CHARACTERISATION OF ACETYLATED, OXIDISED AND ACID-THINNED HYBRID MAIZE STARCHES

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ABSTRACT

Chemical modification of TZL-COMP4 hybrid maize starch was carried out to produce the acetylated (ACE), oxidised (OXI) and acid-thinned (ATI) derivatives. The functional, pasting and morphological characteristics of the native (NAT) and modified starches were determined. The results of functional properties of the starches showed that swelling power and solubility at 55 °C – 95 °C ranged from 174.70±12.27 – 956.04±101.07 g/100g and 0.21±0.12 – 0.58±0.01 g/g, respectively. Oil and water absorption capacity, gelation properties and light transmittance ranged from 214.44±0.02 – 518.57±0.26 g/100g, 10 – 14 %w/v and 6±0.03 - 73±0.10, respectively. Significant ($p < 0.05$) reduction in pasting temperature was observed in ACE and reduced susceptibility to retrogradation was observed in ATI. Granule morphology showed small granules with no disrupted surfaces.

Key words: Biopolymer, Derivatization, Functionality, Structure

1.0 INTRODUCTION

Starch is an important naturally abundant polymer of plant origin with versatile industrial applications. It shows different functionalities and it is the most regularly applied hydrocolloid. Starch is widely used in the food industries, especially in the preparation of soups, dairy, confectionery, snakes, pasta, coatings and products made with meat. The ability of starch to form a viscous paste when heated in water followed by the cooling property makes starch suitable for various uses in the food and non-food industries (Zhang, Kim, & Lim, 2017). Starches are however, rarely used in their native forms because they are unstable with respect to changes in temperature, pH and shear force. Native starch shows a strong tendency for decomposition and retrogradation (Alcázar-alay, Angela, & Meireles, 2015). It has limited use in food processing since it has narrow peak viscosity range, poor process tolerance, lack of clarity, forms a weak cohesive and rubbery paste when heated and undesirable gel when cooling or during storage due to retrogradation and precipitation (Din, Xiong, & Fei, 2015; Majeed, Wani, & Hussain, 2017).They are often modified to develop specific properties such as solubility, texture, adhesive and tolerance to the heating temperature used in industrial processes (Alcázar-alay et al., 2015; Raina, Singh, Bawa, & Saxena, 2007).

Modification of starch include physical, chemical and enzymatic methods (Alcázar-alay et al., 2015). Chemical modification involves the introduction of functional groups on the starch molecules without effecting the morphology or size distribution of the granules. Chemical modifications generate significant changes in starch behavior, gelatinization capacity, retrogradation and paste properties (Alcázar-alay et al., 2015). Modified starch are known to meet the functional properties required in food products such as thickening and stabilization (Zheng & Sosulski, 1998).

Researches have investigated the properties of conventional and unconventional starch sources. It is however, known that the most abundant source of starch that can meet industrial needs are those of corn and tubers. For maize to be relevant in this case, it must be draught tolerant, disease resistant and high yielding of which hybrid maize are suitable in this respect. The objective of this work was to isolate and enhance the property of TZL-COMP4 hybrid maize starch by chemical modification.

2.0 MATERIALS AND METHODS

2.1 SAMPLE COLLECTION

Hybrid maize (TZL-COMP4) seeds were obtained from IITA, Ibadan, Oyo State. All other reagents used were of analytical grade.

2.2 ISOLATION OF STARCH

Starch isolation was done by the method of Lawal and Adebowale (2005) with modification. 2 kg of winnowed maize grains were cracked slightly with a blender before steeping in 10 L of 0.02 M solution of $NaHSO_3$ for 28 h at 30±2 °C, after which the steeping solution was discarded and the swollen grains were washed with distilled water. The swollen grains were blended for 30 min using a blender (Century Electric Blender). The slurry obtained after blending was re-suspended in 5 L of distilled water. It was screened, using muslin cloth and centrifuged for 30 min at 4500 rpm. Starch obtained after centrifugation was re-slurried in 2 L distilled water and protein was separated from starch by toluene emulsification. Toluene was added (20 mL) to starch suspension and it was thoroughly mixed for 30 min and allowed to stand for another 2 h. An emulsion layer of denatured protein was formed at the interface as toluene and water separated. The emulsion layer was discarded. The process was repeated for the starch slurry until emulsion layer became negligible. The starch slurry was then washed with acetone and air-dried for 24 h at 30±2 °C.

