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ISOLATION AND ACETYLATION OF STARCH USING ETHANOIC ACID FOR INDUSTRIAL USES

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Abstract

Starch from Cassava and Potato was isolated using non-conventional method and reagents. The isolated starch was chemically modified using ethanoic acid via acetylation and the success of the modification was evidenced by the changes observed on the functional properties such as, solubility, swelleability and film formability. The solubility of acetylated starch was found to vary with increase in acetylation time at constant temperature. FT-IR analysis further proved the success of the modification reaction from the following peaks 2926-3022 (−C─H stretch of aliphatic (−CH_3) of acetyl group), 1381-1402 (−C−CH_3) deformation in acetyl), 1030-1068 (C−O) stretching vibration in acetyl) and 1739, for carbonyl (C=O). Ash, carbohydrate, energy value, crude protein, phosphorus (P), potassium (K), sodium (Na), and calcium (Ca) of isolated Cassava starch were higher than those obtained from isolated potato starch. However, moisture and fat contents of isolated potato starch were higher than cassava starch although the crude fiber for both starches isolated was significantly similar. The prepared starch acetates gave low water swelleability and solubility making them good candidates for use in food such as stickening agents, thickeners and stabilizers in ice cream yoghurts etc. This research has shown the usefulness of the method adopted for starch extraction and the potential of using ethanoic acid as an acetylation agent

Keywords: Starch isolation**,** vinegar, acetylation, house hold bleach, swellable acetylated starch.

1. Introduction

Starch is a major carbohydrate storage product found in all chlorophyll-containing plants which is formed in the presence of sunlight CO_2 and H_2O (Corn Refinery Association, 2006; Rendon–Villalobos *et al.*, 2010).

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2 \qquad 1.1$$

Starch is made up of two types of polymers and both consist of small unit of glucose chains CRA, 2006; ISI, 2006; Adrina, 2004). The amylose portion has been described as linear while

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the amylopectin as highly branched both present as semi-crystalline granules in all higher plants (Adrina, 2004).

Structurally, researchers over the years have established that linear amylose contains glucose units bonded through glycosidic linkage between C1 of one glucose ring and C4 of the adjourning ring called the α1 → 4 glycosidic bond which can easily be broken via mineral acid or alkaline hydrolysis (Adrina, 2004; Corn refinery Association, 2006; Salwa *et al.*, 2010). However, the predominant model for starch is a concentric semi-crystalline multi-scale structure that allows the production of new nano elements (Herawati, 2012).

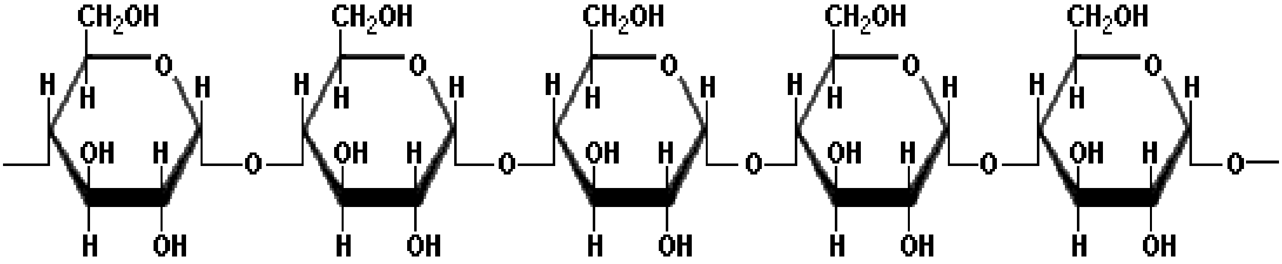

Fig.1 Structure of Amylose

Amylopectin portion of starch has been defined by several research groups as having a linear arrangement of glucose units which are bonded via α1 → 4 glycosidic bond but with alternating branching linkages between two adjacent glucose units through α1 → 6 glycosidic bonds which is the major difference between (Adrina, 2004; Salwa *et al.*, 2010).

