

Derivatisation Improved the Physicochemical and Morphological Properties of *Treculia africana* (Decne) Kernel Starch

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ABSTRACT

Starch finds use in a myriad of industrial applications. In its native form however, its functionalities are limited. In this study, starch was isolated from *Treculia africana*, a lesser-known starch source, kernels and modified to produce the acetylated, oxidized, and acid-thinned derivatives. The effects of modifications on the native starch chemical properties, swelling power and solubility, water and oil absorption capacities, gelation, and morphological were investigated. Significant ($p < 0.05$) reductions in the native starch moisture, ash, crude protein, crude fat, and crude fibre compositions were observed. Starches increased in swelling power and solubilities with increase in temperature. The oxidised starch showed the most significant increase ($p < 0.05$) in oil absorption capacity while the native starch had better water absorption capacity than the modified starches. Improved gelation property was most significant in the acid-thinned starch. Scanning electron microscopy, showed oblong and oval starch granules with rough surface morphology with no significant differences for the native and derivatised starches. The study showed that modification improved *T. africana* kernel starch properties.

Keywords: *Treculia africana*, starch, derivatisation, characteristics, morphology.

1. INTRODUCTION

Starch, a naturally abundant polymer of plant origin, is an important raw material with versatile industrial applications. It shows different functionalities and it is the most regularly applied hydrocolloid. Its use in its native form however, has limitations (Pornsuksomboon, Barta, Mészáros, & Kaewtatip, 2016) such as inability to dissolve in cold water, changing gelling power and viscosity after cooking, syneresis, a consequence of retrogradation (Lawal, 2009), thermal decomposition and low shear resistance among others. To overcome these limitations, starch modifications are usually done to introduce desirable alterations in the starch structure with a resultant ability to predict and control starch behavior (J. Singh, Kaur, & McCarthy, 2007).

Starch modifications are achieved by physical, chemical and biotechnological means. Derivatives obtained have varied uses in pharmaceutical/biomedical, food and non-food industries as binders, disintegrants, lubricants (Olu-owolabi, Afolabi, & Adebowale, 2010), blood plasma expanders, cryoprotective agents for erythrocytes, fat replacers, flavour stabilisers, thickeners, gelling agents, salad dressing, water purification scavengers, flocculants, sizing agents and improvers of printing dyes in textile industry, sanitary product manufacture, binders in insulation of fibreglass, resins of adhesive in plywood, fluid loss control in subterranean drilling (Tharanathan, 2005), floatation and sedimentation agents in ore mining (Kozich & Wastyn, 2012), etc.

The diverse use of starch derivatives and the attendant over-dependence on conventional sources such as corn, wheat, rice, sorghum, potato, tapioca, etc., which serve as major staple foods in developing countries, necessitated the search for alternative sources of starch to meet the ever-increasing demands of the insatiable starch industry. These resulted in researches into new sources of starch from unconventional/under-utilised sources such as mucuna beans (Adebowale & Lawal, 2003b), Cyperus sedge (Paramakrishnan, Jha, & Kumar, 2016), cocoyam (Olayide S Lawal, 2004), bambara groundnut (Adebowale, Afolabi, & Lawal, 2002).

African Breadfruit is a tropical plant that is rich in carbohydrate (73%) (Osabor, Ogar, Okafor, & Egbung, 2009). It grows well in the Western and Eastern regions of Nigeria. It is a rain-forest plant, about 40 m high and with 30 - 50 fruits produced annually with weights in the range of 30 and 40 kg. The use of its kernel is limited to thickening of soup, making cookies, breadfruit cakes and various snacks (Akubor, Isolokwu, Ugbane, & Onimawo, 2000; Onweluzo & Nnamuchi, 2009). However, the use of this kernel as source of starch is an unacknowledged potential. With the dearth of report on its use as starch source, it is reasonable to explore this virgin starch source with the view to maximizing its use as raw material particularly, as alternative source of starch for industrial applications. The optimum employment of African breadfruit starch is however, hinged on its modifications by various methods aforementioned, knowing full well that its potentials in the native states, like every other native starch, are limited. The objective of this work was to determine the effects of acetylation, oxidation and acid-thinning on the physicochemical, pasting, morphological and thermal properties of African breadfruit kernel starch with the view to improving its functional properties and maximizing its potential for industrial applications.

