

Composition, physicochemical properties and retrogradation characteristics of native, oxidised, acetylated and acid-thinned new cocoyam (*Xanthosoma sagittifolium*) starch

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Abstract

New cocoyam starch was modified through oxidation (oNCS), acetylation (aNCS) and acid-thinning (atNCS). Ash content, fat content, crude fibre, protein and amylose contents were reduced following modifications. The starch granules were round and polygonal in shape. The sizes ranged from 15 to 40 μm . Modifications did not alter the granule morphology. The X-ray pattern of native starch was A type, with similar pattern in modified derivatives. Acetylation improved swelling capacity while oxidation and acid-thinning reduced it. Both oxidation and acid-thinning markedly improved solubility, whereas acetylation reduced it. Swelling power of nNCS (native new cocoyam starch), oNCS, and atNCS increased progressively as the pH increased from 2 to 12, except that atNCS had 5 g/g swelling capacity at pH 2 and 4. Swelling power of aNCS was reduced as pH increased until it reached a minimum value of 24 g/g at pH 6 after which further increase in pH resulted in progressive increase in swelling power. Oxidation markedly improved the solubility of native starch at all pH values while acetylation reduced it. Hydrophilic tendency of the starch improved after oxidation and acetylation, whereas acid-thinning reduced it. Oil absorption capacity increased after oxidation and acetylation but was reduced following acid-thinning. Oxidation and acetylation reduced the gelation capacity of native starch while atNCS had better gelating property than nNCS. The pasting temperature of nNCS (76 °C) was reduced after oxidation and acetylation but increased following acid-thinning. Set-back tendency of the native starch was reduced after oxidation and acetylation but increased following acid-thinning. Studies conducted on paste clarity revealed that percentage transmittance (650 nm) increased after chemical modifications. Differential scanning calorimetry showed that oxidation and acetylation reduced peak temperature of gelatinisation (T_p) of native starch, opposite to the increase in T_p after acid-thinning. Enthalpy of gelatinisation (ΔH) was reduced after oxidation and acetylation but increased following acid-thinning. Retrogradation tendency was reduced after oxidation and acetylation but increased following acid-thinning.

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1. Introduction

New cocoyam (*Xanthosoma sagittifolium*) of the family Aracea is an important source of carbohydrate in Tropical Africa. In Nigeria, the corms are usually eaten boiled, mashed or sometimes pounded, frequently mixed with other staples, such as yam or plantain. The source of starch varies all over the world and it depends on the tradition and prevalent climatic conditions. However, it

is starch and starch derivatives of maize and potato that are of commercial interest (Santacruz, Koch, Svensson, Ruales, & Eliasson, 2002). Cassava is also a prominent source of starch on a commercial scale in tropical Africa.

The high carbohydrate content of new cocoyam and its wide availability makes it a very good source of starch for both domestic and industrial uses in Nigeria and tropical Africa. Applications of starch in food systems are primarily governed by gelation, gelatinisation, pasting, solubility, swelling, colour and digestibility (Adebowale & Lawal, 2002b). Depending on the end

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use, one or more of the above particularly detrimental properties are often subjected to suitable chemical modifications through degradation, substitution or cross bonding (Wang & Wang, 2001).

Oxidation as a form of chemical modification involves introduction of carboxyl and carbonyl functional groups, with subsequent depolymerisation of the starch. Such starches have been established to be whiter in colour and have restricted retrogradation or “setting up” on standing (Kuakpetoon & Wang, 2001). Previous investigations have also shown that hypochlorite oxidation penetrates deeply into the granule, acting mainly on the amorphous regions. Oxidised starches find a number of uses in food industries where neutral tasting and low viscosity are required, as in lemon curd manufacture, in salad creams and mayonnaises.

Another prominent method of chemical modification of starches is esterification through acetylation (Adebowale, Afolabi, & Lawal, 2002a). Since the tendency of an aqueous starch dispersion to increase in viscosity on cooling, and finally to gel, depends on the association of amylose molecules, esterification treatment such as acetylation, which retards or eliminates this recrystallisation or retrogradation phenomenon, will effect stabilisation of the starch sol. Cloudiness and syneresis of aqueous dispersions of waxy starches could also be minimised through acetylation of amylopectin outer branches (Morikawa & Nishinari, 2000).

Acid-modified or acid-thinned starch is a granular modification of the native starch achieved through treatment of starch below its gel point in aqueous acid suspension (Wang & Wang, 2001). In this process, the hydroxonium ions attack the glycosidic oxygen atoms and hydrolyse the glycosidic linkages. Recently, Singh and Ali (2000) reported the influence of various acids (HCl, HNO₃, H₂SO₄ and H₃PO₄) on acid degradation of wheat, maize, finger millet, chickpea, green gram, tapioca and potato starches. They reported molecular weight decrease after modifications, H₃PO₄ causing the smallest while HCl and HNO₃ had the greatest reductions. The gelatinisation temperature and the breadth of the gelatinisation endotherm have been shown to increase on acid hydrolysis, while modification increased solubility and gel strength but decreased viscosity of starches (Kim & Ahn, 1996).

Retrogradation is the term that describes the changes that occur in gelatinised starch from an initially amorphous or disordered state to a more ordered or crystalline state. It is the tendency of a starch gel to thicken and form stiff gels. The development of turbidity, opacity and syneresis of water from the paste occurs during retrogradation and it depends on the source of the starch, starch concentration, storage time and temperature (Adebowale & Lawal, 2003).

The aim of the present investigation was to extract the starch of new cocoyam, subject it to chemical modifications, and study some physicochemical properties and retrogradation behaviour of the unmodified and modified starch, with a view to providing relevant information for various utilisations of the starches.

2. Materials and methods

2.1. Materials

New cocoyam was purchased at Ayetoro market, Ogun state, Nigeria. It was identified at the International Institute of Tropical Agriculture, Ibadan, Nigeria. All chemicals used were of reagent grade.

2.2. Starch isolation

The method employed for starch isolation is outlined in Fig. 1. Two kilograms of peeled new cocoyam was washed thoroughly before grating and subsequent sieving (75 µm, W.S. Tyler, Inc., UK). Stirring with distilled water and decanting off supernatants after sedimentation removed impurities. The starch obtained was air-dried at 30 ± 2 °C for 48 h.

2.3. Acetylation

The method of Sathe and Salunkhe (1981) was used. Hundred grams of starch was dispersed in 500 ml of distilled water; the mixture was stirred magnetically for 20 min. The pH of the slurry obtained was adjusted to 8.0 using 1 M NaOH. Acetic anhydride (10.2 g) was added over a period of 1 h, while maintaining a pH range 8.0–8.5. The reaction proceeded for 5 min after the addition of acetic anhydride. The pH of the slurry was adjusted to 4.5 using 0.5 M HCl. It was filtered, washed four times with distilled water and air-dried at 30 ± 2 °C for 48 h.

2.4. Oxidation

The method of Forsell, Hamunen, Autio, Suortti, and Poutanen (1995) was employed with modifications. Fifty per cent slurry of starch was prepared by dispersing 100 g of starch in 500 ml of distilled water. The pH was adjusted to 9.5 with 2 M NaOH. Ten grams of NaOCl was added to the slurry over a period of 30 min, while maintaining a pH range 9–9.5, with constant stirring at 30 ± 2 °C. The reaction proceeded for 10 min after addition of NaOCl. After the reaction, the pH was adjusted to 7 with 1 M H₂SO₄ and the oxidised starch was filtered, washed four times with distilled water and air-dried at 30 ± 2 °C for 48 h.