2.3 STARCH MODIFICATION

2.3.1 PREPARATION OF ACID-THINNED (ATI) STARCH

The method described by Singh and Ali (2008) with slight modification was used for preparing ATI starch using HCI (0.5 M) at 50 °C for 1.5 h. The slurry was stirred frequently after every 20 min during the treatment period, neutralized with 1 M NaOH, and washed with distilled water. The starch was then dried at 40 °C in a convection oven (GenLab) for 24 h.

2.3.2 PREPARATION OF ACETYLATED (ACE) STARCH

Acetylation was carried-out as described by Lawal (2004) with slight modifications. Hundred grams of starch was dispersed in 500 mL of distilled water; the mixture was stirred for 20 min. The pH of the slurry obtained was adjusted to 8.0 using 1 M NaOH. Acetic anhydride (10.2 g) was added over a period of 1 h, while maintaining a pH range 8.0–8.5. The reaction proceeded for 5 min after the addition of acetic anhydride. The pH of the slurry was adjusted to 4.5 using 0.5 M HCl. It was filtered, washed four times with distilled water and air-dried at 30±2 °C for 48 h.

2.3.3 PREPARATION OF OXIDISED (OXI) STARCH

Oxidized starch was prepared by the method of Lawal (2004a) with modifications. Fifty per cent slurry of starch was prepared by dispersing 100 g of starch in 500 mL of distilled water. The pH was adjusted to 9.5 with 2 M NaOH. Ten grams of NaOCl was added to the slurry over a period of 30 min, while maintaining a pH range 9–9.5, with constant stirring at 30±2 °C. The reaction proceeded for 10 min after addition of NaOCl. After the reaction, the pH was adjusted to 7 with 1 M 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.

2.4 PHYSICOCHEMICAL PROPERTIES OF STARCH

2.4.1 PERCENTAGE ACETYLATION AND DEGREE OF SUBSTITUTION

The content of acetyl groups (expressed as percentage in dry basis) and the degree of substitution of acetylation were determined according to the method ofLawal, Adebowale, Ogunsanwo, Barba, & Ilo (2005).Acetylated starch (5 g) was placed in a 250 mL flask, and distilled water (50 mL) was added upon mixing. A few drops ofphenolphthalein indicator were added, and the suspensionwas titrated with 0.1 M sodium hydroxide to a permanentpink end point. After addition of 0.45 M sodium hydroxide (25 mL), the flask was sealed tightly with arubber stopper and shaken vigorously for 30 min. Aftershaking, the stopper was carefully removed and washeddown, together with the walls of the flask, with distilledwater. The saponified mixture containing excess alkaliwas then titrated with standard 0.2 M HCl solution untildisappearance of the phenolphthalein color. The nativestarch was treated in the same manner to obtain a blankvalue.

$$\% \text{ acetyl (dry basis)} = \frac{\text{(Blank titre} - \text{sample titre)(ml)} \times \text{acid molarity} \times 0.043 \times 100}{\text{sample wieght in gram (Dry basis)}} \quad (1)$$

$$\text{Degree of substitution (DS)} = \frac{162A}{4300 - 42A} \quad (2)$$

A = % acetyl (Dry Basis)

2.4.2 CARBOXYL AND CARBONYL CONTENTS

The method of Lawal (2004a) was used for the determination of carboxyl contents. 5 g of oxidized starch sample was slurred in 25 mL of 0.1 M HCl. It would be stirred for 40 min. The slurry was filtered through a medium porosity fritted glass crucible and the residue would be washed with distilled water until it was free of chloride, using silver nitrate test. The chloride-free sample was dispersed in 300 mL of distilled water. The dispersion was heated in a steam bath and stirred continuously until the starch gelatinizes. The hot sample was titrated with 0.1 M NaOH to a phenolphthalein end point. To quantify acidity due to other sources, mainly fatty acids complexed with amylose, a blank titre was determined. 5 g of native starch was titrated to provide for a blank value.