2. MATERIALS AND METHODS

2.1 Materials

Unprocessed African breadfruit was bought from Afigwe Main Market, Anambra State, Nigeria. The seeds were sun-dried for four days and the defective ones screened by hand-picking. The seeds were manually dehulled, dried, milled in a grinder (Marlex Excella, KIL, Daman, India) and kept in LDPE bag until required. Chemicals used were of analytical grade apart from sodium hypochlorite which was reagent grade.

2.2 Isolation and Purification of Starch

Isolation and purification of starch from African breadfruit kernel was done by the method of Lawal and Adebowale (Adebowale, Adeniyi Afolabi, & Lawal, 2002) with modifications. A 1000 g weight of the African breadfruit flour was suspended in 4000 mL of distilled water and the pH was adjusted to 8.0 using NaOH solution (0.2 %^{W/v}) at room temperature for 4 hours with continuous stirring. The suspension obtained was screened using muslin cloth and centrifuged for 30 min at 4500 rpm (ROTANTA 460 R, Hettich GmbH & Co. KG, Tuttlingen, Germany). The starch obtained was washed twice before drying in the air for 48 h at 30±2 °C. The native starch was labelled as NA.

2.3 Starch Modification

2.3.1 Oxidation of starch

Oxidation of NA was done by the Forssel et al. method as reported by Lawal (Olayide S Lawal, 2004) with modifications. 250g starch was suspended in 2500 mL of distilled water. The suspension pH was made 9.5 with 8 % w/v NaOH. NaOCl (10 g, 4% w/w active chlorine) was added to the suspension at the rate of 0.33 g/min at a pH range of 9 – 9.5 while stirring continuously at room temperature. Additional 10 min was allowed for the reaction after adding the NaOCl. The reaction medium pH was adjusted to 7 using 1.0 M HCl solution. The starch suspension was centrifuged, repeatedly washed with distilled water (four times) and centrifuged after each washing. The recovered oxidised starch was air-dried at room temperature for two days and labelled OX.

2.3.2 Acetylation of starch

Native starch was acetylated using the method of Sathe and Salunkhe described by Lawal (Olayide S Lawal, 2004). 20 % w/v starch suspension in 0.5 L was made in distilled water. The pH of the suspension was adjusted to 8 using 4 % w/v NaOH after magnetically stirring for 20 min. Acetic anhydride ((CH₃CO)₂, 10.2 g) was added at the rate of 0.17 g/min at a pH of 8 – 8.5. Additional 5 min was allowed for the reaction after adding the (CH₃CO)₂. The reaction medium pH was adjusted to 4.5 using 1.0 M HCl solution. The starch suspension was centrifuged, repeatedly washed with distilled water four times and centrifuged after each washing. The recovered acetylated starch was air-dried at room temperature for two days and labelled AC.

2.3.3 Acid-thinned Starch

Starch thinning was done by Lawal method (Olayide S Lawal, 2004). 100 g of NA was suspended in 0.5 L of HCl (0.15 M). The starch suspension was magnetically stirred for 8 hrs at 50 °C. The modified starch was centrifuged at 4500 rpm (Rotanta 460 R, Hettich GmbH & Co. KG, Tuttlingen, Germany) for 10 min. The pellet recovered was washed repeatedly with distilled water four times and centrifuged after each washing. The recovered acid-thinned starch was air-dried at room temperature for two days and labelled AT.

2.4 PHYSICOCHEMICAL, PASTING, MORPHOLOGICAL AND THERMAL PROPERTIES

2.4.1 PHYSICOCHEMICAL PROPERTIES

Nwinuka et al. (Nwinuka, Ibeh, & Ekeke, 2005) method was used for determining the moisture, ash, crude fibre, crude protein and crude fat contents of the native and derivatised starches.