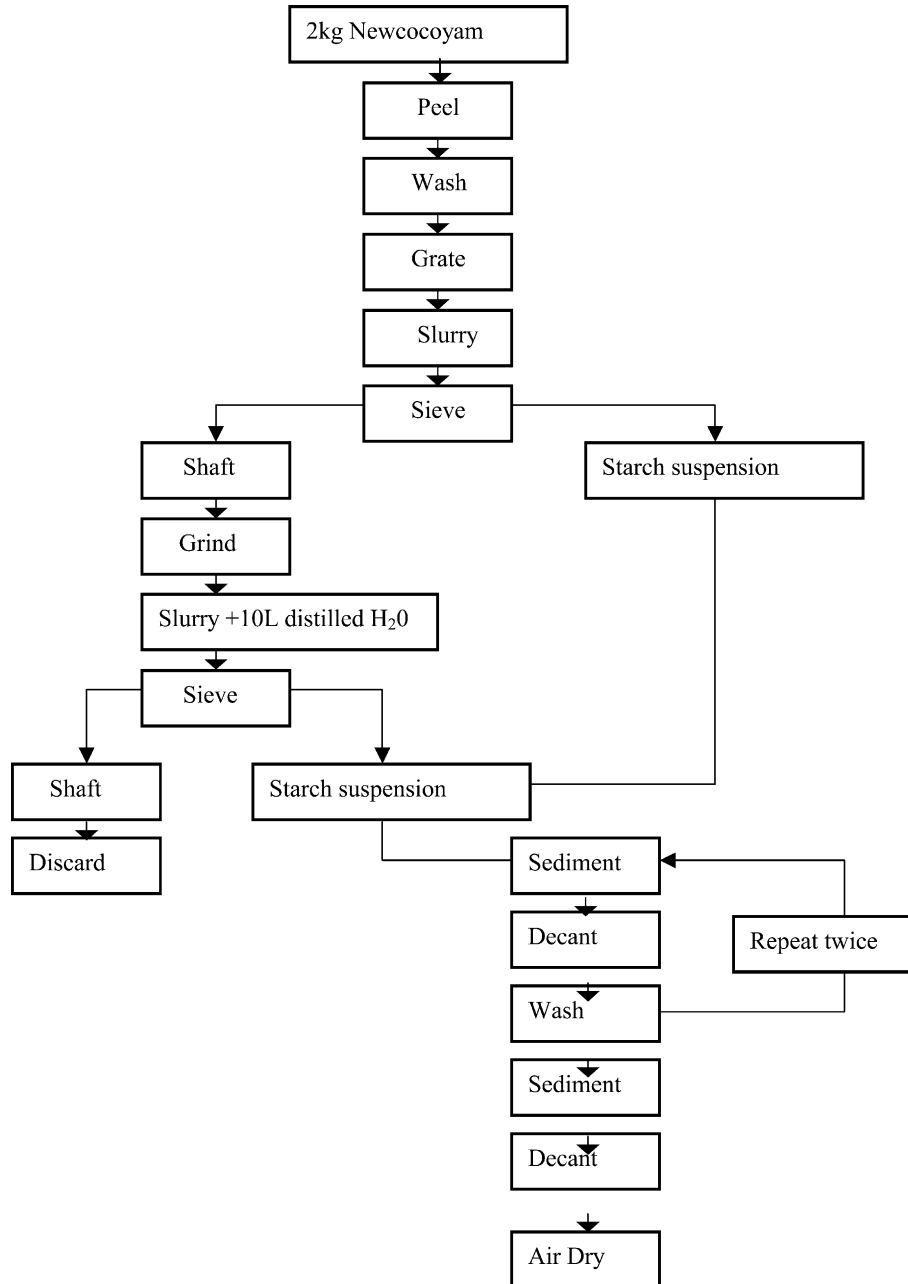


Fig. 1. Schematic diagram for isolation of new cocoyam starch.

2.5. Acid-thinning

Hundred grams of native starch was slurried in 500 ml of 0.15 M HCl. The mixture was stirred magnetically for 8 h, while maintaining a temperature of 50 °C. The acid-modified starch was filtered and the residue obtained was washed four times with distilled water. It was dried in the air for 48 h at 30 ± 2 °C.

2.6. Degree of acetylation

The degree of acetylation was quantified using the method of Sathe and Salunkhe (1981).

2.7. Carboxyl and carbonyl contents

The method of Parovuori, Hamunen, Forsell, Autio, and Poutanen (1995) was used for the determination of carboxyl contents. Five grams of oxidised starch sample was slurried in 25 ml of 0.1 M HCl. The mixture was stirred for 40 min. The slurry was filtered through a medium porosity fritted glass crucible and the residue was washed with distilled water until it was free of chloride, using the silver nitrate test. The chloride free sample was dispersed in 300 ml of distilled water. The dispersion was heated in a steam bath and stirred continuously until the starch gelatinised. The hot sample

was titrated with 0.1 M NaOH to a phenolphthalein end-point. T_0 quantify acidity due to other sources, mainly fatty acids complexed with amylose, a blank titre was determined. Five grams of unoxidised starch was titrated to provide for a blank value:

$$\text{Percent carboxyl} = \frac{(\text{Sample titre} - \text{Blank titre}) \text{ ml} \times \text{Alkali Molarity} \times 0.045 \times 100}{\text{Sample weight (g)}}$$

The hydroxylamine method described by Smith (1967) was used for the determination of carbonyl content. Two grams of oxidised starch was dispersed in 100 ml of distilled water and the suspension was gelatinised by heating in a boiling water bath and then cooled to 40 °C. The pH was adjusted to 3.2 and 15 ml of hydroxylamine reagent were added (the hydroxylamine reagent was prepared by dissolving 25 g of reagent-grade hydroxylamine hydrochloride in water and adding 100 ml of 0.5 M NaOH. The solution was made to 500 ml with distilled water). The sample was covered with aluminium foil and placed in a water bath at 40 °C. After 4 h, the excess hydroxylamine was determined by rapid titration of the reaction mixture to pH 3.2 with 0.1 M hydrochloric acid:

$$\text{Percent carbonyl}(/C=O) = \frac{(\text{Blank titre} - \text{Sample titre}) \text{ ml} \times \text{Acid molarity} \times 0.028 \times 100}{\text{Dry sample weight (g)}}$$

2.8. Chemical composition

Standard Association of Official Analytical Chemistry methods, AOAC (1996) were adopted for estimating moisture, ash, crude fibre, amylose, protein and fat contents.

2.9. Granule size and microscopic appearance

Scanning electron microscopy (SEM) and light microscopy (LM) were used for granule morphology studies. Using SEM, a thin layer of starch granules was mounted on an aluminium specimen holder by double-sided tape. The specimen holder was loaded in a polaron SC 7610 sputter coater (Fison Instrument, UK) It was coated with gold palladium, to a thickness of about 30 nm. The specimen holder was then transferred to a XL-20 series (Phillips) scanning electron microscope and starch samples were examined at 10 kV. Light micrographs of the starch samples were taken with a Diplan-Microscope model GF (Leitz Wetzler, Germany). The method of Sathe and Salunkhe (1981) was used for analysis of size of the starch granules.

2.10. Wide angle X-ray diffraction of starch granules

Diffraction measurements of the powder samples were performed on the crystallography beamline of the Elletra storage ring at Trieste, Italy. The powder was

manually ground and loaded in glass capillaries of 0.3 mm of diameter. Capillaries were sealed with wax and immersed in a sonic bath to obtain a more compact sample. The X-ray beam emitted by the wiggler source on the 2 GeV electron storage ring was monochromatised by a Si(1 1 1) double crystal monochromator and focussed on the sample. Data were collected by rotating the sample to achieve better homogeneity, with a photon wavelength of 1.0 Å, using, as a detector, a Mar 345 imaging plate (MarResearch GmbH, Norderstedt, Germany). Sample to detector-to-detector distance and wavelength were calibrated using lanthanum hexaboride. The scanning region of the diffraction angle (2θ) was from 5° to 45°.

2.11. Physicochemical properties

2.11.1. Swelling power and solubility

Swelling power and solubility determinations were carried out in the temperature range 55–95 °C, using the method of Leach, McCowen, and Scoch (1959).

2.11.2. Effect of pH on swelling power and solubility

Effects of pH on solubility and swelling were investigated using the method of Sathe and Salunkhe (1981). Slurry (1% w/v) was prepared with distilled water and the pH was adjusted to the desired value (2–12) with 0.1 M HCl or 0.1 M NaOH. The slurries were allowed to stand for 1 h, at 30 ± 2 °C, centrifuged at 5000g, for 15 min; 5 ml of the supernatant were dried to constant weight at 110 °C to determine percentage solubility of the starch.

2.11.3. Oil and water absorption capacity

The method of Beuchat (1977) was used to determine oil and water absorption capacity of the starch.

2.11.4. Gelation studies

Samples of starch, 2–18% (w/v), were prepared in test tubes with 5 ml of distilled water. The starch suspensions were mixed with a Vari-whirl mixer for 5 min. The test tubes were heated for 30 min at 80 °C in a water bath, followed by rapid cooling under running cold tap water. The test tubes were further cooled at 4 °C for 2 h. Least gelation concentration was determined as that concentration when the sample from the inverted test tube did not fall down or slip.

