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Assessment of physico-chemical and functional properties of native and modified "Kponan" yam (*Dioscorea cayenensis-rotundata* complex) cultivar starches

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Abstract

The starch of "Kponan" yam cultivar was isolated and was modified through oxidation, acetylation, acid modification and enzymatic modification. The various modified starches of "Kponan" yam cultivar and its native starch were characterized in terms of morphological characteristics, some proximate composition and functional properties. Results obtained showed that the starch granules were Polyhedral and Ovotriangular in shape. The granule size ranged from 7.55µm - 53.47µm. Chemical and enzymatic modifications didn't alter the granule morphology. Proximate composition analysis revealed that moisture, protein, fat and ash contents were reduced after modification and were ranged from 08.26 % dw to 10.11% dw, 0.13 % dw to 0.18 % dw, 0.07 % dw to 0.11 % dw and 0.51 % dw to 0.83 % dw respectively. As for functional properties, WAC, OAC, LGC, syneresis and PC were determined. Our results indicated that modification such as oxidation, acetylation and enzymatic modification increased meaningfully ($p<0.05$) the WAC and OAC of native starch while acid modification decreased them significantly ($p<0.05$). It appeared significant differences ($p<0.05$) between the OAC values of starches, whatever the oil type is. Otherwise, the LGC of the native starch was 9% (w/v) and increased after oxidation (11%) and acetylation (10%), whereas it decreased in acid modified (8%) and enzymatic modified (6%) starches. Syneresis tendency was reduced after oxidation, acetylation and enzymatic modification but increased following acid modification. Studies conducted on paste clarity revealed that percentage transmittance (650 nm) increased after chemical modifications (oxidation and acetylation) and enzymatic modification whereas acid modification reduced it.

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Introduction

Yams are root and tube crops of great antiquity and are widely distributed throughout the tropics with only a few members in the temperate regions of the world (FAO, 1996). It is an important food for about 300 millions people through the world (Ettien *et al.*, 2009). Total world production of yam is estimated to 40 millions tons per year (FAO, 2006). More than 90% of this production occurs in West Africa (Attaie *et al.*, 1988). The most important species of yam in Côte d'Ivoire are *Dioscorea cayenensis-rotundata* complex and *Dioscorea alata* (Ondo *et al.*, 2009). Yam is an excellent source of starch, which provides calorific energy (Coursey, 1973). Indeed, Starch is the major caloric source in a variety of diets of people worldwide. It is also an important ingredient in various food systems as a thickener, gelling agent, and binder. Being the main caloric sources for people in many countries, starch is in high demand.

Starch is an excellent ingredient in food and non-food industries (such as paper, plastic, adhesive, textile and pharmaceutical industries) (Wickramasinghe *et al.*, 2009). Furthermore, the use of native starches has showed some drawbacks because the process conditions (e.g., temperature, pH, pressure, shear stress, etc.) limit their use in industrial applications. These shortcomings may be overcome by modification using chemical, physical and enzymatic methods (Fleche, 1990). The most common methods to modified starch properties are the chemical procedures, treating native starch with specific chemicals reagent. Otherwise, the food such as Corn, potato, and cassava are the most common sources of starch for such industries (Tester and Karkalas, 2002). The starch properties of these foods were investigated by several studies (Emiola and Delarosa, 1981; Farhat *et al.*, 1999; Amani *et al.*, 2004; 2008). Besides, starches from various plant species, especially cereals, have received very extensive attention in food research. However, little attention has been given to starches of yam tuber especially "Kponan" cultivar belonging *Dioscorea cayenensis-rotundata* complex in food research, but desirable functional properties may exist in those starches. Indeed, Publication on yam starches accounts is less than 1% of the total information available for food science and technology abstracts, and the food intelligence databases (Amani *et al.*, 2005). Studies carried out on "Kponan" yam cultivar were limited to physicochemical and functional properties of its flour. Lack of information on the properties of starches from "Kponan" yam cultivar has contributed to limited utilization of these starches in industry. Knowledge on properties of the starches from these crops therefore would unravel the opportunities offered by these root crops and help their utilization (Mweta *et al.*, 2008).

Therefore, the aim of present study was to extract starch from "Kponan" yam cultivar , modification of extracted starch, and comparison of native and modified starches by evaluating their different functional and some physico-chemical properties.

Materials and methods

Raw materials

The "Kponan" cultivar of yam (*Dioscorea cayenensis rotundata* complex) was used in the present study. It was harvested at maturity from fields in the north of Côte d'Ivoire.

Methods

Starch isolation

Yam starches were extracted according to AOAC (1995). One kilogram (1 kg) from yam tuber was weighed, washed and peeled. After peeling, they were cut up into small slices (4x4 cm) with stainless steel knife and steeped in distilled water containing 0.03% (w/v) sodium metabisulphite. The slices were ground in a grinder (Moulinex, Lyon-France) and the paste recovered in 4% (w/v) sodium chloride solution to separate proteins from the starch during 24 h at 25 ± 1 °C. The slurry was sieved successively through 750 µm, 150 µm and 100 µm sieves. Then, the starches were alternatively decanted and washed at least four times with distilled water. The starch suspensions were oven-dried at 45 °C for 48 h [MEMMERT 854, Schwabach German)]. The dry products were ground, quantified and then stored for analyses.

Modified starch preparation

Acetylated starch

The method of Sathe and Salunkhe (1981) was used. Hundred grams of native 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. The obtained acetylated was filtered, washed four times with distilled water and air-dried at 30 ± 2 °C for 48 h.

Oxidized starch

The method of Forssel *et al.* (1995) was employed with modifications. Twenty per cent slurry of native starch was prepared by dispersing 100 g of starch in 200 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 $H_2SO_4$and the oxidized starch was filtered, washed four times with distilled water and air-dried at 30 ± 2 °C for 48 h.