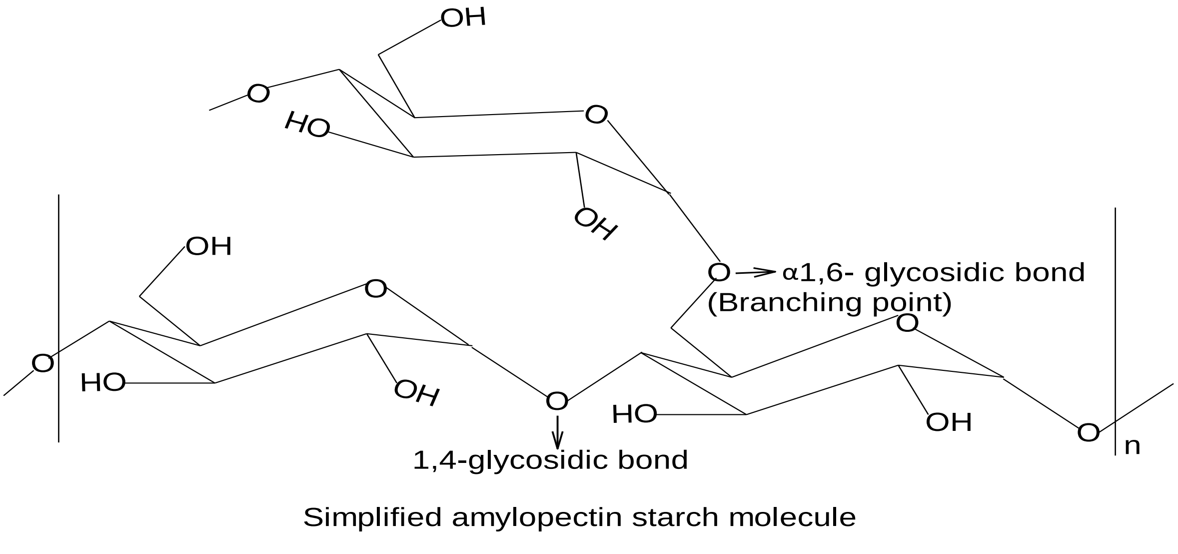

Fig. 2 Structure of Amylopectin

Starch has been reported by several sources as the only caloric source in most diets eaten worldwide and includes cereals such as rice, maize, corn, wheat, barley, tiger nut, millet, chest nuts, mung beans, peas, chick peas, e. t. c and tuber crops (yam, cassava, potatoes, cocoyam) (Awoya *et al.,* 2012; Bello *et al.,* 2010; Salwa *et al.,* 2010; Robbert *et al.,* 1998; Shorgren and Biswas, 2006; ISI 2006; Bente *et al.,* 2007). Starch is a white semi-crystalline powder, odorless and tasteless. It is insoluble in water forming a colloidal solution which sets to a gel on cooling accounting for some of its physical properties (Salwa *et al.,* 2010).

Starch is used as a diet, production of ethanol and glucose, as a stiffening agent, as a sweetener and stabilizer, preparation of starch derivatives with improved properties to meet industries demand and for production of papers, textiles, adhesives, confectioneries, pharmaceuticals and building materials (Adrina, 2004; CRA, 2006; ISI, 2006). Native starch lacks some properties which are required for some applications in most industries and these shortcomings include insolubility in cold water, loss of viscosity, thicken power after cooking, retro-gradation occurs after loss of ordered structure on starch gelatinization which results to water separation in starchy food systems. For these reasons, starch is modified so that it can have wider industrial applications (Taik *et al*., 1999; Gonzalez *et al*., 2002).

Olawale *et al*. (2007) and Sangseethong *et al.* (2010) had identified different industries where the application of modified starch is required. It was reported that conversion of starch food such as cassava into products for starch, food, ply wood, paperboard, textile and pharmaceutical industries could contribute significantly to the transformation of rural African economies and will improve the lots of the rural populace (Emire *et al.,* 2006). Several needs have also been identified particularly in the areas of eco-friendly, readily available and cheap reagents and appropriate technologies for the conversion of cassava and potato to value added products (Taik *et al*., 1999; Olawale *et al*., 2007).

Starch Isolation

Starch has been extracted from numerous tuber plants as well as cereal grains traditionally, industrially or at laboratory scale (Taik *et al.,* 1999). Extraction of starch from fresh tuber roots can be divided into five main stages: preparation (peeling and washing), pulping purification (starch washing), dewatering and drying, and finishing (milling and packaging). Starch isolation is relatively simple as there are only small amount of secondary substances, such as protein, in the roots. A first-grade quality starch can be obtained from starchy tuber crops using only water, and this makes the processing of starch and flour particularly suitable for developing countries and rural industries (Bente *et al.*, 2007; Dzogbefia *et al.*, 2008; Nandan *et al.,* 2011; Izuagie *et al*., 2012).