2.11.5. Brabender viscosography

The Brabender viscosographic pattern of 8% starch paste (36 g of starch on dry weight basis in 450 ml of water) was obtained on a Brabender viscosograph (Type 8012003 W-G) equipped with 700 cmg sensitivity cartridge. The starch suspension was heated from 50 to 95 °C. It was kept at this temperature for 30 min, then cooled to 50 °C and held at this temperature for 30 min. The speed of the rotor was fixed at 75 rpm and the heating as well as cooling rate was 15 °C/min throughout the range of gelatinisation, holding and cooling steps.

2.12. Light transmittance

Paste clarity was studied using the method of Bhandari and Singhal (2002), with modifications. Fifty milligrams (on dry weight basis) of native and modified starches was suspended in 5 ml of distilled water, using 10 ml cotton-plugged test tubes. The test tubes were then heated in a boiling water bath (with occasional shaking) for 30 min. After cooling to ambient temperature, the percentage transmittance (%) was determined at 650 nm against a water blank using a spectrophotometer (Hewlett–Packard spectrophotometer). Also, to monitor tendency for retrogradation, samples were stored for 24 h at 4 °C to effect nucleation, after which they were stored at 30 ± 2 °C for 1–9 days before determining the absorbance.

2.13. Differential scanning calorimetry and retrogradation studies

Gelation and retrogradation of starches were measured using a Perkin–Elmer DSC6 (Norwalk, CT) differential scanning calorimeter, equipped with thermal analysis software, Pyris windows (Perkin–Elmer). Distilled water (6.0 µl) were added to 2.0 mg of starch in DSC pans (BO14-3017). Pans were sealed, reweighed and kept at 30 ± 2 °C for 24 h to ensure equilibration of the starch sample and water. The samples were scanned from 30 to 130 °C at 10 °C/min using empty pans as reference. The heated pans were then cooled immediately and kept at 4 °C inside a refrigerator for 24 h, following which they were kept for 1 or 6 days at 30 ± 2 °C, to make complete storage days of 2 and 7, respectively. Following these periods of storage, the samples were scanned under the same conditions as the first scanning. Indium and zinc were used for calibration, while an empty pan was used as the reference scale. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c) and enthalpy (ΔH , J/g), for gelatinisation and retrogradation, were determined. Experiments were replicated three times.

2.14. Statistical analysis

Analyses were done in triplicate. Analysis of variance was performed to calculate significant differences in treatment means, and LSD ($P < 0.05$) was used to separate means (SAS, 1988).

3. Results and discussion

3.1. Chemical composition of the starches

The yield of native new cocoyam starch, based on the whole corm is 62.3% (Table 1). This value is higher than the 55.1% and 30% earlier reported for old cocoyam (*Colocassia esculenta*) and sweet potato (*Ipomea*

Table 1
Chemical composition of native (nNCS), oxidised (oNCS), acetylated (aNCS) and acid-thinned (atNCS) new cocoyam starches*

Starch	Yield (%)	Moisture (%)	Ash (%)	Fat (%)	Crude fibre (%)	Protein** (%)	Amylose (%)
nNCS	62.32 ^a ± 0.16	8.39 ^a ± 0.12	2.47 ^a ± 0.18	0.09 ± 0.01	0.89 ± 0.29	0.16 ^a ± 0.06	22.7 ^a ± 0.14
oNCS ⁺	89.46 ^b ± 0.18	8.26 ^a ± 0.08	0.74 ^b ± 0.42	ND	ND	0.12 ^b ± 0.05	20.1 ^a ± 0.47
aNCS ⁺⁺	93.15 ^c ± 0.09	8.36 ^a ± 0.27	1.23 ^c ± 0.19	ND	ND	0.13 ^b ± 0.10	21.2 ^b ± 0.32
atNCS	76.67 ^a ± 0.34	8.02 ^a ± 0.05	0.55 ^b ± 0.47	ND	ND	ND	15.4 ^c ± 0.41

ND, not detected.

* All values are means of triplicate determinations ± standard deviation means within columns with different letters are significantly different ($P < 0.05$).

** Nx 6.25.

⁺ Degree of substitution 0.34.

⁺⁺ Degree of substitution 0.30.

batatas), respectively (Lim, Kasemsuwan, & Jane, 1994; Zhang & Oates, 1999). The value is, however, lower than 84.7%, 87.5%, 88.0% and 86.1% earlier reported for *Dioscorea alata*, *Dioscorea cayensis*, *Dioscorea alumetorum* and *Dioscorea rotundata*, respectively (Emiola & Delarossa, 1981). Among the modified starches, atNCS had the lowest yield value of 72.6% compared with 89.4% and 93.1% for oNCS and aNCS, respectively. This observation is attributed to degradation of the amorphous granules during acid-thinning.

The moisture content of a powder plays a significant role in the flow and other mechanical properties (Shieldneck & Smith, 1971). Although it depends largely on the method, extent of drying and the humidity in the surrounding atmosphere, the 8.39% moisture level of unmodified new cocoyam starch observed here is lower than the 10.2% and 9.82% moisture levels reported for cassava (*Manihot esculenta*) starch and arrowroot (*Maranta arundinacea*) starch, respectively (Aiyeye, Akingbala, & Oguntimein, 1993; Raja & Sindhu, 2000).

Functional properties of starches depend on the amylose content to a large extent (Adebowale & Lawal, 2003). Amylose (22.7%) content of native starch is in agreement with ranges of values reported for other tuber starches, 25.47% for potato (Hoover & Hadziyev, 1981), and 22.8%, 21.6% for *D. alata* and *D. cayensis*, respectively (Gallant et al., 1982). Defloor, Dehing, and Delcour (1998) gave the value of amylose content of cassava (*Manihot esculenta*) as 23.6%. New cocoyam and its derivatives have very little protein (<2.0%) and fat (<1%) and this would minimise these components contaminating the starch.

All forms of modification reduced moisture, ash, fat, crude fibre, protein and amylose contents of the native starch. It is also noteworthy that modifications reduced the fat and crude fibre beyond the detection limit. These reductions are due to various degradations that took place during chemical modification processes. Similar observations have previously been reported (Adebowale et al., 2002a).

3.2. Granule size and microscopic appearance

By SEM (Fig. 2) and LM (Fig. 3) investigations, the starch molecules are round and polygonal in shape, with sizes ranging from 15–40 μm . In other tuber starches, round, oval and polygonal shapes with sizes ranging from 2 to 42 μm have been reported for potato starch (Seog, Park, Nam, Shin, & Kim, 1987), and round-oval (28.5–30.6 μm) for *D. cayensis* and *D. rotundata* starch (Emiola & Delarossa, 1981), while round shape (5–4 μm) has been reported for cassava starch (Moorthy, 1994). Fissures were noticed in some of the granules. The extent of fissures in granules is a direct result of drying (Hall & Sayre, 1971). In this study, no noticeable difference was observed between the appearance of the

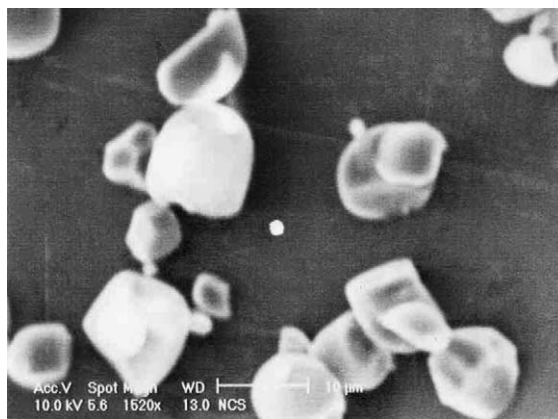


Fig. 2. Scanning electron micrograph of native and new cocoyam starch (1520 \times).

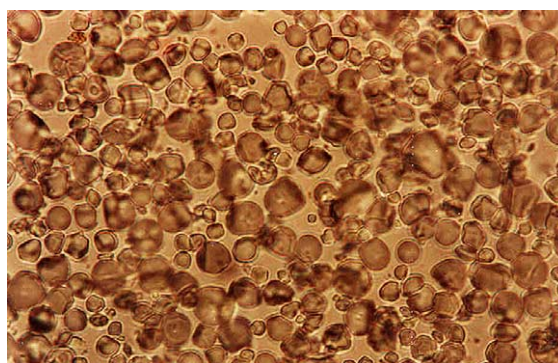


Fig. 3. Light micrograph of native new cocoyam starch.

unmodified starch granule (Figs. 2 and 3) and the modified derivatives (not shown).