Acid modified starch

The method described by Jayakody *et al.* (2007**)** was used. The native starch sample (200 g) was slurried in 600 ml of 2.2 M HCl and the mixture was placed in water bath set at 35°C and stirred magnetically for 8 h. The acid modified starch was filtered. The residue obtained was washed four times with distilled water and air dried at 30 ± 2 °C for 48 h.

Enzymatic modified starch by α-Amylase

Native starch sample (200 g) and enzyme solution (600 µL) were mixed in 0.02 mM sodium phosphate buffer (600 mL, pH 6.9). The mixture was stirred for 2 min. The dispersion was incubated at 37 °C for 96 hr. Ethanol (2,400 mL) was added to inactivate the enzyme and the hydrolyzed starch was collected by centrifuging the solution at 2,280 × g for 10 min. The starch residue was washed with 50% ethanol (300 mL) for three times, and then dried at 35°C in a convection oven overnight.

Granule morphology

Granule morphology of native and modified starches was studied by scanning electron microscopy (SEM). Each starch sample was sprinkled onto a double-backed adhesive carbon tab stuck to a circular aluminum stub. The starch granules were then evenly distributed on the surface of the tape and coated with gold–palladium. Scanning electron micrographs (SEM) were obtained with a scanning electron microscope (Supra 40 VP-Zeiss, Germany, with voltage ranging from 0,1 kV to 30 kV) at 1 kV accelerating voltage using the secondary electron technique.

Frequencies distribution of the average diameter of starch granules

The distributions of the average diameter of starch granules were given on a total of 500 granules (Rasper, 1971). They were carried out according to the rule of Sturge (Scherrer, 1984) and translated by the histograms.

Proximate composition

Approximate analysis contents were carried out according AOAC (1995). Moisture content was determined by air-oven drying at 105 °C overnight. The protein content was determined by Kjeldahl method (% protein= N x 6.25). Fat content was determined by Soxhlet apparatus; using hexane as an organic solvent at 80 °C for 6 h. The ash contents were determined by incinerating in a furnace at 550°C.

Functional properties

Syneresis

Syneresis of native and modified starches was determined according to the method of Singhal and Kulkarni (1990). Starch samples (5 g) were mixed with 100 ml distilled water, using a glass rod. The obtained mixtures were homogenized by manual

agitation and then, they heated at 95°C for 30 min in a water bath with constant stirring. 10 ml of paste were immediately transferred to weighed centrifuge tubes. The weight of the paste was then determined. This was subjected to alternate freezing (4°C) and thawing (30°) cycles (18 h, 3 h, respectively) for 30 days, centrifuged at 3668 rpm for 10 min after each cycle and the syneresis was determined as weight of exudates to the weight of paste.

Water absorption capacity (WAC)

The WAC of "Kponan" yam cultivar native and modified starches were carried out according to Phillips *et al.* (1988) and Anderson *et al.* (1969) methods, respectively. Each starch from yam (2.5 g) was weighed into a centrifuge tube and 30 mL distilled water were added. The content of the centrifuge tube was shaken for 30 min in a KS 10 agitator. The mixture was kept in a water-bath (37°C) for 30 min and centrifuged at 5000 rpm for 15 min. The resulting sediment (M2) was weighed and then dried at 105°C to constant weight (M1). The WAC was then calculated as follows:

$$WAC\ (\%) = \frac{M_2 - M_1}{M_1} X\ 100$$

Oil absorption capacity (OAC)

The OAC of "Kponan" yam cultivar native and modified starches was performed according to the method of Sosulski (1962). Each starch from yam (1) g was mixed with a 10 ml of oil. The mixture was shaken for 30 min in a KS10 agitator and centrifuged Please re-submit your paper along with the attached copyright agreement form.at 4500 rpm for 10 min. The resulting sediment (*M1*) was weighed and the OAC was then assessed as follows:

$$OAC\ (\%) = \frac{M_1 - M_0}{M_0} X\ 100$$

Paste clarity (PC)

The PC of starch was determined according to the method of Craig *et al.* (1989). 1 % aqueous suspension was made by suspending 0.2 g of starch in 20 ml of distilled water in a stoppered centrifuge tube and vortex mixed. The suspension was heated in a boiling water (100°C) bath for 30 min. After cooling, clarity of the starch was determined by measuring percent transmittance at 650 nm against water blank on a spectrophotometer.

Least gelation concentration (LGC)

Appropriate sample suspension of 2, 4, 6, 8, 10, 12, 14 16 and 20 % w/v were prepared in 5 ml distilled water. The test tubes containing these suspensions were heated in a boiling water bath for 1 hour. The tubes are quickly cooled at 4°C. The LGC was determined as concentration when the sample from the inverted test tube did not fall down the slip (Coffman and Garcia 1977).

Statistical analysis

All analyses were carried out in triplicates. Results were expressed by means of ± SD. Statistical significance was established using one-way analysis of Variance (ANOVA) model to estimate the effect of modification main effect on physico-chemical and functional properties of starch from "Kponan" yam cultivar at 5 % level. Means were separated according to Duncan's multiple range analysis ($P \leq 0.05$), with the help of the software STATISTICA 7 (Statsoft Inc, Tulsa-USA Headquarters) and XLSTAT-Pro 7.5.2 (Addinsoft Sarl, Paris-France).

Results

Morphological characteristics

The granular morphological characteristics of native and modified starches are shown in Figure 1 and the physical characteristics in Table 1. In this study, no noticeable differences were observed between the shapes of the native and modified starch granules. They are polyhedral and ovotriangular granule shapes. However, it appeared slight variations in the size of granule. This variation didn't appear significant ($p \leq 0.05$) between Average diameters of native and modified starches, except average diameter of acid modified starch granules (Table1). Indeed, the average diameters the starch granules of native, oxidized, acetylated, acid modified and enzymatic modified starches were 32.05 ± 7.10 µm,

31.09 ± 6.04µm, 30.65 ± 6.23µm, 30.40 ± 5.93µm and 20.89 ± 5.79µm respectively.