$$\text{Percent carboxyl} = \frac{(Sample\ titre - Blank\ titre)\ mL \times Alkali\ molarity \times 0.045 \times 100}{Sample\ weight\ (g)} \quad (3)$$

The hydroxylamine method was used for the determination of carbonyl content. 2 g of oxidised starch was dispersed in 100 ml of distilled water and the suspension was gelatinized by heating in a boiling water bath and then cooled to 40 °C. The pH was adjusted to 3.2 and 15 mL of hydroxylamine reagent was added (The hydroxylamine reagent would be prepared by dissolving 25 g of reagent grade hydroxylamine hydrochloride in water and adding 100 mL of 0.5 M NaOH. The solution was made to 500 ml with distilled water). The sample was covered with aluminium foil and placed in a water bath at 40 °C. After 4 h, the excess hydroxylamine was determined by rapid titration of the reaction mixture to pH 3.2 with 0.1 M hydrochloric acid.

$$\text{Percent carbonyl (C=O)} = \frac{(Blank\ titre - Sample\ titre)\ mL \times Acid\ molarity \times 0.028 \times 100}{Dry\ sample\ weight\ (g)} \quad (4)$$

Values presented as percentages would be numbers of carboxyl (COOH) and carbonyl (CHO) groups per 100 anhydroglucose unit, AGU.

2.4.3 SWELLING POWER AND SOLUBILITY

Effect of temperature on swelling power and solubility determinations were carried out in the temperature range of 55–95 °C, using the method of Lawal (2005). 0.1 g of starch samples were accurately weighed separately and quantitatively transferred into clean dried test tube and weighed (W_1). 10 cm^3 of distilled water was added to the test tube and the mixture was mixed thoroughly for 30 s. The resultant slurries were heated at desired temperatures, varied between 55 and 95 °C for 30 min in a water bath. The mixture was cooled to room temperature and centrifuged at 4500rpm for 15 min. The residue obtained after centrifugation with the water it retained and the test tube was weighed (W_2).

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

Aliquots (5 mL) of the supernatant obtained after centrifugation were dried to a constant weight at 110 °C. The residue obtained after drying the supernatant represented the amount of starch solubilized in water. Solubility was calculated as grams per 100 g of starch on dry weight basis.

The effect of pH on solubility and swelling was studied using the method of Lawal (2005). The slurry (1 %, w/v) was prepared with distilled water and the pH was adjusted between 2 and 12 with 0.1 M HCl or 0.1 M NaOH. The slurries were allowed to stand for 1 h at 30±2 °C centrifuged at 4500 rpmfor 15 min. The supernatant (5 mL) was dried to constant weight at 110 °C to determine percentage solubility of the starch as stated earlier.

2.4.4 OIL AND WATER ABSORPTION CAPACITY.

The method of Lawal (2005) was used to determine oil and water absorption capacity of the starch. 10 mL of distilled water or oil was added to 1 g of sample. The mixture was mixed thoroughly for 30 s and allowed to stand for 30 min. Then, the volume of the supernatant was recorded.

2.4.5 GELATION STUDIES

The method of Lawal (2005) was used to determine gelation studies. Sample of starch, 2–18 % (w/v), were prepared in test tube with distilled water (10 mL). The starch suspensions were mixed for 5 min. The test tubes were heated for 30 min at 80 °C in a water bath, followed by rapid cooling under running cold tap water. The test tubes were further cooled at 4 °C for 2 h. Least gelation concentration was determined as that concentration when the sample from the inverted test tube did not fall down or slip.