3.3. Wide angle X-ray diffraction of starch granules

X-ray diffraction pattern, presented in Fig. 4, shows that native new cocoyam starch gave an X-ray diffraction pattern that has been classified as A type (Wang & Wang, 2001). Although, most tuber starches give the B pattern of X-ray diffractograms, the result obtained in this work is consistent with literature on some tuber starches that gave A patterns of X-ray diffractograms. These include *Ipomea batatas* (Gallant et al., 1982; Moorthy, 1994), *Dioscorea dumetorium* (Gallant et al., 1982), *Colocassia esculenta* (Lim et al., 1994) and *Amorphophallus paenofolius* (Rani, Joh, Moorthy, & Raja, 1998). Modified starches showed X-ray patterns similar to native starch, as all starches showed diffraction patterns of typical A type starch with strong peaks at 15.9°, 17.2°, 18.8°, and 25.0° (2θ). However, acid-thinned derivatives had slightly sharper peaks at $2\theta = 18.8^\circ$ and 25.0° . This observation suggests that starch crystallinity increased following acid-thinning. The cleavage of starch chains in the amorphous region

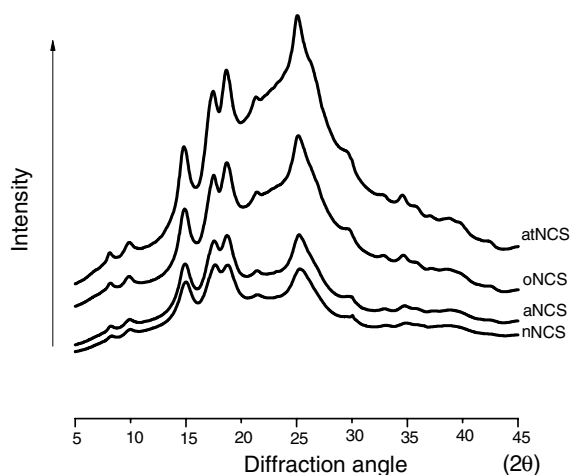


Fig. 4. X-ray diffraction pattern of native, oxidised, acetylated and acid-thinned new cocoyam starch: nNCS, native new cocoyam starch; oNCS, oxidised new cocoyam starch; aNCS, acetylated new cocoyam starch; atNCS, acid-thinned new cocoyam starch.

allows reordering of the chain segments to give more crystalline structure with a sharper X-ray pattern (Wang & Wang, 2001).

Starch crystallites are due to sequential packing of double helices that are formed between the flexible A chains of amylopectin (Wu & Sarko, 1978). Several lines of evidence indicate that amylopectin is the main contributor to crystalline order within the granule (French, 1984). Hence it is reasonable that oxidation did not result in any significant change in the X-ray pattern of native starch because it took place mainly in the amorphous region. Probably the degree of acetylation in this work is not sufficient to alter starch crystallinity. These observations lend credence to similar results presented by Kuakpetoon and Wang (2001) on potato starch.

3.4. Effect of temperature on swelling power and solubility of the starches

Swelling power of all starches increased as the temperature increased (Table 2). This result lends credence to observations of Gebre-Mariam and Schmidt (1996) and Hoover, Sailaja, and Sosulski (1996). It also corroborates our observations on increase in swelling power with temperature for mucuna bean starches (Adebowale & Lawal, 2002b). The 53 g/g (95 °C) swelling power of nNCS is lower than the 90.6 g/g and 80.0 g/g reported even at lower temperature (90 °C) for potato (Kulp & Lorenz, 1981; Seog et al., 1987) but higher than the 20.0 g/g (95 °C) for native maize starch (Collado, Mabesa, Oates, & Corke, 2001). It is also higher than the 51.4 g/g (95 °C) for waxy maize starch (Hoover & Manuel, 1996), the 51 g/g (95 °C) for cassava (Tian, Rickard, & Blanshard, 1991) and the 20.5 g/g (95 °C) for *D. alata* (Emiola & Delarossa, 1981).

Oxidation and acid-thinning reduced the swelling power at all temperatures. Reduction in swelling power due to acid-thinning was more pronounced than the effect of oxidation. The least value of 13 g/g was observed for atNCS at 55 °C, compared with 15 g/g and 16 g/g for oNCS and nNCS, respectively. Similar reduction in swelling power after acid-thinning and oxidation has been reported (Deshpande, Sathe, Rangnekar, & Salunkhe, 1982; Shieldneck & Smith, 1971). Contrarily, at all temperatures investigated, swelling power increased after acetylation of the raw starch. A value of 67 g/g was recorded at 95 °C for aNCS compared with 53 g/g for nNCS.

Solubility of native and all modified derivatives of new cocoyam starch increased as the temperature increased from 55 to 95 °C. Both oxidation and

Table 2

Effect of temperature on swelling power and solubility of native (nNCS), oxidised (oNCS), acetylated (aNCS) and acid-thinned (atNCS) new cocoyam starches*

Starch	Temperature (°C)				
	55	65	75	85	95
<i>Swelling power (°C)</i>					
nNCS	16.24 ^a ± 0.07	24.38 ^a ± 0.56	31.89 ^a ± 0.09	40.57 ^c ± 0.81	53.43 ^b ± 0.01
oNCS ⁺	15.40 ^a ± 0.09	18.76 ^b ± 0.01	22.52 ^b ± 0.01	29.49 ^a ± 0.19	31.67 ^a ± 0.91
aNCS ⁺⁺	23.67 ^b ± 0.01	38.89 ^c ± 0.04	48.98 ^c ± 0.87	54.65 ^b ± 0.87	67.12 ^c ± 0.02
atNCS	13.74 ^c ± 0.05	15.15 ^b ± 0.18	24.76 ^b ± 0.07	24.12 ^a ± 0.06	29.54 ^a ± 0.17
<i>Solubility (%)</i>					
nNCS	26.54 ^b ± 0.17	54.62 ^b ± 0.18	84.12 ^b ± 0.19	142.1 ^b ± 0.14	160.6 ^b ± 0.71
oNCS ⁺	34.18 ^a ± 0.91	59.84 ^c ± 0.89	92.56 ^c ± 0.74	154.3 ^c ± 0.41	174.9 ^d ± 0.01
aNCS ⁺⁺	21.67 ^b ± 0.61	50.91 ^a ± 0.05	64.47 ^a ± 0.06	113.7 ^a ± 0.08	123.8 ^a ± 0.72
atNCS	34.45 ^a ± 0.78	56.86 ^b ± 0.09	87.76 ^b ± 0.09	149.1 ^b ± 0.01	168.7 ^c ± 0.08

* All values are means of triplicate determinations ± standard deviation means within columns with different letters are significantly different ($P < 0.05$).

⁺ Degree of substitution 0.34.

⁺⁺ Degree of substitution 0.30.

acid-thinning markedly improved solubility of the native starch. However, the effect of oxidation was more pronounced than the increase in solubility due to acid-thinning. The maximum value of 174% was observed at 95 °C compared with 168% and 160% of aNCS and nNCS, respectively. Oppositely acetylation led to reduction of percent solubility of the native starch. In a study of the solubility pattern of various starches, Leach et al. (1959) found that 60-fluidity acid-modified corn starch was about four times as soluble as its parent starch in water at 85 °C; they also reported increase in solubility of cornstarch at all temperatures following oxidation. Acid modification also improved solubility of cassava starch (Osunsami, Akingbala, & Oguntimein, 1989) and red bean starch (Kim & Ahn, 1996).

In acid modification, the hydroxonium ion (H_3O^+) attacks the glycosidic oxygen atom and hydrolyses the glycosidic linkage. Acid acts on the surface of the starch granule first, before it gradually enters the inner region. It is believed that the acid preferentially attacks the amorphous region because the crystalline area is not freely accessible to the acid and this allows it to remain intact. Consequently, % relative crystallinity increases after acid-thinning. Increase in crystallinity accounts for reduction in swelling capacity of the acid-thinned starch since swelling is restricted by stiffness of the entangled amylopectin network in the crystalline region of the starch (Cairns, Leloup, Miles, Ring, & Morris, 1990; Kanuma & French, 1971). Reduction in swelling after oxidation is attributed to structural disintegration within the granules of the starch during the process of modification.

The oxidising agent has also been claimed to penetrate deeply into the granule, acting mainly on the amorphous regions (Forssell et al., 1995). Increase in solubility, following acid-thinning and oxidation, is a result of depolymerisation and structural weakening of the starch granule. A similar reasoning has been advanced earlier (Hodge & Osman, 1996; Leach et al., 1959). Acetylation reduces intermolecular associations in the starch granules and this reduces structural limitations against swelling.

