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Effects of chemical modification on functional and physical properties of African star apple kernel (*Chrysophyllum albidnum*) starch

Ibikunle Adeola Ahmed[1*], Sanyaolu Nurudeen Olanrewaju[1], Yussuf Sodiq Tolulope[1] Ogunneye Adeyemi Lawrence[2], Badejo Olayemi Aderanti[1] and Olaniyi Oluwafunmilayo Mary[1]

[1]Department of Chemical Sciences, Faculty of Science, Olabisi Onabanjo University, Ago-Iwoye, Ogun State, Nigeria.
[2]Department of Chemical Sciences, College of Science and Information Technology, Tai Solarin University of Education, Ijebu Ode, Ogun State, Nigeria.
[3]Department of Integrated Science, Adeniran Ogunsanya College of Education, Lagos, Nigeria.

Starch isolated from *Chrysophyllum albidnum* (African star apple) was subjected to modification by acetylation, carboxymethylation and succinylation process. Chemical modifications effect on functional properties as well as physiochemical parameters of starch was analysed. The percentage yield of native starch was 73.22±0.93%; however the value increased after modifications. The proximate determination of the non-starch components of the native starch on a dry weight basis was 19.32±2.40 moisture, 0.0045±0.00020 ash, 0.085±0.030 fat and 0.25±0.12% crude protein, respectively. Chemical modification reduced the values for all the non-starch components. The swelling power and solubility increased as the temperature increased between the ranges of 50–90°C. Native and modified starches absorbed more oil than water and it is pH dependent. Pasting characteristics decreased after acetylation but increased after carboxymethylation and succinylation. The results of bulk densities showed that native and modified starches are very light (<0.8 g/ml). All these characteristics showed that *C. albidnum* starch can be utilized in both food and non-food applications.

Key words: Functional and physical properties, African star apple kernel, chemical modifications, native, starch.

INTRODUCTION

Starch is a raw material with many industrial uses, and hence, there has been an increased demand for the alternative source of starch from different underutilized agricultural materials like legumes, fruits, seeds etc (Adebowale et al., 2009). The seeds of *Chrysophyllum albidnum* (Figure 1) commonly known as African star apple in English, *Agbalumo* (South-West of Nigeria) and *Udara* (South East of Nigeria) can be a good alternative starch source because of its degree of its availability. The pulp of the fruit is consumed in its natural form by pressing hard and the seed is disposed as a waste and hence constitute environmental degradation if not utilized.

Figure 1. Mature fruits (A), seeds (B) and dehulled seeds of *(C) of Chrysophyllum albidnum.*

However, native starches such as the one from seed have very limited industrial applications due to their low solubility in water, restricted swelling power, poor granule dispersibility, high gelatinization temperatures, higher syneresis and resistance to enzymatic hydrolysis (Hazarika and Sit, 2015). Therefore, modification of starch is necessary in order to overcome the limitations stated above. Furthermore, modification of native starch is done to improve its functional properties which can as well lead to increase in its application industrially (Sodhi and Singh, 2005).

Modification of starch can be in physical, chemical and enznymatic forms (Tomasik and Schilling, 2004). Chemical modification involves the introduction of functional groups into the starch molecule, resulting in markedly altered physico-chemical properties and functional properties such as gelatinization, pasting and retrogradation behaviour etc (Liu et al., 1997). This type of modification can be achieved generally through oxidation, etherification, and esterification. Although, many research works have been carried out on chemical modification of starch from different sources; cassava starches (Zhang et al., 2017), glutinous rice starch (Gope et al., 2016), maize starch (Miao et al., 2014), sweet potato starch (Huang et al., 2016), corn starches (Chung et al., 2008), bean starch (Chung et al., 2010), sago starch (Wattanachant et al., 2003), and wheat starch (Van Hung and Morita, 2005).

However, most of the works on chemical modification were carried out on starches from conventional sources and no investigation at our disposal has been reported on isolation of starch from *C. albidnum* kernel and subsequent modification to different derivatives. Therefore, the objectives of this study were to isolate starch from *C. albidnum* kernel, prepared a modified *C. albidnum* starch at three different levels namely esterification (acetylation), etherification (carboxymethylation) and succinylation and then study the effect of chemical modification on physico-chemical and functional properties of the starches.

MATERIALS AND METHODS

Collection of sample

The African star apple fruit (Figure 1) used in this research work was purchased from a local market in Oshodi, Lagos State, Nigeria. The seeds were removed from the fruit and then dehulled manually. The kernel was removed and then stored in a refrigerator until further use.

Chemicals and reagents

The chemicals used in the course of this research work were of analytical grade and they are; succinic anhydride ($C_4H_4O_3$) (BDH), acetic anhydride (Sigma Aldrich), monochloro acetic acid, hydrochloric acid (HCl) (Merk), Sodium hydroxide (NaOH) (BDH), silver nitrate ($AgNO_3$) (BDH) while the solvents used were ethanol (BDH), methanol (BDH), isopropyl alcohol (BDH) and acetone (BDH).

Isolation of starch from African star apple seed

Sit et al. (2013) method used for starch isolation was strictly followed. The African star apple kernel obtained was washed, soaked for about 30 min and then blended using a Laboratory blender (a pm-y44b2) for 10 min. The slurry obtained was suspended in about ten folds of its volumes of distilled water, that is until the distilled water has fully covered the surface of the sample. The mixture was stirred manually for about 20 min. The corresponding suspension was then filtered using a double fold muslin cloth (so as to get fine particles starch). The filtrate was kept for sedimentation process for 4-5 h. The supernatant was discarded and the sediment thus obtained was washed thoroughly with distilled. The final sediment was sun dried for two days. The dried starch was ground and thus kept in air tight plastic containers for further analysis.