Modification

Modifications may involve altering the form of the granules or changing the shape and composition of the constituent of the biopolymers. Modifications are therefore carried out on the native starch to confer it with properties needed for specific applications (Sherry *et al.,* 2005; Dzogbefia *et al*., 2008). Modification can be chemical, physical or enzymatical and can be carried out on native starch via three states as suspensions, paste or solid (Robbert *et al*., 1998; Gonzalez *et al.,* 2002; Sherry *et al*., 2005; Collinson *et al*., 2010; Sangseethong *et al*., 2010; Singh *et al.,* 2011).

Acetylation

Starch esters are obtained as a result of replacement of some hydroxyl groups in starch by acetyl groups. This modification is regarded as acetylation and results in the formation of esters (Sherry *et al*., 2005). Good examples of modified starches are starch acetates, starch succinates and starch phosphates. Starch acetate is prepared via chemical reaction of native starch with acetylating agents such as acetic anhydride, the most common acetylating reagent, in the presence of a strong alkali such as NaOH/KOH as swelling agent for starch granules to enhance the consumption of acetyl groups (Robbert *et al*., 1998; Sherry *et al*., 2005). The reaction is an equilibrium process and proceeds according to a nucleophilic substitution at the unsaturated carbon while the NaOH acts as a promoter (Robbert *et al*., 1998).

According to (Gonzalez *et al*., 2002) chemically modified starch by placing substituent such as acetyl groups along a polymeric backbone, Modification decreases gelatinization temperature and increases transparency, viscosity and freeze–thaw stability as well as alteration of granular morphology as observed via electron microscope. They also, pointed out that acetylated starch showed lower moisture, ash, crude protein and apparent amylose content and pH and slight change in granule morphology than native starch. Modification of starch by acetylation affects the functional properties (water absorption, swelling power and solubility) of starch as the temperature changes (Robbert *et al*., 1998; Gonzalez *et al*., 2002).

Changes observed in acetylated starch have been attributed to bulky acetyl groups (Robbert *et al*., 1998; Gonzalez *et al*., 2002). Starch acetates of moderately high degree of substitution (DS) have been prepared under homogeneous conditions using solvents such as DMSO, DMAc/LiCl, DMF and pyridine (Shorgren *et al*., 2006). Such solvents are expensive and toxic, hence their commercial use is not favourable. According to Richardson *et al*., 2003; Shorgren *et al*., 2006, microwave heating accelerated the esterification and etherification of starches. Recently, it was shown that starch acetates and other esters can be made very efficiently on a micro scale without added catalyst or water simply by heating dry starch with acetic acid and anhydride at 180 ^{o}C for 2–10 min (Shorgren *et al*., 2006).

At this temperature, starch will melt in acetic acid (Shorgren *et al*., 2006). Starch needs to be modified because highly modified starch with a degree of substitution of 2 or 3 are of research interest for their solubility in acetone and chloroform and for their thermo plasticity (Robbert *et al*., 1998). Starches with low modification such as acetylated starch with a degree of substitution of 0.01 – 0.02 are still of commercial interest, their usage being based on properties with respect to thin film forming, binding, adhesives, thickening, stability and texture (Robbert *et al*., 1998). With the development of science and technology and the growing concern on environmental consciousness, there is the need to identify new sources of chemical agents with potentials for acetylation of biopolymers to replace those that are not eco-friendly and are commonly used for modification.

As environmental requirements have become of great importance in today’s society, there is an increasing interest in the industrial use of renewable resources and considerable efforts are being made in the research and development of starch and cellulose as the basic material in new application in order to help solve environmental pollution issues. The aim of this research work was to isolate starch using hypo (house hold bleach) and then prepare acetyl derivatives of the extracted starch using distilled commercial vinegar. Our research group started the investigation of vinegar for potential applicability in acetylation of biopolymers, where we acetylated four different species of wood grown in Nigeria (Azeh *et al*., 2012).

Since, then, we have continued to develop interest in the use of vinegar for acetylation because it is readily available, cost effective and environmentally friendly unlike acetic anhydride which produces acetic acid as by-products and has been restrictly prohibited in some countries from being used for acetylation.