2.4.6 PASTING PROPERTIES

The pasting properties of starch were obtained from Rapid ViscoAnalyser (RVA) (RVA-4, Newport Scientific, Australia) with 2.5 g dried starch dispersed in 25 mL of distilled water. A heating and cooling cycle was programmed in the following manner; the sample was heated from 50 to 95 °C for 3 min, held at 95 °C for 2 min and cooled to 50 °C within 3 min. The gelatinization parameters such as maximum gelatinization temperature, peak viscosity, holding strength, final viscosity, breakdown, and set back were determined.

2.4.7 LIGHT TRANSMITTANCE

Paste clarity was studied using the method of Lawal (2005) with modifications. The native and modified starches (50 mg on dry weight basis) were suspended in 5 mL of distilled water and heated in a boiling water bath (with occasional shaking) for 30 min. After cooling to ambient temperature, transmittance (%) was determined at 650 nm against water blank using UV-Visible spectrophotometer. Also, to monitor tendency for retrogradation, samples were stored for 24 h at 4 °C to effect nucleation, after which they were stored at (30±2) °C for 1 to 9 days before determining the absorbance.

2.4.8 SCANNING ELECTRON MICROSCOPY

The morphology of the starch granules was examined using a scanning electron microscope (Pro SEM, Phenom World). All of the samples were coated with gold and examined in the scanning electron micro- scope under an acceleration.

3.0 RESULTS AND DISCUSSION

3.1 RESULTS

The results of functional properties of native (NAT), acetylated (ACE),oxidized (OXI),and acid thinned (ATI) TZL-COMP4 hybrid maize starches are present in Tables 1-3 and Figures 1-4.The swelling power and solubility at 55 °C – 95 °C ranged from 174.70±12.27– 956.04±101.07 g/100g and 0.21±0.12 – 0.58±0.01 g/g, respectively. Oil and water absorption capacity, gelation propertiesand light transmittance ranged from 214.44±0.02 – 518.57±0.26 g/100g, 10 – 14 %w/v and 6±0.03 - 73±0.10, respectively. Granule morphology showed small granules with no disrupted surfaces.

3.2 DISCUSSION

Results of swelling power and solubility showed that both were temperature dependent (Fig1 and Fig.2). OXI and ACE starches showed improved swelling power over native starch. Increase in swelling power with temperature rise has been reported by Lawal, Adebowale, Ogunsanwo, Barba, & Ilo, (2005), Ačkar, Babić, Šubarić, Kopjar, & Miličević (2010), Huang, Lai, Chen, Liu, & Wang (2010) and Li et al. (2016) for hybrid maize, wheat, yam, taro, and sweet potato starches and normal and waxy wheats.However, Zavareze et al. (2012) reported decrease in swelling power with increase in temperature for oxidised and heat moisture treated potato starches. Swelling power is a measure of hydration capacity and the magnitude of interaction between starch chains within the amorphous and crystalline domains (Mehboob, Ali, Alam, & Hasnain, 2015). Solubility of starches increased with increase in temperature. However, modified starches had lower solubilities than the native starch. Similar lowered solubilities of modified starches relative to native starch has been reported for wheat varieties by Ačkar et al. (2010). Least solubility was recorded for ATI.