3.5. Effect of pH on swelling capacity and solubility of the starches

The effect of pH on swelling and solubility of native, oxidised, acetylated and acid-thinned new cocoyam starch is presented in Figs. 5 and 6. Swelling and solubility of the starches were pH-dependent. Swelling power of nNCS and oNCS increased progressively as the pH increased from 2 to 12. A similar trend was observed for aNCS only in that 5 g/g was recorded at pH 2 and 4, after which the swelling power increased as the pH increased from 6 to 12. It is noteworthy that acetylated starch showed improved swelling over other starches at all pH values investigated. This result agrees with the earlier report on acetylated black gram starch (Deshpande et al., 1982).

Similarly, the solubility of the starches was found to be a function of the pH. For aNCS and aTNCs, solubility increased progressively as the pH increased from 2 to 12. Although maximum values of 89% and 98% were

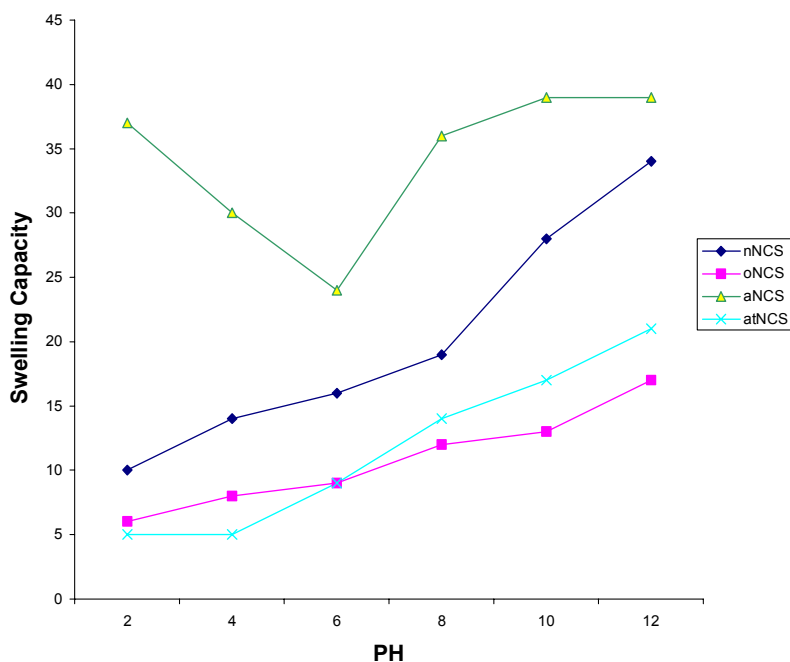


Fig. 5. Effect of pH on swelling capacity of native, oxidised, acetylated and acid-thinned new cocoyam starch: nNCS, native new cocoyam starch; oNCS, oxidised new cocoyam starch; aNCS, acetylated new cocoyam starch; aTNCs, acid-thinned new cocoyam starch.

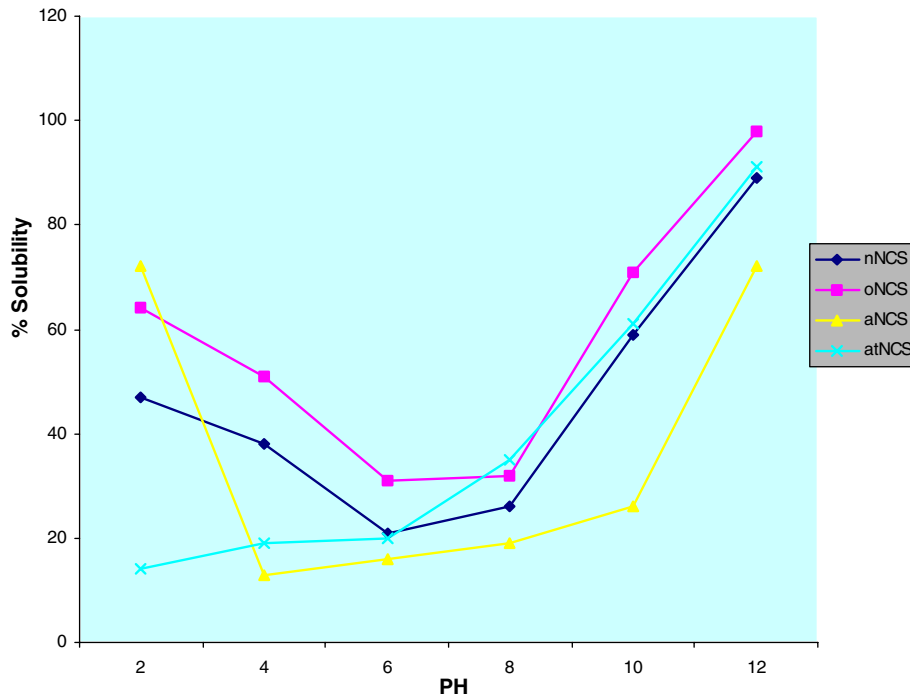


Fig. 6. Effect of pH on solubility of native, oxidised, acetylated and acid-thinned new cocoyam starch: nNCS, native new cocoyam starch; oNCS, oxidised new cocoyam starch; aNCS, acetylated new cocoyam starch; atNCS, acid-thinned new cocoyam starches.

recorded for nNCS and oNCS, respectively, at pH 12, it is also noteworthy that solubility also increased as pH was reduced in the acidic range (2–6). Oxidation markedly improved the solubility of native starch at all pH values contrary to the reduction in solubility after acetylation. Acid-thinning also improved the solubility of the native starch over the alkaline range (pH 8–12). Under alkaline conditions, starches may undergo partial gelatinisation, thus resulting in higher swelling and solubility. This accounts for higher swelling and solubility of the starches at the extreme of the alkaline range.

3.6. Water and oil absorption capacity

Water and oil absorption capacities of native and modified starches are presented in Fig. 7. The results show that hydrophilic tendency of the starches improved after oxidation and acetylation whereas acid-thinning reduced the tendency of the starch to absorb water. However, acetylation had a more pronounced effect on the improvement of water absorption capacity than oxidation. Following a similar trend, both oNCS and aNCS have higher values of oil absorption than unmodified starch. The highest value of 98.6% was observed for aNCS against 94.6% and 92.3% recorded for oNCS and nNCS, respectively, atNCS still showed a lower value (74.6%) of oil absorption capacity than did nNCS. Hence, both hydrophilic and hydrophobic capacities of the native starch were impaired after acid-thinning. Acetylation and oxidation improved the oil

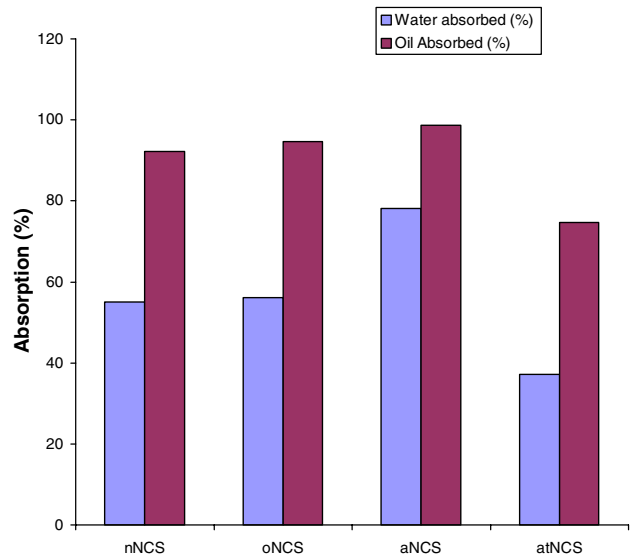


Fig. 7. Water and oil absorption capacity of native, oxidised, acetylated and acid-thinned new cocoyam starch: nNCS, native new cocoyam starch; oNCS, oxidised new cocoyam starch; aNCS, acetylated new cocoyam starch; atNCS, acid-thinned new cocoyam starches.

absorption capacity of black gram starch by almost 2.5 times more than the control (Deshpande et al., 1982), contrary to the report of Sathe and Salunkhe (1981) in which acetylation and oxidation did not improve water and oil absorption capacities of great northern bean starch (Sathe & Salunkhe, 1981). Improvement in water and oil absorption is a result of

introduction of functional groups on the starch molecules, which facilitate a more enhanced, binding capacity than the native starch. Acid-thinning basically reduced oil and water absorption capacities because of reduction of the amorphous region in the starch granules. This reduces the number of available binding sites for water and oil in the starch granule.