Modifications of starch

Esterification (acetylation) process

Sathe and Sakunkhe (1981) method used for acetylation of starch was used. 70 g of starch was weighed and then dispersed in 350 ml (1:5 w/v) of distilled water, and then stirred with the aid of

magnetic stirrer for 20 min. The pH of the slurry obtained was then adjusted using 1 M of NaOH to 8.0. 5 g of acetic anhydride was later added to the starch slurry obtained for a period of one hour at a constant pH range of 8.0- 8.5. The reaction was then allowed to continue for 5 min. The pH of the mixtures (starch slurry and acetic anhydride) was adjusted back to 4.5 using 0.5 M HCl. The mixture was filtered, washed four to five times with distilled water and then finally air dried at 30°C for 48-50 h. The procedure was repeated for 10 and 15 g acetic anhydride respectively.

Etherification (carboxymethylation) process

The carboxymethylation of starch was done using the method described by Lawal et al. (2007); 8 g of NaOH was dissolved in 50 ml of distilled water in a 500 ml beaker, and stirred with the aid of magnetic stirrer until all the NaOH completely dissolved. 400 ml of isopropyl alcohol was added to the dissolved NaOH solution at a constant temperature of 40°C. 70 g of starch was added to the mixture and further stirred for 60 min. 5 g Monochloroacetic acid (MCA) was added to the reacting mixture with continuous stirring at a constant temperature of 40°C. The pH of the mixture was adjusted to 7 (neutral) using acetic acid and allowed to stir for 60 min. The reacting mixture was filtered and the modified starch was suspended in methanol; it was filtered and washed many times using 80% methanol until the filtrate gave a negative response to silver nitrite test for chloride (all the chlorine from MCA was removed). The carboxymethylated starch obtained after filtration was dispersed in acetone, stirred for 20 min and later dried in the oven at 40°C. The procedure was repeated for 10 and 15 g of MCA respectively.

Succinylation process

Awokoya et al. (2011) method used for starch succinylation was

used. 70 g of starch was dispersed in 210 ml of distilled water, and stirred using magnetic stirrer for 60 min. The pH of the slurry was then adjusted to 9.0 using 1M NaOH. 5 g of succinic anhydride was added to the starch suspension (starch succinate) for a period of 120-130 min at a constant pH range of 8.0-9.0. The pH of the slurry was adjusted to 6.0 using 0.5 M HCl. The mixture obtained was filtered and the modified starch washed five to six times using distilled water. The succinylated starch was oven dried for 24 h at 45-50ºC. The procedure was repeated for 10 and 15 g of succinic anhydride respectively.

Determination of degree of substitution

The degree of substitution (DS) is the average number of substituent or attachment that may have taken part in the modification of starch.

Degree of acetylation

Sathe and Salunkhe (1981) method slightly modified was used to determine the percentage acetyl groups and the degree of acetylation in the starch molecules. 5 g of acetylated starch was weighed and then suspended in 50 ml distilled water in a 250 ml flask; the mixture was stirred using magnetic stirrer. 2 drops of phenolphthalein indicator were added and the suspension titrated with 0.1 M sodium hydroxide (NaOH) to a permanent pink end point. 25 ml of 0.45 M NaOH was added to the reacting mixture. The flask was sealed tightly with a rubber stopper and later shaken vigorously for 20-30 min. The stopper was removed carefully and the wall of the flask was carefully washed down with distilled water. The saponified mixture containing excess alkali (NaOH) was then titrated with 0.5 M HCl solution until the pink colour disappeared. The procedure was also repeated for native starch to obtain a blank value.

$$\% \text{ acetyl (dry basis)} = \frac{\left(\text{Blank titre} - \text{sample titre}\right)\text{ml} \times \text{Acid Molarity} \times 0.043 \times 100}{\text{sample weight in g (dry basis)}}$$

(1)

$$\text{Degree of Substitution (DS)} = \frac{162\,B}{4300 - 42\,B}$$

(2)

Where B = % acetyl dry basis, blank titre is native starch while sample titre is the modified starch.

Degree of carboxymethylation (DS)

The DS of the carboxymethylated starch was determined using the standard method described by Jiang et al. (2011); 5 g of carboxymethylated starch was suspended with 50 ml of 95% ethyl alcohol in 500 ml beaker and the mixture agitated for 7 min. Thereafter, 5 ml of 2 M HNO_3 was added and the mixture was boiled using magnetic hot plate for 5 min; it was further agitated for 10 min and then left to settle. After the settlement of the solution, it was filtered using Whatmann no 1 filter paper and the residue washed with 100 ml of 90% ethyl alcohol for about 5-6 times until the nitric acid was completely removed. The precipitate obtained was washed with methanol and transferred to 500 ml beaker, and heated gently until all the ethyl alcohol was completely removed. This was later allowed to cool in a desiccator. 1 g of dry carboxymethylated starch was weighed and added to 100 ml distilled water and 25 ml of 0.5 M NaOH was added, and stirred.