Granule size distributions

The distributions of the starch granule size of native and modified starches are shown in Fig. 2. The range of size distribution, the mode of starch granule size distribution and the average diameter are summarized in Table 1.

Table 1. Physical characteristics of native and modified starch granules of "Kponan" yam (*Dioscorea cayenensis-rorundata complex*) cultivar tubers.

Starch type	Granules Shape	Distribution	range granules size (µm)	Mode (µm)	Average diameter (µm)
Native starch	Polyhedral Ovotriangular	unimodal	7.55 - 53.47	32.81	32.05 ± 7.10^{b}
Oxidized starch	idem	unimodal	15.75 - 51.30	28.25	31.09 ± 6.04^{b}
Acetylated starch	idem	unimodal	9.15 - 49.74	27.92	30.65 ± 6.23^{b}
Enzymatic modified starch	idem	unimodal	9.88 - 45.11	29.26	30.40 ± 5.93^{b}
Acid modified starch	idem	unimodal	7.33 - 40.47	18.93	20.89 ± 5.79^{a}

Means not sharing a similar letter in average diameter column are significantly different p ≤ 0.05 as assessed by the test of Duncan.

The distribution of native starch granules from studied starches was asymmetric and variable (Fig. 2). In fact, the native starch had the greatest range of distribution (7.55µm - 53.47µm), whereas the smallest interval of distribution (7.33µm - 40.47µm) was obtained with acid modified starch (Fig. 2).

Proximate Composition

The proximate composition of the native and modified "Kponan" yam cultivar starches are shown in Table 2.

Moisture content

The moisture content of native and modified "Kponan" yam cultivar starches is shown in Table 2.

Table 2. Proximate composition of native and modified "Kponan" yam (*D. cayenensis-rotundata complex*) cultivar starches (% on dry weight basis).

Starch types	Moisture	Ash	Protein	Fat
Native starch	10.11 ± 0.2^{b}	0.83 ± 0.16^{b}	0.18 ± 0.04^{b}	0.11 ± 0.08^{b}
Oxidized starch	8.87 ± 0.3^{a}	0.51 ± 0.04^{a}	0.14 ± 0.02^{a}	0.08 ± 0.02^{a}
Acetylated starch	8.43 ± 0.11^{a}	0.60 ± 0.09^{a}	0.15 ± 0.02^{a}	0.08 ± 0.02^{a}
AH (α-amylase)	8.26 ± 0.14^{a}	0.54 ± 0.1^{a}	0.15 ± 0.03^{a}	0.08 ± 0.01^{a}
AH (HCl)	8.87 ± 0.14^{a}	0.53 ± 0.23^{a}	0.13 ± 0.01^{a}	0.07 ± 0.03^{a}

Each value is an average of three replicate.

Values are mean ± standard deviation.

Means not sharing a similar letter in a column are significantly different p ≤ 0.05 as assessed by the test of Duncan.

The moisture content of the starches ranged from 08.26 ± 0.14 % dw to 10.11% ±0.20% dw, with the enzymatic modified starch having the least value and the native starch the highest. The moisture content of modified starches was lower than those of native starch. There were significant variations at 0.05 level between the moisture contents of native and modified starches. However, it didn't appear significant at 0.05 level between the modified starches. Slight differences were observed between them.

Protein content

The protein content is presented in table 2. The

values of protein content ranged from 0.13 ± 0.01 % dw to 0.18 ± 0.04 % dw for the acid modified and native starches respectively. The native starch had the highest protein content whereas the acid modified starch had the lowest protein content. The protein content of native starch was higher than those of modified starches. It appeared meaningful (p≤0.05) difference between native and modified starches. However, the protein contents of modified starches didn't differ significantly at 0.05 level. Slight differences were recorded between them.

Table 3. Some functional properties of native and modified "Kponan" yam (*D. cayenensis-rotundata complex*) cultivar starches.

	Starch types				
Property	Native starch	Oxidized starch	Acetylated starch	AH (α-amylase)	AH (HCl)
WAC (%)	40.18 ± 2.74^{b}	52.55 ± 1.38^{d}	71.50 ± 1.53^{e}	48.39 ± 1.60^{c}	25.14 ± 0.70^{a}
LGC (%)	9.00 ± 0.20^{c}	11.00 ± 0.50^{e}	10.00 ± 0.20^{d}	6.00 ± 0.40^{a}	8.00 ± 0.17^{b}

Means not sharing a similar letter in a line are significantly different p ≤ 0.05 as assessed by the test of Duncan.

Fat content

The fat content is indicated in table 2. The values of fat content ranged from 0.07 ± 0.03 % dw to 0.11 ± 0.08% dw for the acid modified and native starches respectively. Fat content of native starch was higher than those of modified starches. It appeared slight differences between the crude fat content of modified "Kponan" yam variety starches. However, the crude fat contents of modified "Kponan" yam variety starches didn't vary meaningfully (p≤0.05).