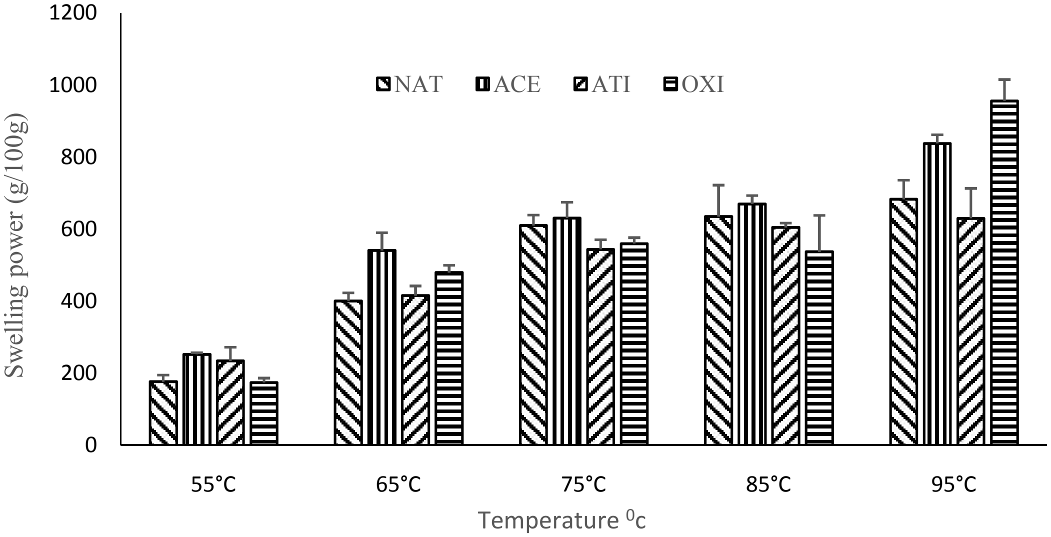


Fig.1. Effect of temperature on swelling power of native (NAT), acetylation (ACE), oxidised (OXI) and acid-thinned (ATI) starches of TZL-COMP4 hybrid maize.

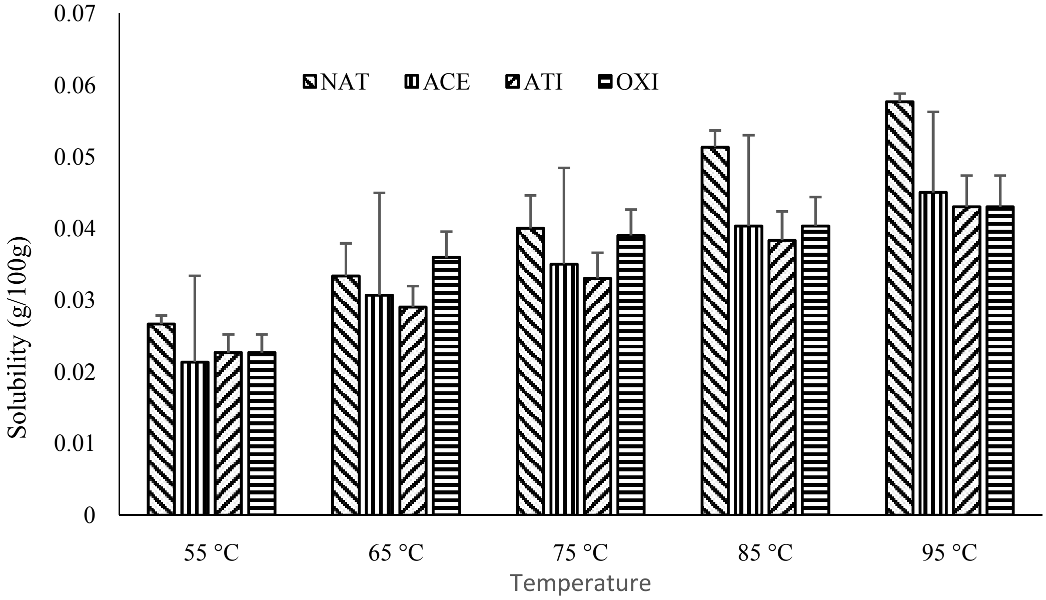


Fig.2. Effect of temperature on solubility of native (NAT), acetylation (ACE), oxidised (OXI) and acid thinned (ATI) starch of hybrid maize

The results of oil and water absorption capacities revealed that acetylation reduced the rate of oil absorption which increased after acid-thinning and oxidation. Similar reports have been reported by Lawal, Adebowale, Ogunsanwo, Barba, & Ilo (2005) who explained that both hydrophilic and hydrophobic properties reduced following acid-thinning. According to Shah, Masoodi, Gani, and Ashwar (2017), water absorption capacity relies upon the molecular structure, crystalline and amorphous regions within the starch and distribution of granular size. The oil absorption capacity involves physical entrapment of oil by capillary action. Lawal (2004), also reported that water absorption capacity increased after succinylation and acetylation. The result of Lawal, Adebowale, Ogunsanwo, Barba, and Ilo (2005) revealed that oxidation increased water absorption capacity and oil absorption capacity of the native starch. This result is in accordance with the observations reported on the water and oil absorption capacities of acetylated, oxidized and acid-thinned new cocoyam starch (Lawal 2004a) and hybrid maize starch (Lawal et al., 2005).