The carboxyl and carbonyl contents of OX were determined by the method of Lawal (Olayide S Lawal, 2004). For the carboxyl content, about 8 % w/v starch sample in 25 mL of 0.1 M HCl was prepared. The starch slurry was occasionally swirled for 30 min and then filtered using suction through a sintered glass funnel of medium porosity. It was washed with 0.4 L of distilled water and the starch was transferred into a 0.5 L beaker. The volume of the starch slurry was adjusted to 0.3 L with distilled water and it was heated with constant stirring over a period of 15 min for gelatinisation in a boiling water bath (Memmert W270, MEMMERT GmbH+Co.KG, Schwabach, Germany). The volume of the dispersion of hot starch was then made up to 0.45 L using distilled

water and titrated with 0.01 M NaOH to pH 8.3. NA was used for blank test. Equation 1 was used to calculate the carboxyl group content.

$$\text{Percent carboxyl} = \frac{(\text{ST}-\text{BT}) \text{ mL} \times \text{NaOH Concentration} \times 0.045 \times 100}{\text{S (g)}} \quad (1)$$

Where ST = Titre value of oxidised sample; BT = Titre value of NA; S = sample mass

To determine the carbonyl content of oxidised starch, 25 % w/v hydroxylamine hydrochloride in 0.5 M NaOH was prepared. The solution was then diluted to 0.5 L with distilled water. 100 mL of 4 % w/v starch sample was put in a 0.5 mL conical flask. The starch dispersion was heated for 20 min in a thermostated water bath (Memmert W270, MEMMERT GmbH+Co.KG, Schwabach, Germany) to attain gelatinisation. It was cooled to 40 °C, and the pH adjusted to 3.2 using 0.1 M HCl. This was followed by the addition of 15 mL of hydroxylamine reagent. A rubber bung was used to stopper the flask and heated at 40 °C for 4 h in a thermostated water bath stirring slowly. Excess hydroxylamine content of the dispersion was determined by swiftly titrating the mixture with standard 0.1 M HCl to a pH value of 3.2. Hydroxylamine reagent only was used to perform blank determination following the same procedure. Equation 2 was used to calculate the carbonyl content of OX.

$$\text{Carbonyl (C=O) content (\%)} = \frac{(\text{BT}-\text{ST}) \text{ mL} \times \text{HCl concentration (M)} \times 0.028 \times 100}{\text{S (g)}} \quad (2)$$

Where BT = Titre value of NA, ST = Titre value of oxidised sample; S = sample mass

The percentage acetyl group content of AC and the degree of substitution were determined using the method of Smith as described by Lawal (Olayide S Lawal, 2004). 5 g AC was added to 50 mL distilled water in a 0.25 L conical flask and thoroughly mixed. The suspension was titrated with 0.1 M NaOH to obtain a permanent phenolphthalein pink end-point. 0.45 M NaOH (25mL) was added and the conical flask tightly stoppered with a rubber bung. It was vigorously shaken for a period of 30 min after which the bung was removed, rinsed into the flask together with the flask walls using distilled water. The mixture, with its excess NaOH, was titrated with 0.2 M HCl solution to a colourless phenolphthalein indicator colour. NA was subjected to the same treatment for a blank titre. Acetyl content (%) and the degree of acetyl substitution were calculated using equations 3 and 4, respectively.

$$\text{Acetyl content (\%)} = \frac{(\text{BT}-\text{ST}) \text{ mL} \times \text{HCl Concentration (M)} \times 0.043 \times 100}{\text{S (g)}} \quad (3)$$

Where BT = Titre value of NA, ST = Titre value of ABCA; S = sample mass

$$\text{Degree of substitution (DS)} = \frac{162A}{4300-42A}; \text{ where } A = \text{acetyl content (\%)} \quad (4)$$