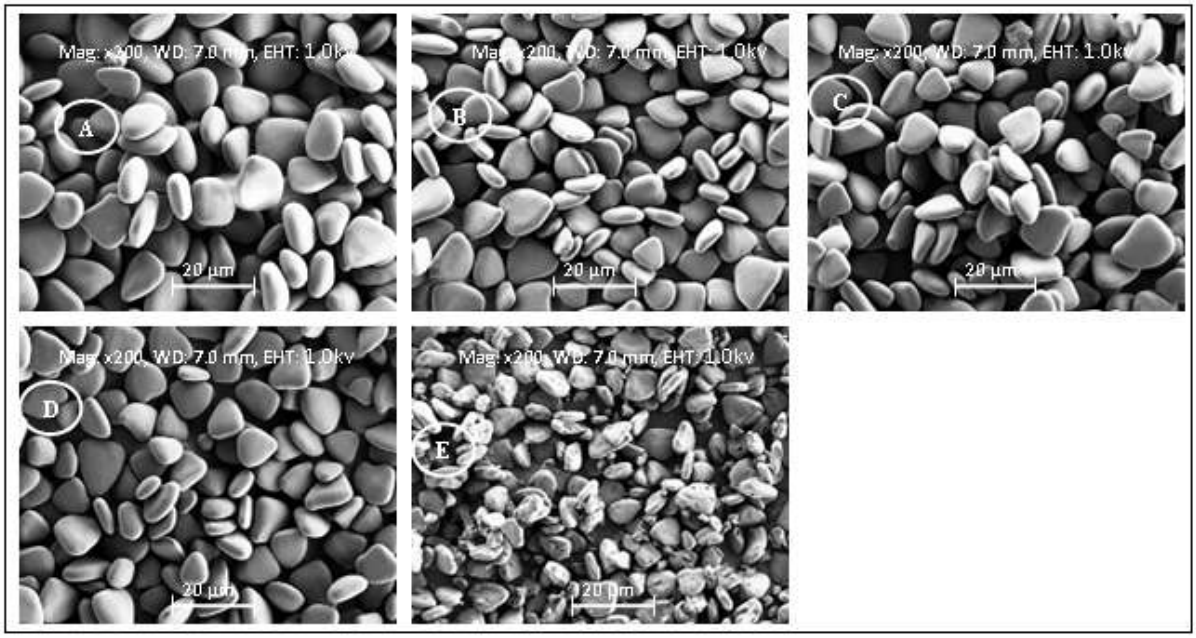

Fig. 1. Scanning electron micrographs of: native (A), oxidized (B), acetylated (C), Acid modified (D) and enzymatic modified (E) "Kponan" yam cultivar starches.

Ash content

The ash content is shown in table 2. The values of total ash content ranged from 0.51 ± 0.04 % dw to 0.83 ± 0.16 % dw for the oxidized and native starches respectively. Total ash content of native starch was higher than those of modified starches. It appeared significant (p≤0.05) differences between the total ash content of native and modified "Kponan" yam cultivar starches. However, the total ash contents of modified

"Kponan" yam variety starches didn't differ meaningfully (p≤0.05).

Functional properties

Water absorption capacity (WAC)

The WAC of native and modified "Kponan" yam cultivar starches ranged from 25.14 ± 0.70% to 71.50 ± 1.53% (Table 3). The highest value of WAC was found for the acetylated starch whereas the acid modified starch had the lowest value of WAC. Otherwise, analysis of variance test indicated that the chemical and enzymatic modifications main effect appeared significant (p≤0.05). Indeed, oxidation, acetylation and enzymatic modification increased meaningfully (p≤0.05) the WAC of native starch while acid modification decreased it significantly (p≤0.05). There were also meaningful (p≤0.05) differences between WAC of oxidized, acetylated, enzymatic modified, acid modified and native starches.