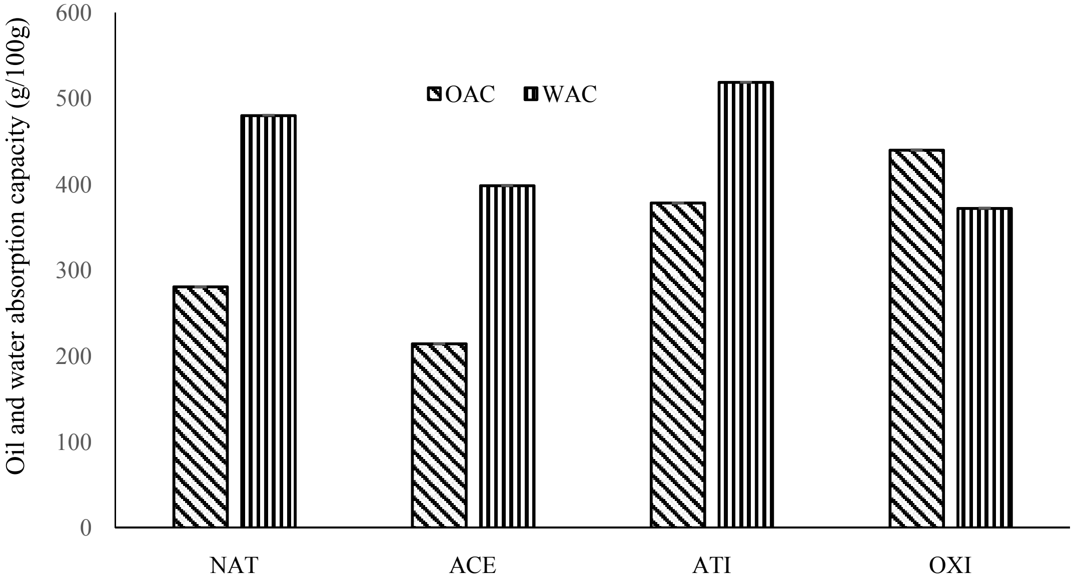


Fig. 3. Oil and water absorption capacities of native and modified starches of native (NAT), acetylation (ACE), oxidation (OXI) and acid thinned (ATI) starches of TZL-COMP4 hybrid maize.

A starch gel is composed of swollen granules, the amorphous region hydrates and swells to a gel phase, during the process of heating (Adebowale & Lawal, 2003). The gelation studies showed that native starch did not form gel until it reached 12 % concentration. ATI and OXI starches however, had an increased least gelation concentration over NAT. Lawal et al. (2005) reported that least gelation concentration increased after oxidation and reduced after acid-thinning. Reduction in least gelation concentration value is an indication of better gelating properties. Starch gelation is a complex process that involves gelatinization, swelling and absorption of water to build a three-dimensional network that offers structural rigidity in various food applications. The building of the structural network involves as well, the bridging of the inter-granular binding forces among the starch molecules, which largely involves hydrogen bonding. The results of Adebowale & Lawal, (2003) indicated a reduction in gelation properties of the native starch after succinylation and acetylation. Lawal, (2005) indicated that the least gelation concentration of native new cocoyam starch was 8 % (w/v). Following annealing, this value decreased drastically, to 2 %(w/v), and heat moisture treatment also reduced the LGC of the native starch.

Table1. Gelation capacity of native(NAT), acetylated(ACE),oxidized (OXI) and acid thinned(ATI) starches of TZL-COMP4 hybrid maize.