2. Materials and Methods

Reagents and solvents

The potato and cassava used in this work were obtained from a Local farm (Emi Tsaduko`s farm located along Sancitagi Shonga Road, Edu Local Government Lafiagi, Shonga, Kwara State. The following analytical grade reagents were used: ethanol, methanol, acetone, sodium chloride, sodium hydroxide. Commercial vinegar was used for acetylation while of commercial hypo (3.5 % sodium hypochlorite) was used for starch extraction.

General experimental procedure for the preparation of samples

Removal of gums substances

Macerated Cassava/Potato tubers were soaked into the solution of sodium hypochlorite (3.5 % in hypo) separately and allowed to stand for 3 h to remove gums and discoloration of samples. Afterwards it was washed and extensively rinsed times with tap water.

Starch isolation from cassava and potato tuber

Cassava/Potato tuber was washed carefully and thoroughly with tap water, peeled, macerated and then blended with a blender equipped with razor blades with the addition of solution of hypo at interval of 1 min during blending and then filtered using a muslin cloth. The filtrate was washed extensively with cold tap water to separate the starch granules from cassava/potato debris and the filtrate was decanted after 24 h the starch milk was re-suspended in hypo solution for 1 h for discolourization and filtered and then air-dried over night at room temperature to obtained white starch cake.

Pre–treatment (Mercerization)

5 g each of oven-dried isolated starch was mercerized using 20 mL of 17 % sodium hydroxide in a beaker. The mixture was placed on a mechanical shaker and shaken for 1 h (at 75 revolutions per minute (rpm). A very thick and colorless gel was obtained for cassava starch samples while a pale–yellow solution was obtained for Potato starch samples.

Starch acetylation with commercial vinegar at constant temperature

Native Cassava starch sample (5 g, dry basis) was placed in a 400 mL beaker and mercerized for 1 h at room temperature (27 – 30 ^{o}C). Then 40 mL of commercial vinegar was added and stirred until homogeneous slurry was obtained. The slurry was heated to 100 °C and maintained for 30 min. The acetylation product was recovered using acetone as precipitating agent. The precipitate was filtered out and air dried at room temperature for three days. The procedure was repeated for 60, 120, 150 and 180 min for Cassava and Potato starch samples. Methanol was used as precipitating agent to recover acetylation products of Potato starch.

Swelling power / water absorption test of acetylated starches

Two sets of the native and acetylated cassava and potato starch samples were prepared. 1 gram of each sample was subjected to water absorption and swelling power test. The two sets of samples were soaked in distilled water for 30 and 60 min. After each round of immersion, the sample was removed, wiped off, then re–weighed and the final weights noted.

Using an expression % water absorption = $H_2 - H_1 / H_1$ X 100, where, H_1 = initial weight of acetylated starch and H_2 = final weight of acetylated starch sample.

Solubility test of acetylated starches

2 g of each sample was subjected to solubility test at room temperature (27 – 30 °C) and also at 50 °C. The two sets of samples were soaked in distilled water for 30 and 60 min and then heated to 50 °C. After each round of immersion, the sample was removed, wiped off, then re–weighed and the final weights were recorded.

Using an expression % Solubility = $S_1 - S_2 / S_1$ X 100, where, S_1 = initial weight of acetylated starch and S_2 = final weight of acetylated starch sample.

Proximate analysis of cassava/potato starch sample

The Proximate analysis of native Cassava/Potato starch samples was carried out at National Cereals Research Institute, Badeggi, Niger state, Nigeria.

Infrared spectroscopy

The IR spectra of the acetylated and control samples were recorded at National Research Institute for Chemical Technology (NARICT), Zaria, Kaduna state, Nigeria. The samples were run as (KBr) pellets, FTIR – 8400S Fourier transform infrared spectrophotometer in the range of 4000 cm^{-1} to 400 cm^{-1}.

3. Results and Discussion

Results of solubility test of acetylated cassava and potato starch samples

Table 1: Percentage water solubility of Acetylated Cassava starch samples for 30 min at ambient temperature.

S/No	ACS	Dry weight (g)	Weight after soaking (g)	Solubility (%)
01	ACS_1	2.0	2.09	Insoluble
02	ACS_2	2.0	2.15	Insoluble
03	ACS_3	2.0	2.18	Insoluble

Table 2: Percentage water solubility of Acetylated Cassava starch samples for 60 min 50ºC

S/No	ACS	Dry weight (g)	Weight after soaking (g)	Solubility (%)
01	ACS_1	2.0	1.93	3.5
02	ACS_2	2.0	1.74	13
03	ACS_3	2.0	1.56	22

Key: ACS_1 is Acetylated Cassava Starch for 30 min, ACS_2 is Acetylated Cassava Starch for 60 min and ACS_3 is Acetylated Cassava Starch for 120 min.

