.42
Peak time	3.73	4.33	3.93	4.27	3.87	4.2	2.73	3
Pasting temperature	71.9	75.85	72.75	76.75	72.8	76.75	74.05	73.25
V3								
Peak viscosity	243.75	155.08	86	174	197.08	146.58	-3.75	-2.58
Trough viscosity	101	81.17	23.17	96.92	87.17	68.17	-4.25	-3.17
Final viscosity	145.42	110.58	36.83	145.25	132.75	96.5	-3.67	-2.75
Breakdown	142.75	73.92	62.83	77.08	109.92	78.42	0.5	0.58
Setback	44.42	29.42	13.67	48.33	45.58	28.33	0.58	0.42
Peak time	3.73	4.2	3.53	4.27	3.73	4.2	1.33	1.4
Pasting temperature	72	76.9	72.8	77.55	72	76	77.5	76.4

Table 2. The pasting profile of the native oxidized, acetylated and acid thinned unfermented and fermented cassava starches (V1, V2 and V3).

starch. Most starches contain about 20 to 25 % w/w of amylose. From the result of this study, the native starches recorded the highest blue value index (19.937 to 22.137 ppm), suggesting that the amylose residue of the native starch is high. On the contrary, the acid thinned samples gave the lowest range (14.160 to 15.077 ppm). This further supports the earlier inference that acid-thinning eroded the amorphous region of the starch granule. However, the result showed very poor correlation between the BVI and SWI ( $R^2 = 0.048$ ) and TSS ( $R^2 = 0.037$ ). Suggesting that the BVI may not be used in predicting the swelling pattern or the solubility of the starches in this study.

## **Pasting properties**

The rapid viscoamylograph was used in the study of the pasting properties of the starches and presented in Table 2. The thermograph for the acid-thinned starch suspensions of the three varieties did not rise much

above the base line and the result cannot be fully discussed because the viscosity measurement appeared to be too low for the sensitivity of the instrument. This may suggest that the acid-thinning seriously impaired the structural composition of the starch resulting in the collapse of the crystalline order within the starch granules (Singh et al., 2003). This effect may also be associated with a re-ordering of the structural composition which may be beyond the scope of this study. The pasting temperature for all the starches ranged from 71.9 to 77.6°C and this was similar to that of native and chemically modified cocoyam starch (Lawal, 2004), but found to be above that reported for the native cassava starch by Piyachomkwan et al. (2002). It was also observed that the time required for each sample to reach the PV was higher in the fermented starches. The reduction of the pasting temperature is the evidence of a structural weakening and disintegration that was brought about during the fermentation process and the modification.

During the cassava starch fermentation process, the



Figure 2. Specific loaf volume of 10% cassava starch with 90% wheat flour.

starch undergoes enzyme and acid modification which is demonstrated by a production of a large presence of organic acids which include lactic, acetic, butyric, and propionic among others (Demiate et al., 1999). The acids and enzymes produced in the different stages of the production of the fermented cassava promote starch granule damage and consequently affect the microstructure (Marcon et al., 2006).

The PV ranged from 151.58 to 317.75 RVU in V1, 154.08 to 249 RVU in V2 and 86 to 243.75 in V3. With the exception of AcUFCS, all the modifications reduced the PV of the native starches. AcUFCS had the highest PV (317.75 RVU). Only the native starch showed that fermentation decreased the hot paste and the final viscosity values. There was no particular characteristic pattern of the hot paste and the final viscosity of the other chemically modified starch samples. The BD value which is a measure of the fragility of the starches was found to decrease after fermentation in the native and acetylated starches. The increase in BD was most pronounced in the AcUFCS. All the oxidized starches displayed low values of BD. The set back (SB) value which is an index of retrogradation (Ancona et al., 2001) appeared highest in most of the oxidized starches. It thus follows that most of the starches with high BD values retrogrades poorly.

The low viscosity values reported for the oxidized starches were caused by the partial cleavage of the glycosidic bonds during the oxidation process and this gave rise to decrease in the molecular weight of the starch molecules. This partially degraded molecule cannot resist shear and thus do not maintain the integrity of the starch granule and this resulted in lower viscosity (Lawal, 2004). When the hot paste is cooled the viscosity is dependent on the re-association tendency of the starch molecules. This ability depends largely on the affinity of the hydroxyl group of one molecule for another (Lawal, 2004). The fermentation process was reported to have a damaging effect on the starch microstructure (Marcon et al., 2006) rendering the starch molecule more amenable to conformational re-ordering and rearrangement.