The effect of temperature variation on swelling power and solubility was carried out, at 55–95 °C, as reported by Lawal (Olayide S Lawal, 2004) with modification. 1 g of starch sample was weighed and transferred quantitatively into a clean dry test tube and weighed. 10 mL of distilled water was added to the test tube and the starch suspension was thoroughly mixed for 30 s and heated at the chosen temperatures (55 – 95 °C) for 30 min on a thermostated water bath (Memmert W270, MEMMERT GmbH+Co.KG, Schwabach, Germany). The mixture was cooled to 27 ± 2 °C and centrifuged for 15 min at 4500 rpm (Centrifuge 80-3 Union Laboratories, England). The starch pellet after and the test tube was weighed. Swelling power (g/100 g) at the chosen temperature was calculated using equation 5

$$\text{Swelling of Starch} = \frac{W_2 - W_1}{\text{Weight of Starch}} \times 100 \quad (5)$$

Where W_1 = mass of dry test tube + dry starch; W_2 = mass of dry test tube + wet starch; S = mass of dry starch sample.

5 mL aliquot of the centrifugation supernatant was oven-dried (OV/125, Genlab Limited, Cheshire, England) at 110 °C to a constant weight. The residue obtained (%) was quantified and represents the extent of solubilisation of starch in water per 100 g of starch sample at the chosen temperature.

The method of Beuchat as reported by Lawal (O S Lawal, 2005) was used for the determination of starch water and oil absorption capacities. 1 g starch sample in 10 mL water or oil (Power oil, Nigeria) was prepared and thoroughly mixed for 30 s. It was then allowed to stand for 30 min. The volume of the water or oil absorbed was then calculated as the difference between the initial volume and the final volume after allowing 30 min. The mass of oil or water absorbed was expressed as g/100 g starch on a dry weight basis.

Gelation studies was performed by the method of Lawal (O S Lawal, 2005). Starch samples (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 g) were suspended in 5 mL of distilled water in test tubes. The starch dispersions were mixed thoroughly for 5 min and heated at 90 °C for 30 min in thermostated water bath. That was followed by cooling rapidly at the cold water tap and refrigeration for 2 hrs at 4 °C. The lowest concentration at which the sample in the inverted tube did not slip was taken as the least gelation concentration.

2.4.2 MORPHOLOGICAL CHARACTERISTIC

The morphologies of the starch granules were examined using a scanning electron microscope (Phenom Pro Desktop SEM, Thermo Fisher Scientific). All of the samples were observed at an acceleration voltage of 25 kV.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties

The results of chemical compositions of native and modified African breadfruit kernel starches are presented in Table 1. Significant ($p < 0.05$) reductions were observed in the percent moisture, ash, crude protein, crude fat and crude fibre following starch modifications. These reductions may be attributed to the degradative and eroding abilities of the oxidant and acid used for hydrolysis and loss of degraded molecules with wash water. Similar observations were made by other workers for hybrid maize (O S Lawal, Adebawale, Ogunsanwo, Barba, & Ilo, 2005), new cocoyam (Olayide S Lawal, 2004), jack bean (Olayide Samuel Lawal, Adebawale, & Adebawale, 2005) and white sorghum (Olayinka, Adebawale, & Olu-Owolabi, 2013) starches. The range of values of moisture contents in native and modified starches are desirable for prolonged shelf life and are similar to those obtained by Olayinka et al. (Olayinka et al., 2013). Low fat and protein contents establish the level of purity of the starch isolates. Similar values were obtained by (Adebawale, Olu-Owolabi, Olawumi, & Lawal, 2005) for breadfruit starch.

Fig. 1 and 2 show how temperature variation affects swelling power and solubility of native and derivatised African breadfruit kernel starches, respectively. Swelling power and solubility of all starches are directly related to temperature and increased with increase in temperature. Similar trend of gradual increase in swelling power and starches solubility with temperature were reported by other workers for *Canavalia ensiformis* (O S Lawal & Adebawale, 2005; Olayide Samuel Lawal et al., 2005), *Kyllinga nemoralis* (Paramakrishnan et al., 2016), *Araucaria brasiliensis* (Thys, Aires, Marczak, & Norena, 2013) *Artocarpus artilis* (Adebawale et al., 2005), *Artocarpus heterophyllus* cultivars (Y. Zhang, Zhu, He, Tan, & Kong, 2016), cocoyam and cassava (Mweta et al., 2008) and corn (Sun, Zhu, Si, & Xiong, 2015). Increase in swelling power was gradual from 55 to 65 °C (1.93 – 4.18 g/g). However, a sharp rise in swelling power was observed between 65 and 75 °C for all starches except AT starch. Solubility increase with temperature, on the other