The reacting mixture was boiled for 16-20 min. After the dissolution of the reacting mixture, it was titrated with 0.5 M HCl using phenolphthalein indicator and the end point was attained when the colour changed from dark pink to colourless. The DS was then calculated using equation Equations 7 and 8 respectively,

$$Z = \frac{GH - TI}{P}$$

(3)

$$\text{Degree of substitution} = \frac{0.162\,X\,Z}{1 - (0.058\,X\,Z)}$$

(4)

where; Z is milliequivalent of consumed acid for each gram of sample, G is volume of NaOH added measured in ml, H is concentration of NaOH added measured in molar concentration, T is volume of consumed HCl measured in ml, I is concentration of HCl used measured in molar concentration, P is sample in grams used. Molecular weight of anhydrous glucose unit is 162 and the net increase of anhydrous glucose unit per each substituted carboxylmethyl group is 58.

Degree of succinylation

The method of alkali Saponification as described by Genung and

Mallatt (1977) was used for the determination of succinyl content. 1 g of succinylated starch was weighed in a conical flask, 50 ml of 75% ethanol was added, and the mixture refluxed for 30 min at a constant temperature of 50°C. The mixture was allowed to cool at room temperature when 40 ml of 0.5 M NaOH was added. The flask was then covered with aluminum foil, allowed to stand at room temperature for 72 h while shaking occasional. Saponification occurred with the addition of NaOH, and the excess alkali was determined by titrating with 0.5 M HCl using phenolphthalein indicator. Native starch was treated in the same manner to obtain a value for the blank. The percentage of succinyl group and the degree of substitution of the samples were calculated as follows;

$$\text{Percentage (\%) succinyl} = \frac{(\text{Blank titre} - \text{sample titre})ml \times 0.1 \times \text{Molarity of acid}}{Weight\ of\ the\ sample}$$

(5)

$$\text{Degree of substitution (D.S)} = \frac{162 \times \% \ succinyl\ content}{1000 - (99 \times succinyl\ content)}$$

Where, Blank titre is the value for native starch in ml, Sample titre is the value for succinylated starch in ml, Molecular weight of anhydrous glucose unit is 162.

Physico chemical properties of native and modified starches

The isolated (native), acetylated, carboxymethylated and succinylated starches were analyzed for pH and proximate contents respectively.

pH

One (1 g) gramme of native starch was weighed into a test tube. 10 ml of distilled water was added to the starch sample and then stirred vigorously for about 5 min; the mixture was allowed to settle for 10 min before the supernatant was carefully decanted. The pH was then evaluated using calibrated pH meter. The procedure was also repeated for acetylated, carboxymethylated and succinylated starch.

Proximate analysis

Moisture, ash, crude protein, crude fat and carbohydrate content were determined according to the standard procedure of AOAC (2002).

Functional properties

Oil and water absorption, bulk density, swelling power and solubility, pasting properties of both native and modified starches were determined using standard methods.

Oil and water absorption capacity

The method described by Lawal et al. (2005) was used for the determination of oil and water absorption capacity (WAC) of the starch. 10 ml of distilled water or oil (Extra virgin Goya oil of 0.9 g/cm^3) was added to 1.0 g of native starch. The mixture was then thoroughly mixed with a mixer for 30 min each; the reacting mixtures were then allowed to stand for 50 min. The volume of the supernatant was decanted and thereafter recorded. The gain in weight was expressed as percentage of oil and water absorption

capacity. The procedure was repeated for acetylated, carboxymethylated and succinylated starch.

$$\text{WAC (\%)} = \frac{\text{Weight of wet sediment}}{\text{weight of dry sample} - \text{weight of dry supernatant}}$$

(6)

Bulk density

The method of Wang and Kinsella (1976) was used to determine the bulk density. 50 g of native starch was weighed into a 250 ml measuring cylinder; the volume occupied by the sample before and after tapping was recorded. The procedure was repeated for acetylated, carboxymethylated and succinylated starch. The bulk density is the ratio of the weight to volume occupied.

$$\text{Bulk density} = \frac{\text{Weight of sample}}{\text{Volume of sample after tapping}} \ (g/ml)$$

(7)

Swelling power and solubility

Swelling power and solubility was determined using the method described by Awokoya et al. (2011). 1.0 g of native starch was accurately weighed and then transferred into a clean dried test tube and weighed (W_1). The native starch was then dispersed in 10 ml of distilled water. The slurry obtained was heated at a temperature range of 50 - 90ºC for 30 min in a calibrated thermostated water bath. The mixture was allowed to cool and then centrifuged at 450-500 rpm for 15-20 min. Approximately 5 ml of the supernatant decanted represents the amount of starch solubilized in water. Swelling power was calculated as g/g of starch on dry weight basis. The residue obtained after centrifugation with the water is retained and was transferred to a clean dried test-tube earlier used and weighed (W_2). The procedure was repeated for modified starches. The swelling and solubility are calculated as follows:

$$\text{Swelling of starch} = \frac{W_2 - W_1}{\text{Weight of starch}}$$

(8)

$$\text{Solubility of starch} = \frac{\text{Weight of dry aliquot}}{\text{Weight of starch}} \times 100$$

(9)

Pasting properties

Starch pasting properties were determined using Rapid Viscosity Analyser (New port Scientific RVA super 4, Central Laboratory, Ibadan, Oyo state). 3.5 g of both native and modified ASAK starch samples was weighed and 25 ml of distilled water was dispensed into a canister. It was place under idle temperature of 50°C for 1 min, heated from 50 to 95°C in 3 min and 45 s, then held at 95°C for 2 min and 30 s. The sample was subsequently cooled to 50°C over a period of 3 min and 45 s, followed by a period of 2 min where the temperature was controlled at 50°C. Initial viscosity, peak viscosity (Pv), time to peak viscosity (Pt), trough viscosity (Tv), breakdown viscosity (Bv), final viscosity (Fv) and setback viscosity (Sv) were recorded by rapid viscosity analyser.