Table 3: Percentage water solubility of Acetylated Potato starch samples for 30 min soaking at ambient temperature

S/No	APS	Dry weight (g)	Weight after soaking (g)	Solubility (%)
01	APS_1	2.0	2.08	Insoluble
02	APS_2	2.0	2.16	Insoluble
03	APS_3	2.0	2.20	Insoluble

Table 4: Percentage water solubility of Acetylated Potato starch samples for 60 min 50°C

S/No	APS	Dry weight (g)	Weight after soaking (g)	Solubility (%)
01	APS_1	2.00	1.92	4
02	APS_2	2.00	1.66	17
03	APS_3	2.00	1.45	27.5

Key: APS_1 is Acetylated Potato Starch for 30 min acetylation; APS_2 is Acetylated Potato Starch for 60 min acetylation; APS_3 is Acetylated Potato Starch for 120 min acetylation.

% Solubility $=\frac{S1-S2}{S1}\ X\ 100$, where, S2 = final weight of acetylated starch sample and S1 = Initial weight of acetylated starch sample.

Tables 2 – 5 showed that acetylated starches do not dissolve at ambient temperature but rather absorbed water molecules and swelled due to the chemical replacement of accessible hydroxyl functional groups by acetyl group in starch samples during acetylation. Acetylated starches showed a decrease in their swelling power and swelling volume compared to native starch (Larotonda *et al*., 2004). This swelling result implied that acetylated starch samples obtained are fit for application as thickeners and stabilizers in ice creams, yoghurts etc. It is also an indication that the acetylated starches synthesized in this work can also be used in pharmaceutical industries to prevent tablet disintegration if used as binders (Larotonda *et al*., 2004, Ohwoarworhua & Osimowo, 2010).

The solubility of acetylated starch prepared increased as the temperature of the dissolving medium was raised as reported by (Gonzalez *et al*., 2002). It was also found that solubility increased with increase in acetylation time. The starch acetates synthesized also showed plastic forming properties as the paste obtained were air-dried forming very hard films after three (3) days drying period.

Results of water absorption and swelling power tests of acetylated cassava and potato starch samples.

Table 5: Percentage water absorption of Acetylated Cassava Starch samples for 30 min at ambient temperature.

S/No	ACS	Dry weight (g)	Weight after soaking (g)	PWS (%)
01	ACS_1	2.0	2.09	4.5
02	ACS_2	2.0	2.15	7.5
03	ACS_3	2.0	2.18	9

PWS: Percentage Water Swelleability.

Table 6: Percentage water absorption of Acetylated Cassava Starch samples for 60 min at ambient temperature.

S/No	ACS	Dry weight (g)	Weight after soaking (g)	PWS (%)
01	ACS_1	2.0	2.18	9
02	ACS_2	2.0	2.30	15
03	ACS_3	2.0	2.38	19

PWS: Percentage Water Swelleability

Table 7: Percentage water absorption of Acetylated Potato Starch samples for 30 min at ambient temperature.

S/No	APS	Dry weight (g)	Weight after soaking (g)	PWS (%)
01	APS_1	2.0	2.08	4
02	APS_2	2.	2.16	8
03	APS_3	2.00	2.20	10

PWS: Percentage Water Swelleability

Table 8: Percentage water absorption of Acetylated Potato Starch samples for 60 min at ambient temperature.

S/No	APS	Dry weight (g)	Weight after soaking (g)	PWA (%)
01	APS_1	2.0	2.16	8
02	APS_2	2.0	2.32	16
03	APS_3	2.0	2.40	20

Key: PWA is Percentage Water Absorption

Set of the samples were prepared as shown in tables 4 – 8 and it was observed that acetylated Cassava and Potato starch samples absorb more water and possess high swelling power than native Cassava and Potato starch samples. This is as a result of hydroxyl functional groups (-OH) that have been substituted during acetylation by acetyl groups (CH_3CO-). This phenomenon depends on the degree of substitution by acetyl groups (Shorgren *et al*., 2006, Sherry *et al*., 2005, Gonzalez *et al*., 2002).