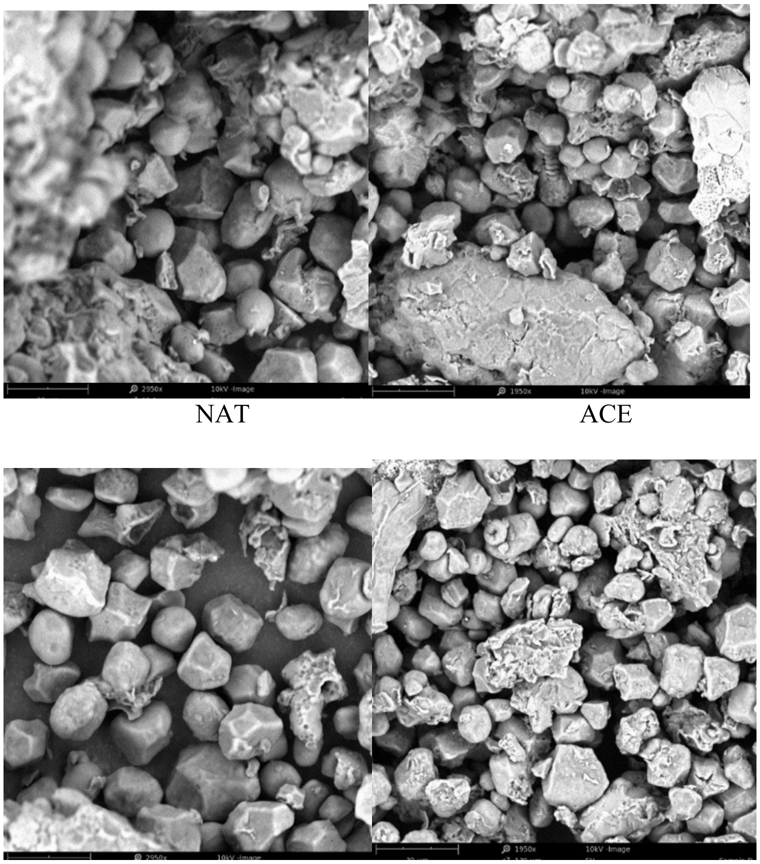
Concentration (%)	Starch Sample			
	NAT	ACE	ATI	OXI
2	Liquid	Liquid	Liquid	Liquid
4	Liquid	Liquid	Liquid	Liquid
6	Liquid	Liquid	Liquid	Liquid
8	Viscous	Viscous	Viscous	Viscous
10	Viscous	Viscous	Gel	Gel
12	Gel	Gel	Gel	Firm Gel
14	Gel	Firm Gel	Firm Gel	VFG
16	VFG	VFG	VFG	VFG
LGC	12	14	10	10

LGC = least gelation concentration; VFG = very firm gel; NAT = native; ACE = acetylated; ATI = acid-thinned; OXI = oxidized.

The scanning electron microscopy revealed that NAT and ATI had the smallest granule size, and dual modified ACE had the largest granule size. Xiao et al. (2012) explained that scanning electron microscopy revealed that starch granules of native and modified rice starch samples were small, and no noticeable differences were observed among the appearances of morphologies of the native and chemically modified starch granules after performing cross-linking, oxidation and dual modification on rice starch. The microscopy did not show any form of surface destruction for ACE starch however, ATI starch showed a significant destruction in the surface structure. However, Singh et al., (2007) reported that microscopy did not show any destruction of granular structure of starch upon acid thinning and he attributed that it may be due to the low level of hydrolysis.