FT-IR Spectroscopy characterization of native and modified starches

The FT-IR Spectra of native, acetylated, carboxymethylated and succinylated starch were taken to determine the changes in the

Table 1. Degree of modifications of starches of Native African star apple.

S/N	Starch (g)	Acetylated		Carboxymethylated	Succinylated starch	
		% Acetyl	DS	DS	% succinyl	DS
1	5	4.042±0.23[a]	0.158±0.012[a]	0.0360±0.024[a]	4.000±1.40[a]	1.070±0.021[a]
2	5	3.913±0.17[a]	0.153±0.042[a]	0.0290±0.010[b]	5.500±2.60[ab]	1.960±0.082[a]
3	5	3.784±0.21[b]	0.148±0.13[b]	0.0170±0.012[c]	7.000±2.10[c]	3.690±1.24[b]

Values obtained are mean ± standard deviation. Means in the columns with different superscripts are significantly different between samples at p ≤ 0.05 from Duncan's multiple range tests.

functional groups. 2 mg of the samples were pulverized, mixed uniformly with 200 mg pure KBr powder; pellets were made by compression and then analysed using Perkin Elmer, England (Spectrum BX) Fourier Transform Infrared Spectrophotometer in the transmission wavelength range of 4000-400 cm^{-1}. Samples used were oven dried (50°C) for 1 h to remove moisture gained during storage.

Statistical analysis

All analysis was carried out in triplicates and the average values were used with the exception of starch modifications which were carried out in duplicates. The data were statistically analyzed using SPSS version 16 Software (statistical package for social sciences). Duncan's multiple range tests at 5% significance level were used to determine the differences between mean of samples.

RESULTS AND DISCUSSION

Degree of acetylation, carboxymethylation and succinylation

Percentage acetyl and degree of substitution (DS) (acetylation) decreased significantly (p≤0.005) with increased amount of acetic anhydride. The value of percentage acetyl ranged from 3.784-4.042 while DS varied between 0.148-0.158 of the acetylated starch of Native African star apple (Table 1). Acetylated starches performed different functions depending upon the DS. The acetylated starch prepared was within the range of 0.01-0.2 and therefore may be useful as adhesion, stabilizing and binding agent and also in the food industry (Luo and Shi, 2012). Francisco et al. (2012) reported percentage acetyl content value of 6 and 0.24% for degree of substitution for barley starch; while similar observation was also reported by Liu et al. (1997) for acetylated maize starches to have acetyl group content ranging between 2.71- 4.22%; DS also ranged from 0.105- 0.165 using 10% w/v acetic anhydride. Huang et al. (2007) reported DS from 0.064-0.071 for pulse starches. The differences in percentage acetyl value reported in different literatures may be due to difference in reaction conditions and the source of starch used. The results of DS of carboxymethylated starch show that DS decreased as the amount of MCA increased from 0.0170 to 0.0360 and 5 to 15 MCA, respectively. Similar

observation was also reported by Awolu and Olofinlae (2016). The low value observed for carboxymethylation in this research work will make it more suitable for industrial and food application. There was a linear increase in the percentage succinyl content and the DS with increased concentration of succinic anhydride from 5-15% w/w. This observation may be due to increase in reaction contact between the starch and the succinylating agent, which facilitated the formation of starch derivatives with higher DS (Awokoya et al., 2011).

Effect of chemical modifications on physico-chemical properties of starches

Proximate analysis such as moisture content, total ash, fat and crude protein were used to evaluate the quality and purity of the native starch as well as the effects of the chemical modifications on the proximate compositions. The proximate composition of the native starch was compared with the acetylated, carboxymethylated, succinylated starches and the results are shown in Table 2. Native African star apple seed starch has 19.32±2.40% moisture content which decreased to 8.44±1.61% upon acetylation (ACS), 12.39±2.40% upon carboxymethylation (MCS) and 12.39±2.40% upon succinylation (SUS). Generally, the moisture content of modified starches was low because of the removal of water binding proteins during the alkali extraction stage. Furthermore, the low moisture content of modified starches suggests a prolong shelf stability during storage as a result of mould growth prevention and lowering moisture induced biochemical reactions (Onimawo and Aklubor, 2012). Similar observations have also been reported by Gope et al. (2016) while Lawal (2004b) reported increase in moisture content after succinylation; Awolu and Olofinlae (2016) reported increase in moisture content after acetylation of water yam starch. These observations may be due to the drying methods and the extent of drying and humidity of the surrounding atmosphere. The percentage yield of native starch is 45.22±0.93% on dry basis starch, while after modification, the percentage yield increased from 45.22±0.93 to 54.37±2.15, 59.14±1.47 and 52.86±0.51% for acetylated, carboxymethylated and succinylated

Table 2. Proximate analysis of Native African star apple seed and modified starches (n=3).