The results indicate that both swelling power and solubility were temperature dependent and values increased with increase in temperature for both starches. It was also noted that as the temperature of the medium increased, starch acetate molecules became more thermodynamically activated resulting in increase in granular mobility exposed non accessible –OH groups and enhanced penetration of water molecules which facilitated their improved swelling capacities.

Results of proximate analysis of cassava and potato starch samples

Table 9: Proximate Composition of Extracted Cassava, Potato and EPR starches

S/NO.	SD	CHO	FAT	PRO	ASH	MOISTURE	EV	P	K	Na	Ca
									(mg/100g)		
01	Cassava Starch	93.11	0.10	3.76	0.80	2.23	388.38	464	70	67	70
02	Cassava Starch	93.08	0.13	3.78	0.81	2.20	388.61	463	72	69	71
03	Potato Starch	91.70	0.29	2.85	0.30	4.86	380.81	38	30	61	45

04	Potato Starch	92.06	0.25	2.89	0.31	4.49	382.05	39	32	63	47
05	EPR Starch)	91.55	0.30	3.95	0.05	3.70	384.70	1001.60	22	29	13
06	EPR (Starch)	91.95	0.28	3.96	0.07	3.74	384.16	1001.63	24	30	15

SD = Sample Description; CHO = Carbohydrate; PRO = Protein; EV = Energy; CHO is by difference and Energy value is by calculation. Unit of the minerals is in mg/100g.

Pharmaceutical grade starches have the specifications of white coloration, tastelessness odourlessness absence of foreign matters, insolubility in water and 96 % ethanol, high energy values, low crude protein and fat (especially solani amylum or potato pharmaceutical-grade starch). The proximate analysis results of extracted and laboratory-grade starches showed that, extracted potato starch has the highest moisture content than cassava and laboratory grade starch. This explained why microbial resistance of potato starch is less and hence can easily spoil. It also had lowest crude protein value (2.85 %), energy value (1593.31Kj/100g), and Phosphorus (38mg/100g) (Awoya *et al.*, 2012). Though its' carbohydrate and fat content are slightly the same with that of laboratory grade starch reagent (EPR). This is an indication that, the reagents and method employed for starch extraction can also be used for the extraction of pharmaceutical-grade analytical starch.

In the order hand, cassava starch has the highest ash content, carbohydrate, and energy value, Potassium, Sodium and Calcium as compared to EPR starch. This implied that, the method and chemicals used will be viable for application in pharmaceutical industry, extraction of foods and pharmaceutical grade starch. In general, the extracted potato and cassava starch samples had highest ash, carbohydrate, energy value (especially cassava sample), moisture (especially potato sample), K, Na, and Ca as shown via proximate analysis while laboratory starch reagent is lower in all these as compared to cassava and potato starch isolated. Pharmaceutical grade native potato starch also called solani amylum has characteristics of lower crude protein and fat which was also observed in the potato starch isolated in this work.

This explained the novelty of the method used for the isolation of samples (potato and cassava starches) and is valid enough to be used for obtaining pharmaceutical-grade starch of any type (Bente *et al.*, 2002, Mistry *et al.*, 1992, Larotonda *et al.*, 2004). Extracted Cassava and EPR starches had close protein and energy values. A close carbohydrate values were also observed between potato, cassava and EPR starches. It is also observed that, the major component of starch is carbohydrate in all starchy materials with other classes of food such as fat, proteins, minerals etc present in minute quantity which varies from starchy crops to crops as can be seen from the extracted starch samples and the EPR starches used in this work (ISI, 2006; Nandan *et al*., 2011, Olawale *et al*., 2007, Klanarong, 2009, Taik *et al*., 1999, Miyazaki *et al*., 2006, Singh *et al*., 2011, Gonzalez *et al*., 2002, Sangseethong *et al*., 2010).

Infrared spectra studies

Table 10: Infrared assignment of acetylated and native starch samples

Frequency (cm^{-1})	Assignments	References
3367.83 – 3456.55	–OH bonded stretching vibrations	Larotonda *et al*., 2004; Ramazan et al., 2002.
2926.11 – 3022.55	C–H stretching vibrations in starch	Larotonda *et al*., 2004; Ramazan *et al*., 2002.
1581.68 – 1633.76	water absorbed in the amorphous parts of starches	Ramazan *et al*., 2002.
1381.08 – 1402.30	C–CH_3 deformation in acetyl groups	Larotonda *et al*., 2004.
1030.02 – 1068.60	C–O stretching medium	Bello *et al*., 2010.
1739.85	C=O stretching of acetate group	Chowdary *et al*., 2011; Adebajo *et al*., 2006, Larotonda *et al*., 2004; Rendon – Villalobos *et al*., 2010.