Table 2 shows the pasting properties of NAT, ACE, OXI and ATI starches of ITZL-COMP4 hybrid maize. The peak viscosity, which is the maximum viscosity developed during or soon after the heating portion, ranged from 2297.00 to 133.00 RVU. OXI starch gave the highest (2297.00 RVU at a temperature of 85.60 °C) while ATI had the lowest (172.00 RVU at a temperature of 83.15 °C). This variation in the peak viscosity might be as a result of the amylose contents of the starches. Oguntunde (1987) reported that the associative bonding of the amylose fraction is responsible for the structure and pasting behaviour of starch granule. Peak viscosity has been reported to be closely associated with the degree of starch damage and high starch damage results in high peak viscosity (Sanni et al., 2001). Pasting temperatures of the starch samples ranged from 76.65 °C for ACE to 85.69 °C for NAT and OXI. The range of values obtained were similar to those of native and modified corn starches of Sandhu, Kaur, Singh, & Lim (2008). The pasting temperature is one of the properties which provide an indication of the minimum temperature required for sample cooking, energy cost involved and other components stability. Shimelis et al. (2006) reported that final viscosity is used to indicate the ability of starch to form various paste or gel after cooling and that less stability of starch paste is commonly accompanied with high value of breakdown. Sanni et al. (2001) reported that lower setback viscosity during the cooling of gari indicates higher resistance to retrogradation.

Light transmittance of all the starches increased as storage period increased from 1st day to the 9th day. Light transmittance was time dependent (Table 3). All modified starches had higher light transmittance on Day 1 than the native starch. Highest transmittance however, was observed in ATI.



NAT ACE

OXI ATI

Fig. 4. Scanning electron micrographs of native (NAT), acetylated (ACE), oxidized (OXI) and acid-thinned (ATI) TZL COMP4 hybrid maize starches

Table 2. Pasting properties of native(NAT),acetylated(ACE),oxidized (OXI)and acid thinned(ATI)TZL COMP4 hybrid maize starches.

Starch sample	Pasting temperature	Peak viscosity	Peak time	Setback	Breakdown	Final viscosity
NAT	85.60	376.00	5.27	295.00	348.00	323.00
ACE	76.65	1932.00	4.93	1758.00	955.00	2735.00
OXI	85.60	2297.00	5.87	666.00	434.00	2529.00
ATI	83.15	172.00	5.20	1165.00	226.00	1111.00

Table 3. Light transmittance of native (NAT), acetylated (ACE), oxidised (OXI) and acid thinned (ATI) TZL COMP4 hybrid maize starches.

Samples	1st day	3rd day	4th day	5th day	6th day	7th day	8th day
NAT	20±0.10	40±0.44	43±0.23	46±0.12	73±0.10	60±0.34	65±0.80
ACE	23±0.05	42±0.26	43±0.15	60±0.10	66±0.15	70±0.15	73±0.31
OXI	36±0.12	66±0.05	70±0.10	72±0.36	56±0.40	63±0.40	66±0.98
ATI	50±0.14	47±0.32	30±0.20	27±0.64	18±0.11	12±0.05	9±0.04

This development is associated with the electrostatic repulsion resulting from functional groups introduced on oxidized starch, which facilitated better paste clarity. Similar time-dependent reduction in transmittance (%) has been reported for hybrid maize starch (Lawal et al., 2005) and elephant foot yam starch (Sukhija et al., 2016), banana starch paste (Bello-Perez, Romero-Manilla & Paredes- Lopez (2000) and corn and amaranth starches (Bhandari and Singhal, 2002). Craig, Maningat, Seib, and Hoseney (1989) reported that starch pastes with more disintegrated granules gave higher light transmittance than those with more remnants of swollen granules.Also, in a previous study conducted on new cocoyam starch, Lawal (2004a) reported increased light transmittance following acetylation. Chemical substitution of the OH groups on the starch molecules by succinyl and acetyl moiety hampered the formation of ordered structure following gelatinisation, and these developments retarded retrogradation, which resulted in a more fluid paste with improved clarity. Improved paste clarity is a useful property in the manufacture of some confectionary products.

CONCLUSION

Starch was isolated from TZL-COMP4 maize breed. The light transmittance (%T), solubility, oil and water absorption capacity, and least gelation concentration were significantly affected. Introduction of carboxyl and carbonyl groups improved functional properties of modified starches over its native form. Increase in swelling and water absorption properties of modified starches over native starch indicated that modified TZL-COMP4 maize starches are potential industrial thickeners. Modification improved oxidised starch pasting properties.

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