S/N	Samples	MC (%)	Ash (%)	Fat (%)	CP (%)	pH	Yield (%)
1	NS	19.32±2.40[a]	0.0045±0.00020[a]	0.085±0.030[c]	0.25±0.12[a]	5.80±0.10[c]	45.22±0.93[c]
2	ACS	8.44±1.61[b]	0.0067±0.0015[a]	0.14±0.010a	0.17±0.012[a]	6.30±0.18[bc]	54.37±2.15[b]
3	MCS	12.39±2.40[b]	0.0057±0.0081[a]	0.15±0.010a	0.19±0.060[a]	6.98±0.50[a]	59.14±1.47[a]
4	SUS	11.19±3.56[b]	0.0032±0.0019[a]	0.12±0.012[b]	0.21±0.065[a]	6.37±0.15[b]	52.86±0.51[ab]

Values obtained are mean ± standard deviation. Means in the columns with different superscripts are significantly different between samples at p ≤ 0.05 from Duncan's multiple range tests.
MC=moisture content, CP=crude protein.
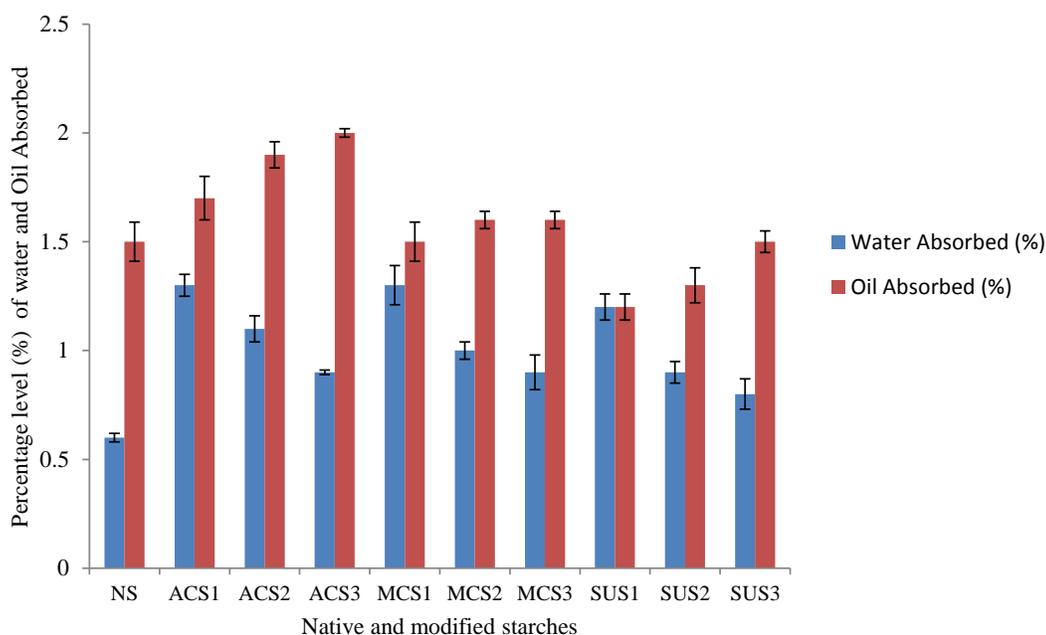
Figure 2. Percentage level of water and oil absorbed of native and modified starches.

starch, respectively. This observation may be due to the substitution of the hydroxyl groups on the starch molecules and also the effect of swelling of starch polymer as a result of different reagents used. Previous works on chemically modified water yam starch (Awolu and Olofinlae, 2016), starch of mucuna bean (Adebowale and Lawal, 2003) and glutinous rice starch (Gope et al., 2016) also showed similar pattern. Both acetylation, carboxymethylation and succinylation processes reduced the ash and crude fat content of native starch from 0.0045 and 0.085, respectively to 0.0067 (ACS), 0.0057 (MCS), 0.0032 (SUS); while there was a decrease in the value of crude protein (CP) contents of native starch when compared to modified starch. Although both the native and modified starches have low protein contents, there was a reduction in the value of native to modified starches; this is attributed to extensive purification through alkaline solubilisation and degradative effect in amylose fraction of starch granules after modification.

Similar observations were reported by Adebowale and Lawal (2003).

Effect of chemical modification on functional properties of starches

The functional properties of both the native and modified starches play an important role in the manufacturing and food industries. The functional properties of native African star apple for both native and modified starches are presented as follows.