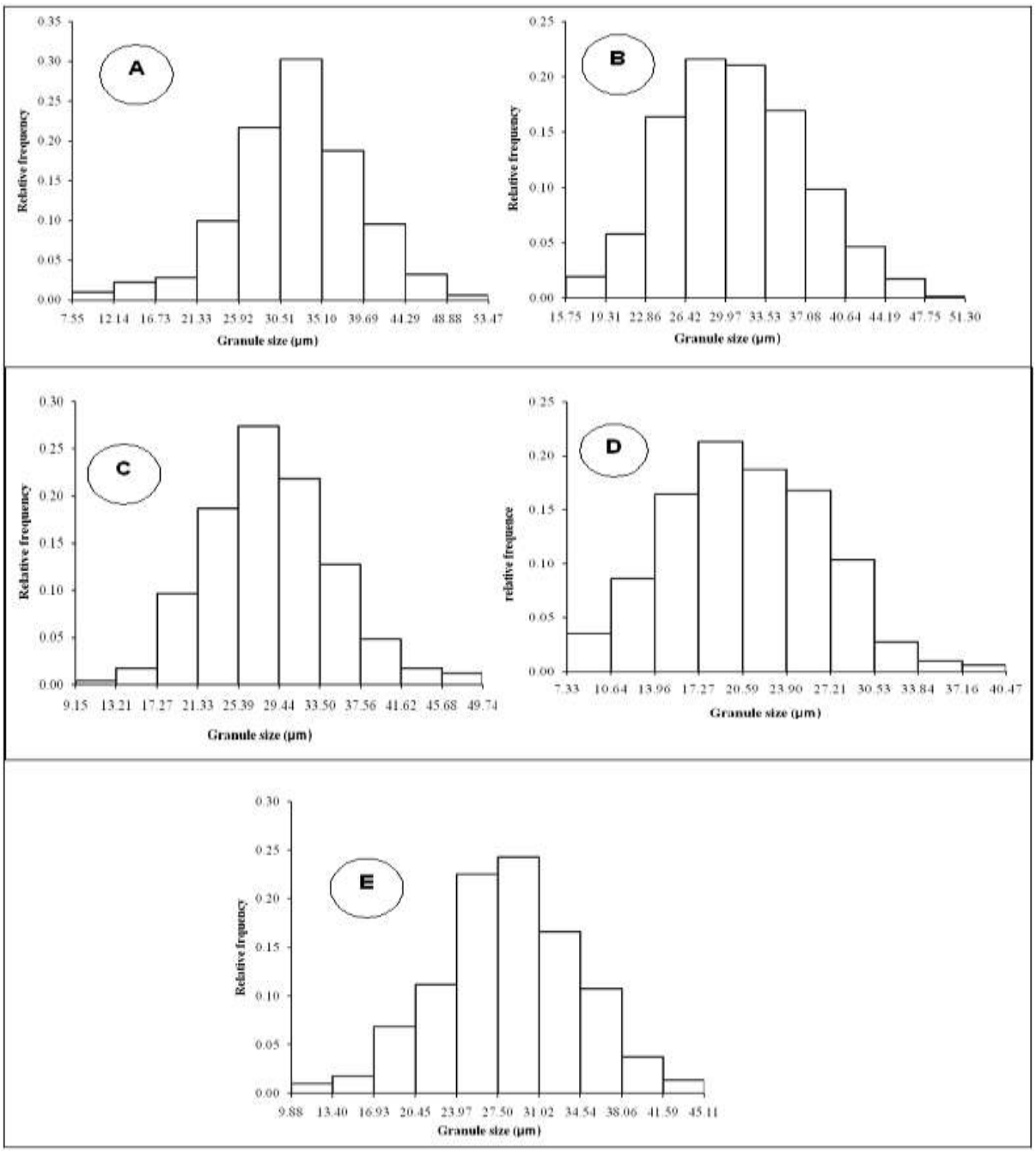

Fig. 2. Frequency distribution of native (A), oxidized (B), acetylated (C), enzymatic modified (E) and acid modified (D) starch granule average diameters of "Kponan" yam cultivar tubers.

Least gelation concentration (LGC)

The gelation properties of the native and modified yam starches are presented in table 3. In line with the least gelation concentration (LGC) which is considered an index of gelation capacity was ranged from 6% to 11%. The obtained result indicated that lowest value of LGC was observed in enzymatic modified starch, while the oxidized starch had the highest value of LGC. Indeed, the LGC of the native starch was 9% (w/v) and it increased significantly ($p \leq 0.05$) after oxidation (11%) and acetylation (10%). On the other hand, the LGC decreased meaningfully ($p \leq 0.05$) after acid modified (8%) and enzymatic modified (6%) starches.

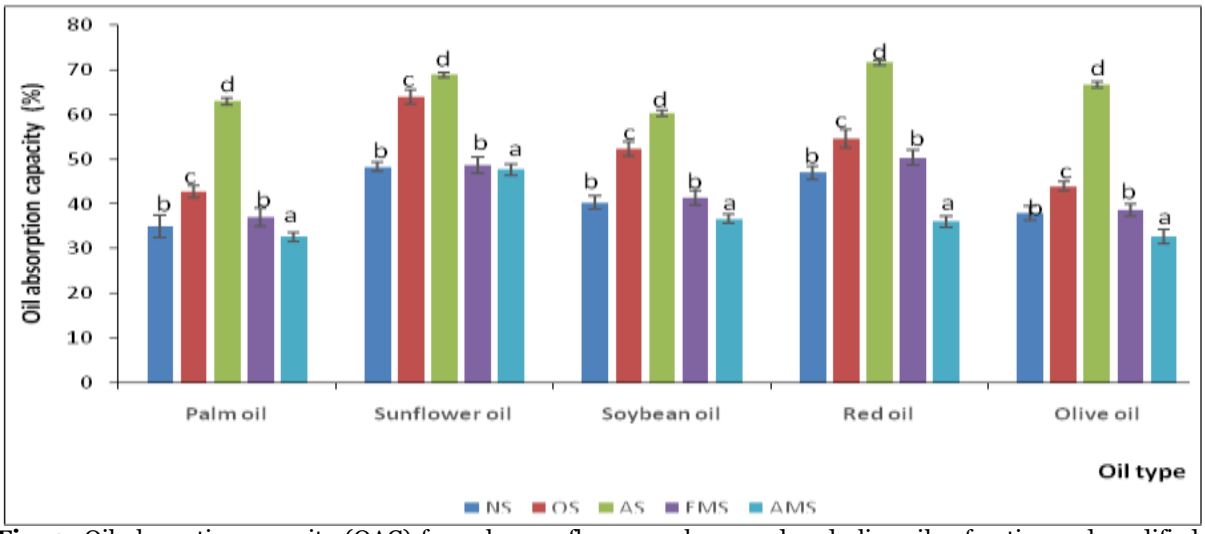

Fig. 3. Oil absorption capacity (OAC) for palm, sunflower, soybean, red and olive oils of native and modified "Kponan" yam (*D. cayenensis-rotundata complex)* cultivar starches.

NS: native starch; OS: oxidized starch; AS: acetylated starch; EMS: Enzyme modified starch; AMS: Acid modified starch

Oil absorption capacity (OAC)

The OAC of native and modified "Kponan" yam cultivar starches varied from 32.67 ± 1.58 % to 63.00 ± 1.53 %, 47.67±1.00 % to 64.00±1.53%, 36.67±0.66% to 60.33±0.79, 36.00 ± 0.66 % to 71.67 ± 1.58% and from 36.67±1.58% to 66.67±1.00% for "palm oil", "sunflower oil", "soybean oil", "red oil" and "olive oil" (Fig. 3). The obtained result showed that the highest value of OAC was obtained with acetylated starch, while the acid modified starch had the lowest value of OAC, whatever the oil type is. Besides, the Analysis of variance (ANOVA) revealed that the chemical and enzymatic modifications main effect had meaningful ($p \leq 0.05$) effect on OAC. Indeed, oxidation, acetylation and enzymatic modification increased meaningfully ($p<0.05$) the OAC of native starch whereas acid modification decreased it significantly ($p<0.05$). It appeared also significant differences between the OAC values of native and modified starches, whatever the oil type is.