3.7. Gelation properties

Taking the least gelation concentration as the index of gelation capacity, the gelation properties of native, oxidised, acetylated and acid-thinned new cocoyam starches are presented in Table 3. The lowest concentration for gelation (LGC) of native cocoyam starch is 8% (w/v). This value increased after oxidation and acetylation, suggesting that nNCS is a better gelating food additive than oNCS or aNCS. However, examining the physical appearance of the starch gels, with increase in concentration, reveals that a firm gel is formed at 12% (w/v) when using aNCS compared with oNCS.

The introduction of carbonyl, carboxyl and acetyl groups after modification caused inter-molecular repulsion in the starch gel, which accounts for weaker gels in oNCS and aNCS. In contrast, in the present investigation, acid-thinning improved gelation. The minimum

concentration required for gelation is 6% (w/v), an improvement over 8% (w/v) of the unmodified starch. This observation agrees with the earlier report of Wang and Wang (2001) on improvement of gelation capacity of corn starch, potato starch and rice starch following acid-thinning. Acid-modified red bean starch and cassava starch has also been reported to have improved gel strength over the unmodified starch (Kim & Ahn, 1996; Osunsami et al., 1989).

The crystalline region is an ordered arrangement of double helical amylopectin structures. Embedded in the amorphous region, amylose has been proposed to disrupt the crystalline packing of amylopectin (Atichokudomchai, Shobsngob, & Padvaravinit, 2001; Jenkins & Donald, 1995). In this sense, the erosion of the amorphous regions by acid hydrolysis may result in a reduced hindrance of double helical chains approaching each other, thus facilitating formation of Van der Waals forces and hydrogen bonding, leading to stronger gelation properties.

3.8. Pasting characteristics

Pasting characteristics of native and modified starches of new cocoyam are presented in Table 4. Pasting temperature of native new cocoyam starch (76 °C) were

Table 3
Gelation properties of native (nNCS), oxidised (oNCS), acetylated (aNCS) and acid-thinned (atNCS) new cocoyam starches

Sample temperature (°C)	nNCS	oNCS ⁺	aNCS ⁺⁺	atNCS
2	–Liquid	–Liquid	–Liquid	Liquid
4	–Liquid	–Liquid	–Liquid	–Liquid
6	Viscous	–Viscous	–Liquid	+Gel
8	+Gel	–Viscous	–Liquid	+Gel
10	+Gel	+Gel	+Gel	+Gel
12	+Firm gel	+Gel	+Firm gel	+Firm gel
14	+Firm gel	+Firm gel	+Firm gel	+V. firm gel*
16	+V. firm gel	+Firm gel	+Firm gel	+V. firm gel
18	+V. firm gel	+V. firm gel	+V. firm gel	+V. firm gel
LGC ^a	8	10	10	6

LGC, least gelation concentration.

* Very firm gel.

⁺ Degree of substitution 0.34.

⁺⁺ Degree of substitution 0.30.

Table 4
Pasting characteristics* of native (nNCS), oxidised (oNCS), acetylated (aNCS) and acid-thinned (atNCS) new cocoyam starches showing pasting temperature (T_p), peak viscosity (P_v), hot paste viscosity (H_v), cold paste viscosity (C_v), stability (ST) and set back (SB)

Starch	T_p (°C)	P_v (BU)	H_v (BU)	H_{v30} (BU)	C_v (BU)	BD (BU)	SB (BU)
nNCS	76	495	440	420	840	75	345
oNCS ⁺	70	320	220	200	520	120	200
aNCS ⁺⁺	72	430	310	280	480	150	50
atNCS	85	410	250	295	850	–150	440

Breakdown (BD) = $P_v - H_{v30}$. SB = $C_v - P_v$. BU, Brabender units.

* Starch concentration 8% (w/v).

⁺ Degree of substitution 0.34.

⁺⁺ Degree of substitution 0.30.

reduced after oxidation and acetylation but increased following acid-thinning. Compared with other starches, the pasting temperature of nNCS is above the 62 and 63.4 °C reported for cassava starch (Creda & Wosiacki, 1985; Piyachomkwan et al., 2002) and *D. abyssinica* starch (Mariam & Schimdt, 1998) but below the 82 °C reported for *D. dumetorium* and *D. esculenta* starches (Rasper & Coursey, 1967). All forms of modification studied reduced the peak viscosity (P_v) of the native starch. Hot paste viscosity (H_v), after holding for 30 min at 95 °C (H_{v30}), and cold paste viscosity (C_v) were also reduced following oxidation and acetylation. Cold paste viscosity increased following acid-thinning.

The breakdown value of a starch paste, defined as the difference between the peak viscosity and the viscosity after holding for 30 min at 95 °C (Muhammad, Hussin, Man, Ghazali, & Kennedy, 2000), a measure of fragility of the starch (Thayumanavan & Kumari, 1998), increased following oxidation and acetylation but reduced markedly after acid-thinning. The setback value (SB), an index of retrogradation tendency in the starch paste (Ancona, Guerro, Matos, & Ortiz, 2001) was reduced after oxidation and acetylation but increased following acid-thinning.

Reduction of pasting temperature, following oxidation and acetylation is a consequence of structural weakening and disintegration during the modification processes. Heating the starch granule in excess water leads to further granule swelling, additional leaching of soluble components and total disruption of granules. This process results in formation of starch paste. Viscosity of starch, as a food component, is a vital factor for consideration in its applicability to food systems. Reduction in peak viscosity and hot paste viscosity after oxidation, acetylation and acid-thinning has been reported (Adebowale et al., 2002a; Atichokudomchai et al., 2001).

The decrease in viscosity after oxidation was caused by partial cleavage of the glycosidic linkages upon oxidation, resulting in a decrease in molecular weight of starch molecules. This partially degraded network was not resistant to shear and could not maintain the in-

tegrity of the starch granule, thereby producing a lower viscosity. When hot pastes are cooled, the extent of increase in viscosity is governed by reassociation tendency of the starch. This phenomenon is largely determined by the affinity of hydroxyl groups of one molecule for another. Modified starches, having been subjected to conformational reordering and rearrangement, are less prone to such reassociation. Introduction of functional groups to replace the hydroxyl groups limits formation of such binding forces. This accounts for reduction in cold paste viscosity and setback value of oNCS and aNCS compared with the unmodified starch.

3.9. Paste clarity

The influence of storage days on paste clarity of starches is presented in Table 5. Percentage transmittance (650 nm) increased after chemical modifications. Acetylation produced the most marked increase in % transmittance. In all the starches, % transmittance was reduced as the number of days of storage increased. It is, however, noteworthy that pronounced reduction in % transmittance was only observed in nNCS and atNCS. Similar time-dependent reduction in % transmittance has been reported for banana starch (Bello-Perez, Romero-Manilla, & Paredes-Lopez, 2000). Increase in % transmittance after modification is due to chemical substitution of the hydroxyl groups in starch molecules by the acetyl moiety, carbonyl and carboxyl functional groups. This causes repulsion between adjacent starch molecules and apparently reduces interchain association, which facilitates improved % transmittance.

Marked reduction of % transmittance of native starch is a result of retrogradation tendency. This effect is minimised in oNCS and aNCS because such associative bonding forces, responsible for retrogradation, have been reduced by the introduction of other functional groups. The leaching of the amorphous region during acid hydrolysis enhances interactive bond formation between the amylopectin molecules; this facilitates retrogradation of atNCS, thus explaining reduction in % transmittance in acid-thinned starch.

Table 5

Influence of storage days on paste clarity of native (nNCS), oxidised (oNCS), acetylated (aNCS) and acid-thinned (atNCS) new cocoyam starches*

Starch sample	Percentage transmittance (650 nm)					
	1st day	2nd day	4th day	6th day	8th day	10th day
nNCS	26.49 ^a ± 0.07	18.48 ^b ± 0.04	13.32 ^a ± 0.84	11.43 ^a ± 0.12	10.85 ^a ± 0.29	6.94 ^a ± 0.29
oNCS ⁺	34.56 ^b ± 0.32	33.32 ^a ± 0.33	33.24 ^b ± 0.09	32.18 ^b ± 0.32	32.17 ^b ± 0.08	32.16 ^b ± 0.47
aNCS ⁺⁺	38.98 ^c ± 0.44	38.09 ^c ± 0.10	37.92 ^b ± 0.14	37.98 ^c ± 0.42	36.84 ^c ± 0.33	36.87 ^b ± 0.84
AtNCS	33.57 ^b ± 0.29	17.54 ^b ± 0.74	12.74 ^a ± 0.44	10.70 ^a ± 0.34	9.05 ^a ± 0.13	4.78 ^a ± 0.73

* All values are means of triplicate determinations ± standard deviation means within columns with different letters are significantly different ($P < 0.05$).