hand, was gradual for all starches. Luo et al. (Luo, Huang, Fu, Zhang, & Yu, 2009) reported a similar jump in swelling power between 65 and 74 °C for crosslinked waxy potato starch while Adebowale et al. (Adebowale et al., 2002) reported noticeably high swelling power between 75 and 95 °C for unmodified bambara groundnut starch. NA starch had a significantly ($p < 0.05$) higher increase in swelling with temperature, reaching 11.60 ± 0.13 g/g at 95 °C. That was followed by AC and OX starches with 9.98 ± 0.27 and 9.15 ± 1.79 g/g, respectively. The least swelling power was exhibited by AT starch. High swelling power with increase in temperature has been attributed to weakening of the bindings in intra-granular starches, which facilitated unrestricted swelling as temperature increased. Higher swelling power by native starches over modified starches were also reported by Remya et al. (Remya, Jyothi, & Sreekumar, 2018), Adebowale and Lawal (Adebowale & Lawal, 2003b) and Liu et al. (Liu et al., 2015) for modified lentil and banana, mucuna and common buckwheat starches. On the contrary, Singh and Adedeji (M. Singh & Adedeji, 2017) and Adebowale et al. (Adebowale et al., 2005) reported increase in swelling power of acid-modified and acetylated, oxidised and heat–moisture-treated breadfruit starches over their native counterparts, respectively. Increase in swelling power of AC starch could be attributed to introduction of bulky functional groups in the starch chain which facilitated entrance of water into the granules of starch. Oxidation of starch has been reported to reduce swelling power due to possible chain scission which disrupts structure of granules and hence ability to hold water. AT starch had lower swelling power similar to the reports of previous workers. Sandhu et al. (Sandhu, Singh, & Lim, 2008) reported that acid-thinning reduced swelling power of normal and waxy maize starches. Similar reports were given by Lawal (Olayide S Lawal, 2004) after oxidation and acid-thinning of new cocoyam at varying temperatures and Xiao et al. (Hua-xi Xiao, Lin, Liu, & Yu, 2012) for oxidized rice starch. All the modifications, but acid-thinning, reduced African breadfruit native starch solubility significantly ($p < 0.05$). Significant increase in solubility of starch following acid-thinning was observed (10.33 ± 0.58 – 56.67 ± 1.16 g/100g). Dey and Sit (Dey & Sit, 2017), Sandhu et al. (Sandhu et al., 2008), and Lawal et al. (Lawal et al., 2005) all reported increase in solubility of starches following acid-thinning. This increased solubility can be attributed to erosion of the amorphous amylose content of starch which is leached into the medium of suspension.

Table 2 shows the results of gelation properties of native and modified African breadfruit starches. A measure of gelation ability, the least gelation concentration, LGC, represents the minimum concentration of starch suspension in water that produced gel. From the results obtained, gelation tendency increased with increase in the concentration of starch suspension in water. LGC ranged from 6 – 10 %w/v with acid-thinning reducing LGC (6 %w/v) of native starch among the modifications while oxidation increased gelation concentration (10 %w/v). Similar reduction of LGC by acid-thinning has been reported for corn, potato and rice and jack bean (O S Lawal & Adebawale, 2005; Wang & Wang, 2001). Reduced LGC can be attributed to molecular reordering of starch granules after imbibition of water and swelling due to bridging of intergranular binding forces among starch molecules (O S Lawal et al., 2005). Increase in LGC of OX may be attributed to fragmentation and molecular disintegration (Adebawale & Lawal, 2003a) and the introduction of carbonyl and carboxyl groups on the starch chain which reduced hydrogen bonding required for gelation (O S Lawal & Adebawale, 2005). NA and AC had 8 % w/v LGC, a value similar to that reported for jack bean by Lawal and Adebawale (O S Lawal & Adebawale, 2005).