Syneresis

The retrogradation tendency of gels prepared from native and modified starches was measured by determining syneresis (percentage of separated water) during storage at 4°C. The curves of syneresis showed similar trends (Fig. 4). Syneresis of starches was increased at day 0 for acid modified starch, while it decreased for acetylated modified and oxidized modified starches. Then, it increased quickly from 0 day to 2 day and from 0 days to 3 days for native starch and other starches respectively. After this respective time, the syneresis was increased slightly as the number of days of storage increased in all starches. Otherwise, it varied from 14.2% to 70.70% and from 29.41% to 85.5% at day 0 and day 30 respectively **(**Fig. 4**)**. Besides, data of this study showed that acid modified starch had higher increment in syneresis than native starch. On the other hand, enzymatic modified, acetylated and oxidized starches possessed lower increment in

syneresis than native starch. Among these modified starches, the lowest value of syneresis was recorded with oxidized starch followed by, acetylated and enzyme modified starches.

Paste clarity (PC)

The effect of storage days on paste clarity of the native and modified "Kponan" yam variety starches is shown in fig. 5. The obtained paste clarity curves indicated similar trends. Paste clarity of starches was increased at day 0 for acetylated modified and oxidized modified starches, whereas it decreased for acid modified starch. Then, paste clarity (%Transmittance) decreased quickly from day 0 to day 1 for native and modified starches. After this time, paste clarity was reduced slightly as the number of days of storage increased in all the starches. In this study, the results showed that acid modified starch had lower increment in paste clarity than native starch. On the other hand, enzyme modified, acetylated starch and oxidized starch possessed higher increment in paste clarity than native starch. The paste clarity ranged from 21.40 %T to 47.70%T and from 11%T to 27%T at day 0 and day 30 respectively. Besides, Oxidation produced the most remarkable increase in % transmittance followed by acetylation, enzyme and acid modifications.

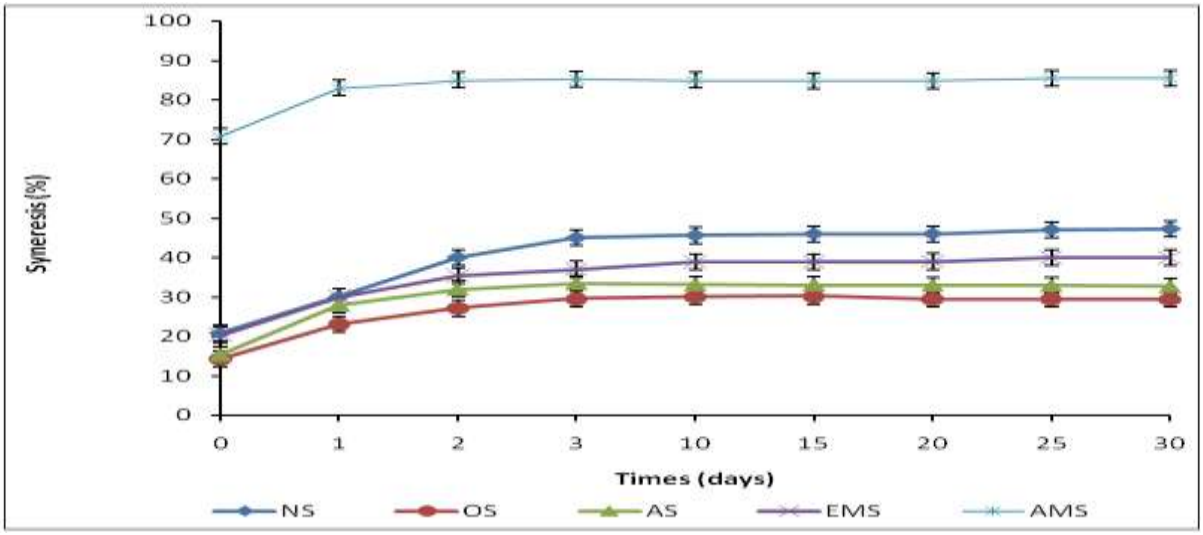

Fig. 4. Syneresis study of native and modified "Kponan" yam cultivar starches

NS: native starch; OS: oxidized starch; AS: acetylated starch; EMS: Enzyme modified starch; AMS: Acid modified starch.

Discussion

Morphological characteristics

Data of this study showed that there didn't appear significant change in shape of native and modified "kponan" yam cultivar starches. This suggested that chemical and enzymatic modifications were not found to significantly affect the granule shapes (Ayucitra, 2012). Similar results were indicated by Ayucitra (2012) on native and acetylated starches from Corn. Besides, the observed shapes were agreed with those recorded by several other authors (Moorty, 2002; Lindeboom *et al.*, 2004). These authors reported the ovotriangular, oblong, oval, polyhedral and ellipsoid shapes in the whole tubers of *Dioscorea cayenensis-rotundata* complex. Indeed, the morphology of starch granules depends on biochemistry of the chloroplast or amyloplast, as well as physiology of the plant (Badenhuizen, 1969).

Granule size distributions

Otherwise, the change of granule size of native and modified starch from "Kponan" yam cultivar tubers didn't appear meaningful ($p \leq 0.05$), except that of acid modified starch. This may be explained that chemical and enzymatic modifications didn't generally influence meaningful starch granule size

Ayucitra (2012). Our results were similar to those of Tetchi *et al.* (2007) who reported 32 µm as the average diameter of "Kponan" cultivar (*Dioscorea cayenensis-rotundata* complex). These values found to be higher than those obtained for white tacca and yellow tacca starches by Nwokocha *et al.* (2011), who noted that the average diameter size of starch granules of 12.32 µm and 6.89 µm respectively. Furthermore, all observed granule range size of native and modified starches were higher than the reports of De Vizcarrondo *et al.* (2004) which indicated the average diameter size of starch granules varying from 21.8 µm to 35.0 µm for *Dioscorea bulbifera*. Compared to other root and tuber starches, our result were also higher than the findings of Amani *et al.* (2004) who published the average diameter size of starch granules ranging from 6.43 µm to 38.55 µm for *Zingiber officinale* Roscoe.