Oil and water absorption capacities

The water and oil absorption capacities of the starches under investigation are presented in Figure 2. All the starches absorbed more oil than water. Chemical
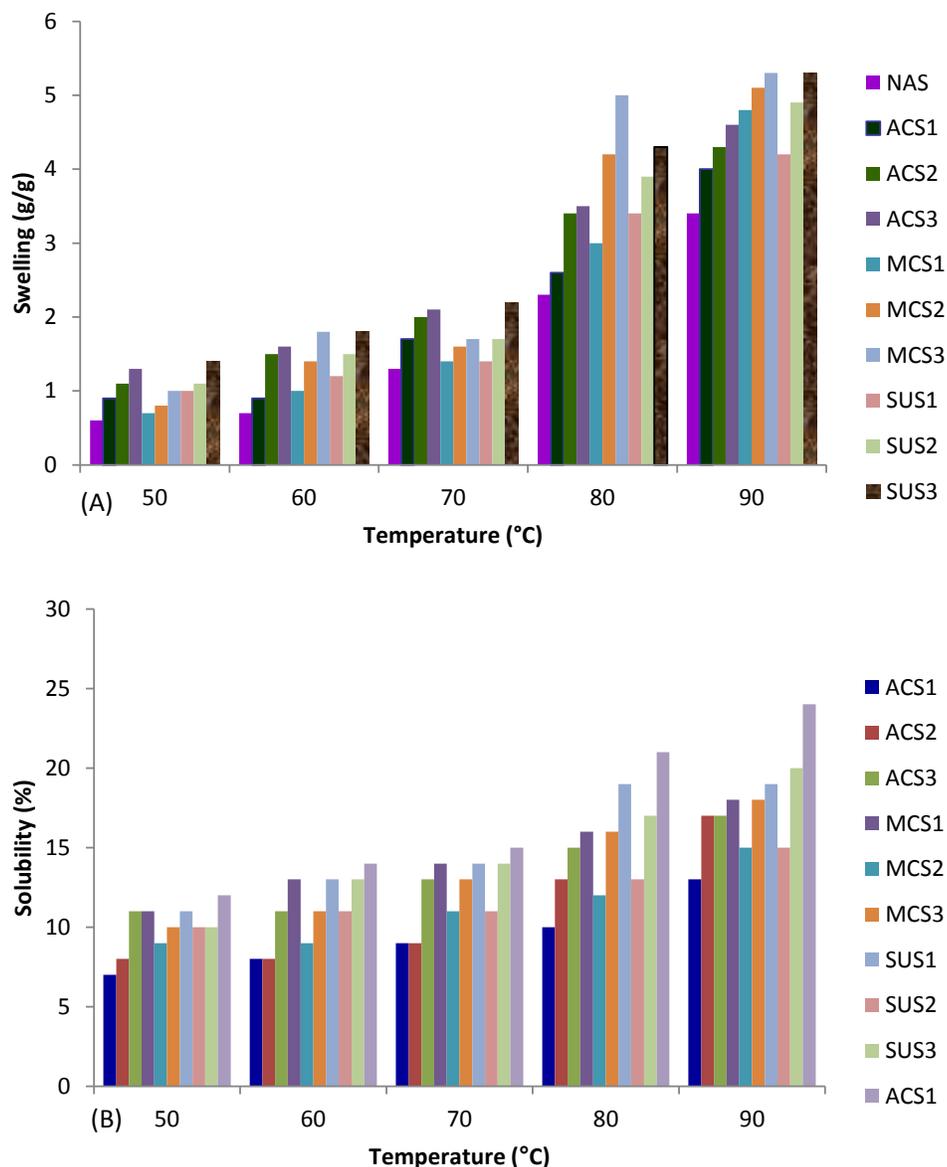
Figure 3. (a): Effect of temperature on swelling power of native and modified starches, **(b):** Effect of temperature on solubility of native and modified starches.NAS is Native African Star apple Starch. ACS (1-3) is acetylated starch at 5 (ACS1), 10 (ACS2) and 15(ACS3) g. MCS (1-3) is Carboxymethylated starch at 5 (MCS1), 10 (MCS1) and 15 (MCS1) g.SUS (1-3) is succinylated starch at 5 (SUS1), 10 (SUS2) and 15 (SUS) g.

modification increased the water absorption capacity of the native starch, with acetylation producing a marked effect (1.49%) compared with 0.52% recorded for the native starch followed by carboxymethylation starches. Acetylation increased the oil absorption capacity of the native starch (2.00%), while a reduction in the oil absorption capacity was observed for the carboxymethylated (1.52%) and succinylated starches (1.49%). This result differs from the results of Deshpande et al. (1982), who reported that both acetylation and oxidation caused an increase in the oil absorption

capacity of black gram starch; but similar with the work reported on the starch of mucuna bean (Adebowale and Lawal, 2003).

Swelling power and solubility

The temperature dependent swelling power and solubility of native and modified starches is represented in Figure 3(a) and (b). The swelling power and solubility increased with increased temperature. It was also observed that at
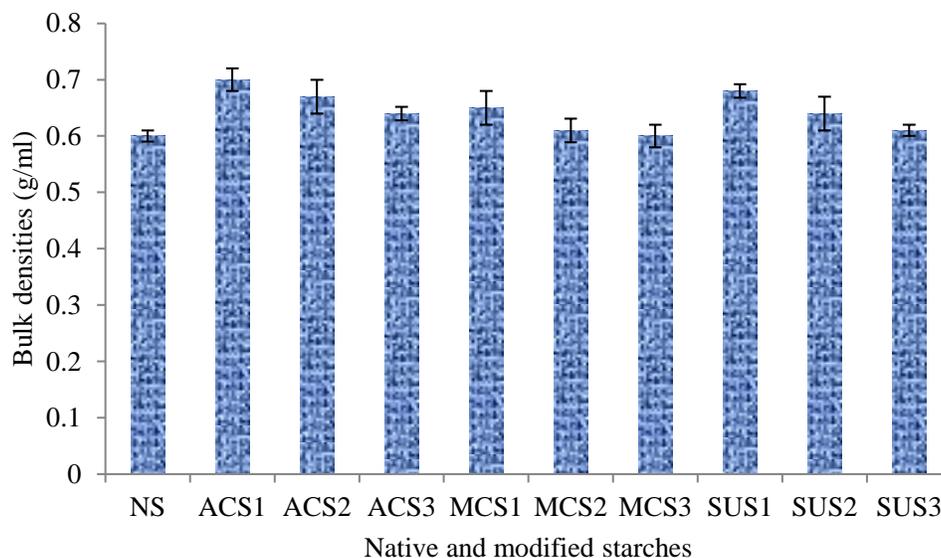
Figure 4. Bulk density of native and modified starches.