## Baking expansion and sensory evaluation

The results showed that the acetylated starch had effective baking expansion; their specific volumes ranged from 8.00  $\pm$  0.38 to 11.08  $\pm$  0.18 ml/g (Figure 2). Demiate et al. (2000) have reported high specific volume 11.5 cm<sup>3</sup>/g for cassava starch immersed in 1% lactic acid solution for 4 h and sun dried for 8 h. The report of Bertoloni et al. (2000) showed that the baking expansion might involve the re-association of size-reduced starch molecules of amylose and/or amylopectin in the amorphous regions. Explaining the expansion process during baking, Fan et al. (1999) demonstrated that the expansion during baking can be associated to the bubble growth in the viscous fluid and as the viscosity increased the internal bubble pressure also increased giving rise to a large tensile stresses on the cell surface resulting in cell rupture at the end of oven rise. Similarly, Bertolini et al. (2001) attributed the expansion of the fermented cassava starch to the pressure increased by water evaporation and the low melt viscosity which will reduce the resistance force to the expansion. According to Vatanasuchart et al. (2005), the depolymerised starch dough would possess low viscosity of the bubble wall and consequently low viscous resistance for the bubble growth and this resulted in baking expansion. They further indicated that extensive degradation may lead to the loss of integrity of the bubble walls, which ruptured at

Starch samples		Overall acceptability	
Starch samples —	V1	V2	V3
NaUFCS	4.71±0.49 <sup>a</sup>	3.14±0.38 <sup>a</sup>	4.29±0.76 <sup>a</sup>
NaFCS	4.14±0.90 <sup>b</sup>	3.00±0.82 <sup>a</sup>	3.71±0.49 <sup>b</sup>
OxUFCS	$5.57 \pm 0.53^{\circ}$	4.00±0.58 <sup>b</sup>	4.43±1.13 <sup>c</sup>
OxFCS	4.71±0.49 <sup>a</sup>	3.76±0.72 <sup>c</sup>	3.28±0.52 <sup>d</sup>
AcUFCS	6.58±0.74 <sup>d</sup>	5.28±1.25 <sup>d</sup>	5.57±0.72 <sup>e</sup>
AcFCS	5.57±1.13 <sup>c</sup>	4.43±0.78 <sup>e</sup>	$5.00 \pm 1.15^{\circ}$
AtUFCS	3.71±0.76 <sup>e</sup>	2.57±0.53 <sup>t</sup>	2.57±0.53 <sup>9</sup>
AtFCS	3.00±0.56 <sup>t</sup>	2.00±0.58 <sup>g</sup>	1.86±0.38 <sup>h</sup>
LSD	0.06	0.086	0.06

Table 3. Scores for the overall acceptability of the loaf samples.

Mean values within each column bearing different superscript are significantly different ( $p \le 0.05$ ).

lower strains causing no expansion of the starches.

The results of the sensory scores of wheat/starch bread are presented in Table 3. Acetylation impacted the most positive improvement followed by oxidation when compared with the native starch sample while acid thinned samples were poorly scored. The improvement after acetylation and oxidation may be due to chemical substitution of the hydroxyl groups in starch molecules by the acetyl moiety, carbonyl and carboxyl functional groups which causes repulsion between adjacent starch molecules and apparently reduces inter-chain association (Lawal, 2004).

#### Conclusion

The starches from different varieties differed significantly in functional and pasting properties. The starches investigated in this study displayed unique characteristics different from the native starch. The acetylated starches were found to possess remarkable functional properties and it gave highest expansion volume comparable to that obtained for the lactic acid treated cassava starch (Demiate et al., 2000).

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#### REFERENCES

Abbey BW, Ibe CO (1988). Functional properties of raw and heated processed cowpea (*Vigna unguiculata* Walp) flour. J. Food Sci., 53: 1775-1777.