⁺ Degree of substitution 0.34.

⁺⁺ Degree of substitution 0.30.

3.10. Gelatinisation and retrogradation studies

The results of gelatinisation and retrogradation transition temperature and enthalpy are presented in Table 6. Oxidation, acetylation and acid-thinning influenced the onset temperature (T_o), peak temperature (T_p), concluding temperature (T_c), the enthalpy of gelatinisation (ΔH) and retrogradation after storage for 2 (ΔH_2) and 7 (ΔH_7) days. The gelatinisation temperature range of native new cocoyam starch (77.15–84.22) is comparable to those of other tuber crops starches, such as cassava (Valetudie, Colona, Bouchet, & Gallant, 1995), potato (Collado, Mabesa, & Corke, 1999) and old cocoyam (Jane et al., 1992). Oxidation and acetylation reduced peak temperature of gelatinisation (T_p) of the native starch from 79.80 to 75.97 and 75.13 °C, respectively, contrary to the increase in T_p after acid-thinning. However, gelatinisation increased after oxidation and acetylation but was reduced slightly after acid-thinning. ΔH value, which represents the amount of thermal energy involved in the gelatinisation process, was reduced from 4.07 J/g in nNCS to 3.98 and 3.52 J/g in oNCS and aNCS, respectively. Acid modification, however, increased ΔH value of the native starch to 5.31 J/g. This result corroborates the observation of Wang and Wang (2001) on increase in peak temperature and gelatinisation enthalpy of potato starch after acid-thinning.

Gelatinisation involves the uncoiling and melting of external chains of amylopectin that are packed together as double helices in clusters. Cooke and Gidley (1992) have shown, through studies of starches isolated at various steps of the gelatinisation process, that the relative decrease in double helix content parallels the relative decrease in both crystallinity and residual gelatinisation enthalpy, but occurs at higher temperatures than the relative decrease in granular birefringence. They also established, through their studies on granular and model crystallites, that ΔH is due mainly to disruption of the double helices, rather than the longer-range disruption of crystallinity. In view of this direct relationship between double helix content and crystallinity, it is supposed that leaching of the amorphous region by acid hydrolysis increased starch crystallinity and consequently increased both gelatinisation temperature and enthalpy. ΔH is expected to involve cleavage of hydrogen bonds and other associative bonding forces between starch molecules; such bonds must have been limited by oxidation and acetylation. This accounts for reduction in T_p and ΔH following these chemical modifications.

For nNCS and atNCS, ΔH_{77} (retrogradation enthalpy after seven days) is greater than ΔH_{72} (retrogradation enthalpy after 2 days). Also, for oNCS and aNCS, ΔH_{77} is greater than ΔH_{72} but the increases observed in these two cases are minimised. T_p of the starches also increased as time of storage increased. For all the starches, enthalpy at the end of storage days (ΔH_{77}), is lower than

Table 6
The transition temperatures and enthalpies associated with gelatinisation and retrogradation of native (nNCS), oxidised (oNCS), acetylated (aNCS) and acid-thinned (atNCS) new cocoyam starches

Starch	1st day scanning			2nd day scanning			7th day scanning							
	T_p	T_c	$T_c - T_o$ (°C)	ΔH (J/g)	T_o	T_p	T_c	$T_c - T_o$ (°C)	ΔH_2 (J/g)	T_o	T_p	T_c	$T_c - T_o$ (°C)	ΔH_7 (J/g)
NNCS	77.15	79.80	84.22	7.07	4.07	51.07	62.09	69.74	18.67	1.83	58.09	67.64	74.36	16.27
oNCS ⁺	61.08	75.97	84.23	23.15	3.98	48.96	60.98	67.31	18.35	1.52	52.54	62.12	67.42	14.87
aNCS ⁺	60.76	75.13	85.40	24.64	3.52	47.71	58.77	67.53	19.82	1.78	52.92	61.31	69.58	17.66
AtNCS	78.59	81.98	85.6	7.01	5.31	57.14	69.78	71.72	14.58	2.08	64.07	69.97	72.57	8.5

T_o , onset of gelatinisation temperature; T_p , peak of gelatinisation temperature; T_c , conclusion of gelatinisation temperature; ΔH , enthalpy of 1st day scanning; ΔH_2 , enthalpy of retrogradation after 2 days of storage; ΔH_7 , enthalpy of retrogradation after 7 days of storage.

⁺ Degree of substitution 0.34.

⁺⁺ Degree of substitution 0.30.

gelatinisation enthalpies (ΔH). Similar observations have been reported for chemically modified potato starch (Morikawa & Nishinari, 2000).

Recrystallisation of starch molecules occurred during gel storage, and reheating of aged starch gel in a DSC produced an endothermic transition which was absent in freshly gelatinised samples. The enthalpy of retrogradation values was also observed at lower temperature ranges than for gelatinisation (Perera & Hoover, 1999). Recrystallisation of starch molecules has been reported to occur in a less ordered manner in stored starch gels than in native starches. This explains the observation of retrogradation endotherms at a temperature range below that for gelatinisation. Retrogradation is a time-dependent process; thus longer storage enhances structural reordering after gelatinisation. This explains higher values of ΔH_{r7} compared with ΔH . Chemical modifications convert such rearrangement of molecular chains to the ordered structure after gelatinisation and this explains why increase in enthalpy of retrogradation after seven days is minimised in oNCS and aNCS.

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References

- Adebowale, K. O., Afolabi, T. A., & Lawal, O. S. (2002a). Isolation, chemical modification and physicochemical characterisation of Bambarra groundnut (*Voandzeia subterranean*) starch and flour. *Food Chemistry*, *78*, 305–311.
- Adebowale, K. O., & Lawal, O. S. (2002b). Effect of annealing and heat moisture conditioning on the physicochemical characteristics of bambarra groundnut (*Voandzeia subterranea*) starch. *Nahrung/ Food*, *46*, 311–316.
- Adebowale, K. O., & Lawal, O. S. (2003). Microstructure, functional properties and retrogradation behaviour of mucuna bean (*Mucuna pruriens*) starch on heat moisture treatments. *Food Hydrocolloids*, *17*, 265–272.
- Aiyele, F. B., Akingbala, J. O., & Oguntimein, G. B. (1993). Chemical factors affecting acetylation of cassava starch. *Starch*, *45*, 443–445.
- Atichokudomchai, N., Shobsngob, C., & Padvaravinit, S. (2001). A study of some physicochemical properties of high-crystalline tapioca starch. *Starch*, *53*, 577–581.
- Ancona, D. A. B., Guerro, L. A. C., Matos, R. I. C., & Ortiz, G. A. (2001). Physicochemical and functional characterisation of baby lima bean (*Phaseolus lunatus*) starch. *Starch*, *53*, 219–226.
- AOAC (1996). Official methods of analysis. Association of official Analytical chemistry, Arlington.
- Beuchat, L. R. (1977). Functional and electrophoretic characteristics of succinylated peanut flour protein. *Journal of Agriculture and Food Chemistry*, *25*, 258–261.
- Bhandari, P. N., & Singhal, R. S. (2002). Effect of succinylation on the corn and amaranth starch paste. *Carbohydrate Polymers*, *48*, 233–240.
- Bello-Perez, L. A., Romero-Manilla, R., & Paredes-Lopez, O. (2000). Preparation and properties of physically modified banana starch prepared by alcoholic alkaline treatment. *Starch*, *52*, 154–159.
- Cairns, P., Leloup, V. M., Miles, M. J., Ring, S. G., & Morris, V. J. (1990). Resistant starch: An X-ray diffraction study into the effect of enzymatic hydrolysis on amylose gels in vitro. *Journal of Cereal Science*, *12*, 203–206.
- Collado, L. S., Mabesa, R. C., & Corke, H. (1999). Genetic variation in the physical properties of sweet potato starch. *Journal of Agriculture and Food Chemistry*, *47*, 4195–4201.
- Collado, L. S., Mabesa, L. B., Oates, C. G., & Corke, H. (2001). Bihon-type noodles from heat-moisture-treated sweet potato starch. *Journal of Food Science*, *66*, 604–609.
- Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinisation. Origin of the enthalpic transition. *Carbohydrate Research*, *227*, 103–112.
- Creda, M. P., & Wosiacki, G. (1985). Characterisation of Pinharo starch. Part II. *Starch*, *37*, 404–407.
- Defloor, I., Dehing, I., & Delcour, J. (1998). Physicochemical properties of cassava starch. *Starch*, *50*, 58–64.
- Deshpande, S. S., Sathe, S. K., Rangnekar, P. D., & Salunkhe, D. K. (1982). Functional properties of modified black gram (*Phaseolus mungo* L.) starch. *Journal of Food Science*, *47*, 1528–1533.
- Emiola, L. C., & Delarossa, L. C. (1981). Physicochemical characteristics of yam starches. *Food Biochemistry*, *5*, 115–130.
- Forssell, P., Hamunen, A., Autio, K., Suortti, T., & Poutanen, K. (1995). Hypochlorite oxidation of barley and potato starch. *Starch*, *47*, 371–377.
- French, D. (1984). Organization of starch granules. In R. L. Whistler, J. N. Be Miller, & E. F. Paschall (Eds.), *Starch chemistry and technology* (pp. 183–247). New York: Academic Press.
- Gallant, D. J., Bewa, M., Buy, Q. H., Bouchet, B., Szylił, O., & Sealy, L. (1982). On ultrastructural nutritional aspects of some tropical tuber starches. *Starch*, *34*, 255.
- Gebre-Mariam, T., & Schmidt, P. C. (1996). Isolation and physicochemical properties of enset starch. *Starch*, *48*, 208–214.
- Hall, D. M., & Sayre, J. (1971). A scanning electron microscope study of starches. Part III. Miscellaneous starches. *Textile Research Journal*, *41*, 880–883.
- Hodge, J. E., & Osman, E. M. (1996). Carbohydrates. In O. R. Fennema (Ed.), *Food chemistry* (p. 47). New York: Marcel Dekker.
- Hoover, R., & Hadziyev, D. (1981). Characterisation of potato starch and its monoglyceride complexes. *Starch*, *33*, 290–300.
- Hoover, R., & Manuel, H. (1996). The effects of heat moisture treatment on the structure and physicochemical properties of normal maize, waxy maize, Dull waxy maize and amylo maize V starches. *Journal of Cereal Science*, *23*, 153–162.
- Hoover, R., Sailaja, Y., & Sosulski, F. W. (1996). Characterisation of starches from wild and long grain brown rice. *Food Research International*, *29*, 99–107.
- Jane, J., Shen, L., Chen, J., Lim, S., Kasemsuwan, T., & Nip, W. K. (1992). Physical and chemical studies of Taro starches and flours. *Cereal Chemistry*, *64*, 528–535.
- Jenkins, P. J., & Donald, A. M. (1995). The influence of amylose on starch granules structure. *International Journal of Biological Macromolecules*, *17*, 315–321.