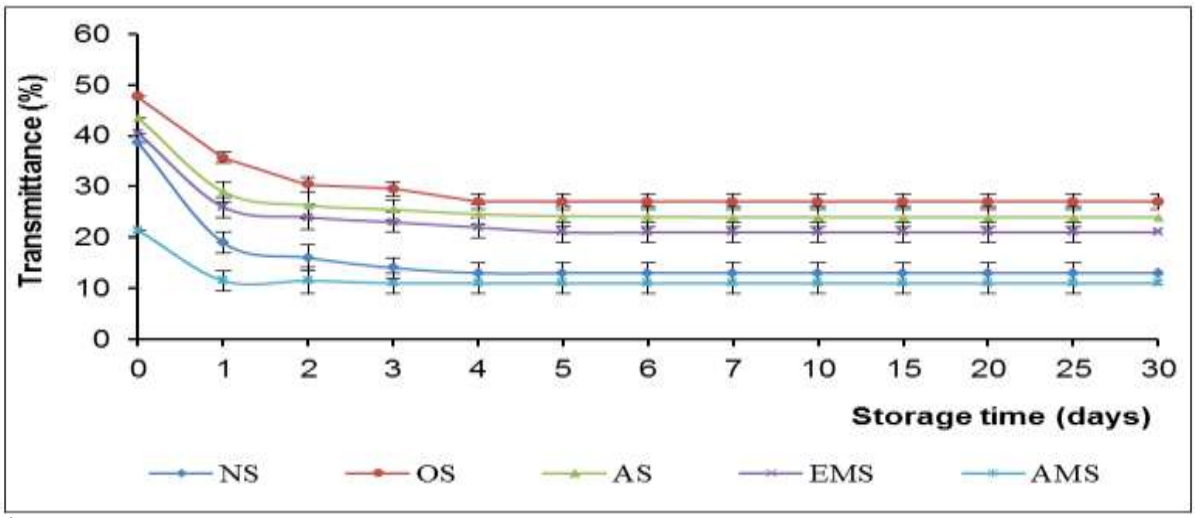

Fig. 5. Effect of storage days on paste clarity of native and modified "Kponan" yam cultivar starches
NS: native starch; OS: oxidized starch; AS: acetylated starch; EMS: Enzyme modified starch; AMS: Acid modified starch.

Proximate Composition

The moisture contents were reduced significantly ($p<0.05$) in acetylated, oxidized, enzymatically modified and acid modified starches. This reduction was supported by Olayinka *et al.* (2013), who indicated that moisture content decrease in modified sorghum starches. Indeed, the result revealed that the moisture contents of modified starches were all below 9 %, thereby giving the starch a better shelf life. Moisture content of dry starch varies from 6-16%, depending on the process used for drying the starch (Moorthy, 2002). This biochemical parameter is important in the storage of starch, levels greater than 12% allow for microbial growth. Higher levels of moisture can lead to microbial damage and subsequent deterioration in quality. Chew *et al.* (2011) reported that reduced moisture content ensured the inhibition of microbial growth, hence is an important factor in food preservation. Moisture levels of modified "Kponan" yam variety starches were lower than that reported on cassava (*Manihot esculenta*) starch (10.20%) (Alyeleye *et al.*, 1993); arrowroot (*Maranta arundinacea*) starch (9.82%) (Raja and Sindhu, 2000). Besides, our results were similar than those carried out on cocoyam starch by Lawal (2004) who found the moisture levels ranging from 8.02% to 8.39%.

The crude protein, crude fat and total ash contents of the native "Kponan" yam variety were reduced following modification. These reductions are due to various degradation that took place during the modification processes and were in agreement with report by Adebowale *et al.* (2002) on Bambarra (*Voandzeia substerranean*) starch and flour. Similar result was recorded by Lawal (2004) on new cocoyam (*Xanthosoma sagittifolium*) starch.

Functional properties

Water absorption capacity (WAC)

Significant differences were observed between WAC of oxidized, acetylated, enzymatic modified, acid modified and native starches. In order, our results showed that acetylated starch had the highest value of WAC followed by oxidized, enzymatic modified, native and acid modified starches. Similar results were found by Chibuzo (2012) on native and chemical modified sweet potato (*Ipomoea batatas* L.) starch. These results were found to be lower than the reported of Chibuzo (2012), who recorded the values of 4.80ml/g, 0.87ml/g and 0.73ml/g for acetylated, oxidized and acid thinning respectively. Otherwise, the gotten results indicated that WAC was increased significantly ($p \leq 0.05$) after acetylation, oxidation and enzymatic modifications while it was decreased after acid modification. This observation showed that hydrophilic tendency of the native starches may be improved after oxidation, acetylation and enzymatic modification whereas acid modification could be reduced the tendency of the starch to absorb water. Our findings were agreed with the reports of Akintayo *et al.* (2000) on lima bean starches. On the other hand, they were contrary to the results of Sathe and Salunkhe (1981) which showed that modification didn't affect water absorption capacities of the Great Northern bean starch.

Least gelation concentration (LGC)

The results showed that LGC increased of the native starch after oxidation and acetylation, whereas it decreased the enzymatic and acid modification. So, the LGC values of oxidized and acetylated starches were found to be higher than those mentioned of enzymatic and acid modified starches. According to Akinayo *et al* (1999), more LGC is weak, better is the gelation capacity of the food component. Indeed, the change of obtained LGC values may be bound to the relative reports of different food constituents. Thus, our results suggested that enzymatic and acid modified starches were better gelating food additives than native, acetylated and oxidized starches though acid modified starch had the best and enhanced gelating property. The gotten results were similar to those found by Chibuzo (2012) who revealed that the acetylation and acid modification had effect on the gel strength of the native starch from sweet potato (*Ipomoea batatas* L.). This author mentioned contrary to our findings that oxidation influence oxidation had no effect on the gel strength of the native starch. Besides, the results of this study were in agreement with reports by Lawal (2004) on cocoyam starch.