all temperatures, all modified starches had higher swelling power than the native starch (Balbir et al., 2010). This result agrees with the observations of Gebre-Mariam and Schmidt (1996), who indicate that swelling power of *enset* starch increased as temperature increased. It also corroborates with the observations on the increase in swelling power with temperature for mucuna bean starches (Adebowale and Lawal, 2002b). For succinylation, the swelling power of the starches increased as the DS increased due to increase in hydrophilicity. Comparing among these modified starch samples, at all temperatures succinylated starch samples were observed to have a better swelling power and solubility. In all cases increase in swelling power and solubility was observed at all levels of starch modifications (Adebowale, 2002 and Lawal, 2004b). Following the introduction of acetyl, carboxymethyl and succinyl bulk groups on starch molecules, structural re-organization occurs as a result of steric hindrances. These result in repulsion, facilitating an increase in water percolation within the granules after modifications. Similar observation has been reported for rice starch by Gonzalez and Perez (2002).

Bulk density

Bulk density is a measurement of heaviness of solid samples, which is important in determining the type of packaging material required, material handling and application in wet processing in the food industry (Kinsella, 1987). Samples with high bulk densities (> 0.7 g/ml) are considered heavy. Hence, native African Star apple starch in this study is light and could be used in the food processing industry. The bulk densities of native and modified African star apple kernel starch are shown in Figure 4. The bulk densities for both native and modified starches were in the range of 0.60 to 0.70. Bulk density of native starch was 0.60 g/ml; whereas in the acetylated, it was 0.64 - 0.70 g/ml, carboxymethylated was 0.60 to 0.65 g/ml and succinylated starch was 0.61 to 0.68 g/ml, respectively. However, there were no significant differences in the bulk density between native and acetylated starches. Similar result was also reported for Indian Horse Chestnut starch by Akhtar (2014).

Pasting properties of native and modified starches

The results on the pasting properties of both native and modified starches are presented in Table 3. Pasting temperature (T_p) of the native starch reduces following chemical modifications. Peak viscosity (P_v), Trough viscosity (T_v), Final viscosity (F_v) and set back (S_v) decrease after acetylation but increase following carboxymethylation and succinylation. Reduction in pasting temperature following succinylation has been reported by Lawal (2004a). It was also observed that pasting temperature decreases as the Degree of Substitution increases (Lawal, 2012). This reduction occurs as a result of structural weakening and disintegration during the modification processes. When a starch granule is heated in excess water, it leads to further granule swelling and this results in the formation of a viscous starch paste (Awokoya et al., 2011). However, increases were observed in the peak viscosity value of native ASAK starch after succinylation. This observation is similar to that observed by Liu et al. (1997) about normal maize starch.

The set back (Sv) values observed after the addition of

Table 3. Results of pasting properties on both native and modified starches.

Samples	Peak viscosity (RVA)	Trough viscosity (RVA)	Breakdown viscosity (RVA)	Final viscosity (RVA)	Set back viscosity (RVA)	Peak time (Min)	Pasting temperature (°C)
NAS	460.83	334.67	126.17	470.83	136.17	5.07	84.10
ACS1	376.08	319.42	56.67	433.58	114.17	5.80	81.70
ACS2	345.58	238.17	107.43	321.08	82.92	5.27	80.80
ACS3	352.75	253.75	99.00	347.50	93.75	5.27	80.80
MCS1	325.00	178.25	146.75	273.00	94.75	4.73	80.00
MCS2	54.00	13.67	40.33	24.83	11.17	4.27	-
MCS3	377.92	257.00	120.92	335.17	78.17	4.80	80.00
SUS1	402.00	234.25	167.75	281.75	47.50	4.73	81.60
SUS2	485.50	330.75	154.75	410.25	79.50	4.87	81.70
SUS3	958.25	424.25	534.00	810.75	386.50	3.73	72.60

15 g MCA for carboxymethylation (78.17 RVA) were lower than those obtained after the addition of 15 g Acetic anhydride and 15 g Succinic anhydride for both acetylation and succinylation (93.75 and 386.5 RVA).This indicates the tendency of the starch to associate and retrograde. The increased set back value observed in succinylation is associated with a cohesive paste, while the decrease in this value indicates that the paste was not cohesive (Adewole et al., 2012). High set back value is useful for domestic products. The trough viscosity is indicative of the additional breakdown of granules due to stirring, reflecting and stability of the hot paste. It provides a measure of the tendency of the paste to break down during cooking (Normita et al., 2002). Trough viscosity of native ASAK decreases after acetylation (319.42-253.73 RVA), while those of carboxymethylation (178.25-234.25 RVA) and succinylation (234.25-424.25 RVA) increases. This indicates that native, carboxymethylation and succinylation of ASAK starch have the ability to withstand breakdown during cooling than the acetylated starch. The hold period reduces following acetylation (376.08-246.63RVA) and increases in both carboxymethylation and succinylation of ASAK starch. The holding strength is the ability of the granules to remain undisrupted.