Results of oil and water absorption capacities of native and modified African breadfruit starches are presented in Fig. 3. Oil and water absorption capacities ranged from 39.20 ± 0.43 – 117.60 ± 0.09 g/100g and 163.33 ± 0.58 – 220.00 ± 0.20 g/100g, respectively. Modifications led to increase in oil absorption capacity (OAC) of native African breadfruit starch with significant increase ($p < 0.05$) recorded by OX. Similar observation of increase in OAC following oxidation has been reported for bambara groundnut starch (Adebawale et al., 2002) and jack bean starch (O S Lawal & Adebawale, 2005). OAC of AT (68.6 ± 0.32 g/100g) was higher than that observed for NA (39.20 ± 0.43 g/100g). This was contrary to the observation of Alimi and Workneh (Alimi & Workneh, 2018) who reported decrease in OAC of citric acid modified acha and iburu starches after modification. Native starch however, had a better water absorption capacity (WAC) which was significantly greater than that of AT. Low WAC by AT is attributable to eroded amylose content following acid treatment. This gives credence to its low swelling power.

3.2 Morphological characteristics

Fig. 4 presents the SEM of native and modified African breadfruit kernel starches. All the starches have diameters of about 10 μm similar to those reported by Zabot et al. (Zabot et al., 2018) for annatto seeds. Oblong and oval particles with rough surfaces characterised all the starches. No

significant morphological difference appeared on starch particle surfaces following oxidation, acetylation and acid-thinning. Unchanged surface morphology of OX is similar to the reports of Sangseethong et al. (Sangseethong, Termvejsayanon, & Sriroth, 2010) for hypochlorite oxidized cassava starch, Kuakpetoon and Wang (Kuakpetoon & Wang, 2001) for potato, corn and rice starches and Halal et al. (Halal et al., 2015) for barley starches but contrary to the report of Sukhija et al. (Sukhija, Singh, & Riar, 2016) for elephant foot yam starch and Vanier et al. (Vanier et al., 2012) for bean starch. Vanier et al. (Vanier et al., 2012) also reported that acid hydrolysis at a mineral acid concentration of 3.16 M resulted in exo-erosion of starch granule surface.

4. CONCLUSION

Acetylated, oxidized and acid-thinned starches were produced from African breadfruit kernel native starch. The physicochemical properties of native starch were significantly affected by modification. Improved solubility and gelation ability and reduced pasting properties were observed in acid-thinned starch. Starch morphology remained unchanged following modifications. The native starch is a potentially good thickener for reducing water contents of preparations owing to its high, water absorption capacity while the oxidised African breadfruit kernel starch can function as flavor retention agent. The acid-thinned starch has the potential of usage in gelling, in quick-cook preparations with low viscosity, and frozen products with low tendency to syneresis.

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Table 1. Native (NA), acetylated (AC), oxidized (OX) and acid-thinned (AT) starches of African breadfruit kernel chemical compositions*.

Sample	Yield (%)	Moisture (%)	Ash (%)	Crude protein (%)	Crude fat (%)	Crude Fibre (%)
NA	69.56±1.32	11.44±0.26 ^a	0.38±0.31 ^a	0.97±0.44 ^a	0.72±0.08 ^a	0.76±0.37 ^a
AC	94.71±0.54	9.52±0.48 ^b	0.24±0.07 ^b	0.55±0.38 ^b	0.58±0.57 ^b	0.46±0.41 ^b
OX	96.75±0.98	10.45±0.04 ^c	0.31±0.38 ^c	0.34±0.23 ^c	0.48±0.47 ^c	0.49±0.19 ^b
AT	93.41±0.05	9.05±0.11 ^b	0.29±0.29 ^c	0.52±0.26 ^b	0.42±0.20 ^d	0.55±0.28 ^c

*Means ± SD of triplicate determinations. Yield of native starch, NA, was based on dry matter of African breadfruit kernel. Yields of derivatives are based on recovery after modification. Means within columns with different superscripts are significantly different at 95% confidence interval. OX: COOH = 0.35 per 100 anhydrous glucose unit; CHO = 0.19 per 100 anhydrous glucose unit; AC: percent acetyl substituent = 1.84%.