- Kanuma, K., & French, D. (1971). Nageli amylopectin and its relationship to starch granule structure I. Preparation and properties of amylopectins from various starch types. *Biopolymers*, *10*, 1673–1680.
- Kim, R. E., & Ahn, S. Y. (1996). Gelling properties of acid-modified red starch gel. *Agricultural Chemistry and Biotechnology*, *39*, 49–53.
- Kuakpetoon, D., & Wang, Y. J. (2001). Characterisation of different starches oxidised by hypochlorite. *Starch*, *53*, 211–218.
- Kulp, K., & Lorenz, K. (1981). Heat-moisture treatment of starches. I. Physicochemical properties. *Cereal Chemistry*, *58*, 46–48.
- Leach, H. W., McCowen, L. D., & Scoch, T. J. (1959). Structure of the starch granule I. Swelling and solubility patterns of various starches. *Cereal Chemistry*, *36*, 534–544.
- Lim, S. T., Kasemsuwan, T., & Jane, J. L. (1994). Characterisation of phosphorus in starch by ³¹P nuclear magnetic spectroscopy. *Cereal Chemistry*, *71*, 468–472.
- Mariam, T. G., & Schimdt, P. C. (1998). Some physicochemical properties of dioscorea starch from Ethiopia. *Starch*, *50*, 241–246.
- Morikawa, K., & Nishinari, K. (2000). Effect of concentration dependence of retrogradation behaviour of dispersions for nature and chemically modified potato starch. *Food Hydrocolloids*, *14*, 395–401.
- Moorthy, S. N. (1994). Tuber crop starches. Central Tuber Crops Research Institute, Sreekariyam, Thiruvananthapuram, Kerala, India, pp. 1–40.
- Muhammad, K., Hussin, F., Man, Y. C., Ghazali, H. M., & Kennedy, J. F. (2000). Effect of pH on phosphorylation of sago starch. *Carbohydrate Polymer*, *42*, 85–90.
- Osunsami, A. T., Akingbala, J. O., & Oguntimein, G. B. (1989). Effect of storage on starch content and modification of cassava starch. *Starch*, *41*, 54–57.
- Parovuori, P., Hamunen, A., Forsell, P., Autio, K., & Poutanen, K. (1995). Oxidation of potato starch by hydrogen peroxide. *Starch*, *47*, 19–23.
- Perera, C., & Hoover, R. (1999). Influence of hydroxypropylation on retrogradation properties of native, defatted and heat-moisture treated potato starches. *Food Chemistry*, *64*, 361–375.
- Piyachomkwan, K., Chotineerant, S., Kijkhunasattian, C., Tonwitawat, R., Prammanee, S., Oates, C. G., & Sriroth, K. (2002). Edible canna (*Canna edulis*) as a complementary starch source to cassava for the starch industry. *Industrial Crops and Products*, *16*, 11–21.
- Raja, M. K. C., & Sindhu, P. (2000). Properties of steam-treated arrowroot (*Maranta arundinacea*) starch. *Starch*, *52*, 471–476.
- Rani, V. S., Joh, J. K., Moorthy, S. N., & Raja, K. M. (1998). Effect of pre-treatment of fresh *Amorphophallus paeranoiifolius* on physico-chemical properties of starch. *Starke*, *50*, 72–77.
- Rasper, V., & Coursey, D. G. (1967). Properties of starches of some West African yams. *Journal of the Science of Food and Agriculture*, *18*, 240–244.
- Santacruz, S., Koch, K., Svensson, E., Ruales, J., & Eliasson, A. C. (2002). Three under-utilised sources of starch from the Andean region in Ecuador: Part I. Physico-chemical characterisation. *Carbohydrate Polymers*, *49*, 63–70.
- SAS (1988). SAS/STAT users guide, Release 6.03. SAS Institute Inc., Cary, NC.
- Sathe, S. K., & Salunkhe, D. K. (1981). Isolation, partial characterisation and modification of the great Northern bean (*Phaseolus Vulgaris* L.) starch. *Journal of Food Science*, *46*, 617–621.
- Seog, H. M., Park, Y. K., Nam, Y. J., Shin, D. H., & Kim, J. P. (1987). Physicochemical properties of several sweet potato starches. *Han guk nanghwa Hakhoechi*, *30*, 179–185.
- Shieldneck, P., & Smith, C. E. (1971). Production and uses of acid modified starch. In R. L. Whistler & E. F. Paschall (Eds.), *Starch: Chemistry and technology* (pp. 173–215). New York: Academic Press.
- Singh, V., & Ali, S. Z. (2000). Acid degradation of starch. The effect of acid and starch type. *Carbohydrate Polymers*, *41*, 191–195.
- Smith, R. J. (1967). Characterisation and analysis of starches. In R. L. Whistler & E. F. Paschall (Eds.), *Starch: Chemistry and technology* (pp. 620–625). New York: Academic Press.
- Thayumanavan, B., & Kumari, S. K. (1998). Characterisation of starches of proso, foxtail, barnyard, kodo and little millets. *Plants Food for Human Nutrition*, *53*, 47–56.
- Tian, S. J., Rickard, J. E., & Blanshard, J. M. V. (1991). Physico-chemical properties of sweet potato starch. *Journal of the Science of Food and Agriculture*, *57*, 459–491.
- Valetudie, J. C., Colona, P., Bouchet, B., & Gallant, D. J. (1995). Gelatinisation of sweet potato, Tania and yam tuber starches. *Starch*, *47*, 298–306.
- Wang, L., & Wang, Y. (2001). Structures and physicochemical properties of acid-thinned corn, potato and rice starches. *Starch*, *53*, 570–576.
- Wu, H. C. H., & Sarko, A. (1978). The double helical molecular structure of crystalline B-amylose. *Carbohydrate Research*, *61*, 7–40.
- Zhang, T., & Oates, C. G. (1999). Relationship between amylase degradation and physicochemical properties of sweet potato starches. *Food Chemistry*, *65*, 157–163.