***Functional group analysis of native and modified starches by FTIR***

The FTIR analysis confirmed the preparation of carboxymethylated, succinylated and acetylated starch by the addition of MCA, succinic anhydride and acetic anhydride in the etherification, succinylation and acetylation reaction, respectively. The FT-IR spectrum of native and chemically modified African star apple starches is shown in Figure 5. As shown in the figure, the broad band for both native and modified starches ranged from 3200- 3400 cm^{-1}; these correspond to OH stretching and it is due to hydrogen bonding involving the OH

groups on the starch molecules. The band between 2927 cm^{-1} and 2930 cm^{-1} region is assigned to CH$_2$ symmetrical stretching vibrations (Mano et al., 2003). The bands at 1642 and 1420 cm^{-1} were attributed to the scissoring of the OH bonds of water molecules and CH bending while the remaining bands in the range of 880 and 750 cm^{-1} are due to skeletal stretching vibrations of starch molecules and thus confirm the carbohydrate nature of African star apple starch. Acetylated starches show new strong absorption bands at 1730-1742 cm$^{-1;}$ this indicates (C=O stretching of acetyl group) 1362-1369 cm^{-1} for C-H in acetyl group and 1160-1138 cm^{-1} shows absorption bands for C-O stretching of acetyl group. Thus, this is an evidence of acetylation. On the other hand, the absence of absorption bands between 1751-1849 cm^{-1} is an indication that the starch prepared from the native sample is free from unreacted acetic anhydride and bye-products such as carboxylic acid (Diop et al., 2011). The succinylated starch derivative shows two new bands characteristics in the region between 1718.83 - 1724 cm^{-1} and 1150-1152 cm^{-1}. 1718.83 -1724 cm^{-1} is due to the carbonyl group of the ester (evidence that succinylation reaction has occurred) while 1150-1152 cm^{-1} is attributed to the C=O stretching in the ester molecules. Other bands are 1472 cm^{-1} (C-C bonded to hydroxyl group), and 1642 cm^{-1} is primarily attributed to water molecules (Sun et al., 2000).

The carboxymethylated starch derivative shows new absorption bands at 1641- 1646 cm^{-1} for carbonyl group (C=O stretching), 1413- 1427 cm^{-1} for -CH2 scissoring, and -OH bending vibration at 1344-1348 cm^{-1}. Similar observations were reported by Bhattacharyya et al. (1995) and Zeljko et al. (2000) for carboxymethylated potato, corn and maize starch respectively.

Conclusion

Physico-chemical properties of native and chemically
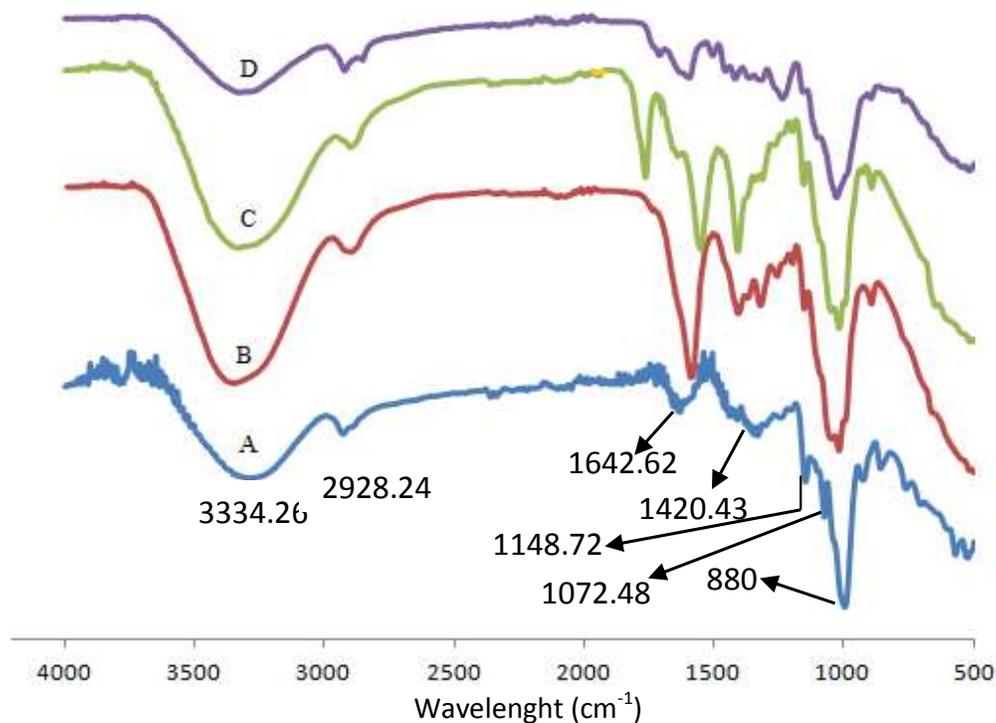
Figure 5. The FTIR spectra of native African star apple (*C. albidnum*) kernel starch (A) and a representative acetylated (B), carboxymethylated (C) and succinylated starch (D).

modified starches of *C. albidnum* were investigated. Increased moisture content shows a more suitability of the modified starched for industrial purposes. Swelling capacity and solubility were temperature dependent. Both solubility and swelling capacity increased with increasing temperature. Acetylation, carboxymethylation and succinylation process increased swelling power and solubility. The pH increased after modification weak acidic region (6.30–6.98). The results of pasting properties and FT-IR spectra revealed that considerable alterations enhanced the properties of *C. albidnum* starches with chemical modifications. The modification of the native starch was confirmed by FTIR spectroscopy. Above all, the starch obtained from the *C. albidnum* can compete with other starches from other sources due to its percentage yield.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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