Table 2. Gelation properties of native (NA), acetylated (AC), acid-thinned (AT) and oxidized (OX) starches of African breadfruit kernel

Concentration (% w/v)	NA	AC	AT	OX
2	L	L	L	L
4	L	L	V	L
6	V	V	G	V
8	G	G	G	V
10	G	G	G	G
12	G	G	G	G
14	G	G	G	G
16	G	G	G	G
LGC	8	8	6	10

LGC = Least Gelation Concentration; L = liquid; V = viscous; G = gel

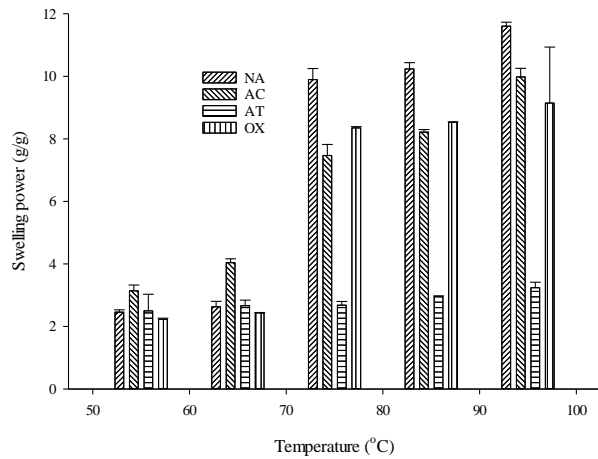


Fig. 1 Mean swelling power of native (NA), acetylated (AC), acid-thinned (AT), and oxidized (OX) African breadfruit kernel starches

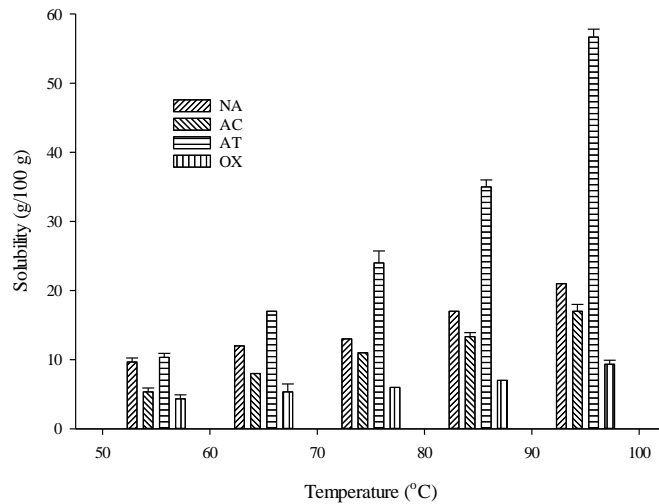


Fig. 2 Mean solubility of native (NA), acetylated (AC), acid-thinned (AT), and oxidized (OX) African breadfruit kernel starches

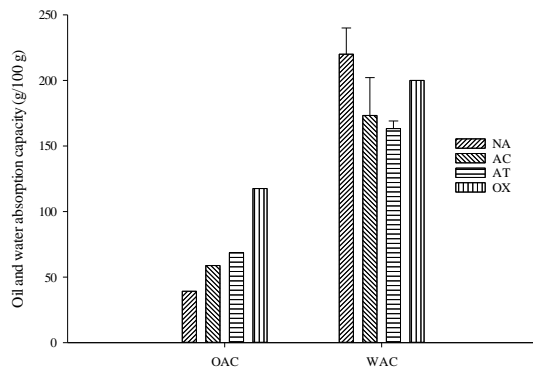


Fig. 3 Oil and water absorption capacities of native (NA), acetylated (AC), acid-thinned (AT), and oxidized (OX) starches of African breadfruit kernel