- Akintayo ET, Oshodi AA, Adebowale KO (2000). Functional properties of Lima bean (*Phaseolus lunatus*) unmodified and modified starches. Nig. J. Sci., 32: 187-193.
- Ancona DAB, Guerro LAC, Matos RIC, Ortiz GA (2001). Functional and functional characterisation of baby lima bean (*Phaseolus lunatus*) starch. Starch, 53: 219-226.
- Atichokudomchai N, Shobsngob S, Varavinit S (2000). Morphological properties of acid-modified tapioca starch. Starch/Starke, 52: 283-289.
- Bertolini AC, Mestres C, Colonna P (2000). Rheological properties of acidified and UV irradiated starches. Starch/Starke, 52: 340-344.
- Bertolini AC. Mestres C, Lourdin D, Della Valle G, Colonna P (2001). Relationship between thermomechanical properties and baking expansion of sour cassava starch (*Polvilho azedo*). J. Sci. Food Agric., 81: 429-435.
- Cairns P, Leloup VM, Miles MJ, Ring SG, Morris VJ (1990). Resistant starch: An X-ray diffraction study into the effect of enzymatic hydrolysis on amylose gels *in vitro*. J. Cereal Sci., 12: 203-206.
- Camargo C, Colonna P, Buleon A, Richard-Molard D (1988). Functional properties of sour cassava (*Manihot utilissima*) starch: Polvilho azedo. J. Sci. Food Agric., 45: 273-289.
- Carcea M, Acquistucci R (1997). Isolation and functional characterization of Fonio (*Digitaria exillis* Stapf.) starch. Starch, 49: 131-135.
- Carioca JOB, Arora HL, Pannir Seluam PV, Tarares FCA, Kennedy JF, Knill CJ (1996). Industrial utilization of starch and its derived products in Brazil. Starch/Starke, 48: 322-326.
- Demiate IM, Dupuy N, Huvenne JP, Cereda MP, Wosiacki G (2000). Relationship between baking behaviour of modified cassava starches and starch chemical structure determined by FTIR spectroscopy. Carbohydrate Polymers, 42: 149-158.
- Demiate IM, Barana AC, Cereda MP, Wosiacki G (1999). Organic acid profile of commercial sour cassava starch. Ciênc. Tecnol. Aliment. 19: 127-130.
- Deshpande SS, Sathe SK, Rangnekar PD, Salunkhe DK (1982). Functional properties of modified black gram (*Phaseolus mungo* L.) starch. J. Food Sci., 47: 1528-1533.
- Fan JY, Mitchell JR, Blanshard JMV (1999). A model for the oven rise of dough during baking. J. Food Engin., 41: 69-77.
- Forssel P, Hamunen A, Autio K, Suortti T, Poutanen K (1995). Hypochlorite oxidation of barley and potato starch. Starch/Starke, 47: 371-377.
- Galliard T, Bowler P (1987). Morphology and composition of starch. In: Galliard T (ed), Starch properties and potential. Chichester: Wiley. pp. 57-78.
- Kawabata A, Sawayama S, Nagashima N, Delrosario R, Nakamura M (1984). Some functional properties of starches from cassava, arrow root and sago. J. Jpn Soc. Starch Sci., 31: 224-232.
- Lacerda ICA, Miranda RL, Borelli BM, Nunes AC, Nardi RMD, Lachance MA, Rosa CA (2005). Lactic acid bacteria and yeasts associated with spontaneous fermentations during the production of sour

cassava starch in Brazil. International J. Food Microbiol., 105: 213-219.

- Lawal OS (2004). Composition, functional properties and retrogradation characteristics of native, oxidized, acetylated and acid-thinned new cocoyam (*Xanthosoma sagittifolium*) starch. Food Chem., 87: 205-218.
- Lawal OS (2005). Studies on the hydrothermal modifications of new cocoyam (Xanthosoma sagittifolium) starch. Int. J. Biol. Macromolecules, 37: 268-277.
- Marcon MJA, Vieira MA, Santos K, De Simas KN, Dias De Mello Castanho Amboni R, Amante ER (2006). The effect of fermentation on cassava starch microstructure. J. Food Process Eng., 29: 362-372.
- Piyachomkwan K, Chotineeranat S, Kijkhunasattian C, Tonwitowat R, Prammanee S, Oates CG, Sriroth K (2002). Edible canna (*Canna edulis*) as a complementary starch source to cassava for the starch industry. Ind. Crops Prod., 16: 11-21.
- Sathe SK, Salunkhe DK (1981). Isolation, partial characterisation and modification of the great Northern bean (*Phaseolus vulgaris* L.) starch. J. Food Sci., 46: 617-621.
- Singh N, Singh J, Kaur L, Sodhi NS, Gill BS (2003). Review-Morphological, thermal and rheological properties of starches from different botanical sources. Food Chem., 81: 219-231.

- Udensi EA, Onuora JO (1992). Chemical and functional properties of some soyabean flours in the Nigerian market. Book of Abstracts. 16<sup>th</sup> Annual conference of NIFST, Enugu, Nigeria.
- Ukpabi UJ, Ndimele C (1990). Evaluation of the quality of gari produced in Imo State. Nig. Food J., 8: 105-110.
- Vatanasuchart N, Naivikul O, Charoenrein S, Sriroth K (2005). Molecular properties of cassava starch modified with different UV irradiations to enhance baking expansion. Carbohydr. Polymers, 6: 80-87.
- Wang L, Wang YJ (2001). Structures and functional properties of acidthinned corn, potato and rice starches. Starch/Starke, 53: 570-576.
- XLSTAT (2011). XLSTAT-Pro version 2011.1.01 Statistical Software. Addinsoft New York 10001. www.xlsat.com.
- Yusuf AA, Ayedun H, Logunleko AGO (2007). Proximate composition and functional properties of modified *Mucuna sloanei* starch. ASSET Series B., 6: 143-150.