Oil absorption capacity (OAC)

Data was showed that oxidation, acetylation and enzyme hydrolysis increased meaningfully ($p \leq 0.05$) the OAC. This result suggested that these modifications enhanced the hydrophobic tendencies of the starches. Similar results were recorded by Uzomah and Ibe (2011), who indicated that Acetylated and oxidized starches had the strongest affinity for oil absorption. Our results were in agreement with the findings of Yusuf *et al.* (2007) on unmodified and modified Jack bean (*Canavalia ensiformis*) starches. The obtained results showed oxidation, acetylation and enzyme hydrolysis could be used to improved absorption improve oil capacity of "Kponan" yam variety. Otherwise, the acid hydrolysis reduced significantly ($p \leq 0.05$) the OAC. The result of this study supported the findings of Lawal (2005), who published that acetylation and oxidation had a more pronounced effect on the oil absorption capacity of native cassava starches than acid thinning. Indeed, The increased hydrophobic tendencies of the acetylated and oxidized starches have been related to the attachment of functional groups on the starch molecule, while the decrease in acid thinned samples have been related to the erosion of the amorphous region by the acid.

Syneresis

This phenomenon described release of water by gels that have been kept for longer periods or refrigerated or frozen. This is an important factor to be considered when formulating refrigerated and frozen foods (Thomas and Atwell, 1999). Our results revealed that acid modified starch had the highest increment in syneresis while the lowest increment in syneresis was

obtained with oxidized starch. Indeed, lowest tendency to syneresis from oxidized starch showed that this modified starch is more stable to freeze-thawing than others. Hence, it would be better suited for use in freeze products than others (Mweta *et al.*, 2008). Furthermore, enzyme modified, acetylated starch and oxidized starches possessed lower increment in syneresis than native starch. In this work, our findings supported the reports of Lawal (2009) on hydroxyalkylation of finger millet (*Eleusine coracana*) starch. Similar trends were observed on corn starches by Ayucitra (2012), who noted that the syneresis of acetylated starch gels found to be lower than that of native starch. According to Singh *et al.* (2004), the alteration in the retrogradation properties of acetylated starches may also be due to the increase in water retention capacity of the starch molecules due to the presence of acetyl groups in the refrigerated stored gels .This author showed also that acetylation served to reduce syneresis. Otherwise, the fall in syneresis for acetylated modified, oxidized modified and enzyme modified starches may be attributed to reduction in the inter chain bonding between the starch molecules Lawal (2009). These modifications (acetylation, oxidation and enzyme modification) could be used to stabilise starch gels in low temperature conditions that may cause retrogradation. On the other hand, an increase in syneresis indicates a lack of freeze-thaw stability.

Paste clarity (PC)

The paste clarity of "Kponan" yam variety starch was increased at day 0 after chemical modifications. This increase in paste clarity (% transmittance) after modification may be 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 paste clarity (% transmittance) Lawal (2004). Otherwise, decrease in paste clarity of all starches was observed with an increase of the storage time at 4°C. Similar trends were obtained by Ogungbenle (2007) on effect of Chemical Modification on Starch of Some Legume Flours. Our results were in agreement with the findings of Chibuzo (2012), who reported that the percentage transmittance of native and modified starches was reduced as the storage days increased. This work showed that the oxidized modified starch had the highest amount of paste clarity (% transmittance), while the lowest paste clarity was recorded by acid modified starch. Indeed, the high paste clarity observed for starch signified that the starch granules of these samples are fragile during pasting and remnants of granules are absent from the paste (Callghan and Lelieve, 1985). On the other hand, the low paste clarity found in "Kponan" yam variety starch may be explained by the presence of molecules less susceptible to retrogradation. Besides, Stuart *et al.* (1989) observed that more opaque paste gave low paste clarity (%Transmittance). This implied that native and acid modified starches are more opaque than other starches studied. Indeed, an increase in opacity of starch pastes during storage could be attributed to many factors like leached amylose and amylopectin chains, granular remnants, granular swelling, amylose and amylopectin chain length (Jacobson *et al.* 1997). Furthermore, Oxidation produced the most remarkable increase in % transmittance followed by acetylation, enzyme modifications. These modification improved paste clarity (% transmittance). Indeed, improved paste clarity is a useful property in the manufacture of some food products, such as salad dressings and confectionery products.

Conclusion

The results of this work indicated that the granules shape of native and modified starches was all polyhedral and ovotriangular. Indeed, chemical and enzymatic modifications didn't affect meaningfully ($p \leq 0.05$) the granule morphology. On the other hand, they reduced the proximate composition such as that moisture, protein, fat and ash contents. Besides, oxidation, acetylation and enzymatic modification increased meaningfully ($p \leq 0.05$) the WAC and OAC of native starch while acid hydrolysis decreased them significantly ($p \leq 0.05$). An increase of WAC and OAC showed that the modifications such as oxidation,

acetylation and enzymatic modification improved hydrophilic or hydrophobic tendency. Otherwise, LGC of the native starch was increased after oxidation and acetylation, whereas it decreased in acid modified and enzymatic modified starches. This suggested that enzymatic and acid modified starches were better gelating food additives than native, acetylated and oxidized starches. This study indicated that syneresis tendency was reduced after oxidation, acetylation and enzymatic modification but increased following acid modification. Studies conducted on paste clarity revealed that percentage transmittance (650 nm) increased after chemical modifications (oxidation and acetylation) and enzymatic modification whereas acid modification reduced it. Furthermore, the modifications such as acetylation, oxidation and enzyme modification could be used to imoprove the both parameters (syneresis and paste clarity).

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