The IR absorption spectra of native starches (potato and cassava), acetylated potato and cassava starch samples are shown in **Table 10.** The strong absorption bands observed at 3581.93, 3456.55, 3450.77, 3443.05, 3441.12, 3439.19, 3433.41, 3427.62, 3421.83, 3419.90, 3412.19, 3408.33, 3398.69, 3398.69, and 3367.62cm^{-1} as separately seen in each IR spectra are feature absorption bands of –OH group linkages. The acetylation of cassava and potato starch samples at constant temperature (100^{o}C) at varying time showed an increase in –OH absorption bands for 30 min acetylation (3408.33 cm^{-1} potato starch) and 120 min acetylation

(3450.77 cm^{-1} potato starch) but sharp decrease was noticed as acetylation reaction continues to 150 min (3398 cm^{-1} potato starch).

To further investigate the effect of time, the reaction was left and monitored till 180 min but a reversed reaction was observed to be the case as absorption band had increased to 3433 cm^{-1} at 180 min. This same observation was noted for cassava starch samples treated under the same condition. This is an indication that, reaction time play significant role in acetylation reaction as increase in reaction time led to deacetylation of the products formed being a reversible process (Larotonda *et al.*, 2004; Ramazan *et al.*, 2002). Due to the presence of prodigious hydroxyl functional groups in starch, appropriate reaction time is required for acetylation/elimination of all the accessible –OH functionalities in starch (Azeh, 2010).

The controlled sample showed lower absorption bands which implied that, no acetylation had occurred. The absorption bands at 1068-1030 cm^{-1} is assigned to the stretching vibrations of C–O in starch which occurred as a result of acetylation (Azeh, 2010; Mirna, 2010; Bello *et al.*, 2010). The results of acetylation at constant time while varying the temperature and at constant temperature while varying the time, showed a steady increase in absorption band at 1047 cm^{-1} for samples acetylated at ambient temperature and at 1057 cm^{-1} at 40 ^{O}C for 30 min acetylation time, respectively. This is an indication that acetylation proceeded with increasing temperature (Azeh, 2010; Bello *et al.*, 2010). The C=O stretching band of acetate group at 1739 cm^{-1} for acetylated potato starch sample for 120 min acetylation was a clear evidence that acetylation had taken place.

The absorption band at 3022-2926 cm^{-1} has been assigned to C–H stretching vibrations in starch due to asymmetric stretching of aliphatic $-CH_3$ group in acetate. This also indicated that acetylation had occurred in starch (Azeh, 2010; Larotonda *et al.*, 2004; Ramazan *et al.*, 2002). The absorption spectra band at 1402-1381 cm-^{1} in the IR spectra of acetylated samples are ascribed to C–H deformation of $-CH_3$ group in acetyl ($-C-CH_3$) which confirmed the formation of ester bond due to acetylation in starch (Azeh, 2010; Ramazan *et al.*, 2002). The band at 1633-1581 cm^{-1} is attributed to water absorbed in the amorphous part of acetylated and native starch (Larotonda *et al.*, 2004).

Effect of acetone and methanol on native and acetylated starches

The introduction of 17 % sodium hydroxide (NaOH) solution on native starch samples promoted the rate of chemical reaction by increasing the surface area of the starch granules. This explained why the starch granules swelled as 17 % NaOH solution was introduced (Miyazaki *et al*., 2006; Singh *et al.*, 2011; Gonzalez *et al*., 2002; Azeh, 2010; Cheku, 2012; Adebayo *et al*., 2004; Larotonda *et al*., 2004; Gunorubon, 2012; Awoye *et al*., 2012). The degree of substitution has been reported to increase with increase in NaOH concentration from 10–40 % but a decrease in DS is observed for a 50 % NaOH concentration for cassava and potato starches.

The Viscosity of acetylated starch has been said to decrease as NaOH concentration is increased (Rachtanapun *et al.,* 2012). Acetone was used as a precipitating agent to recover acetylated cassava starch while methanol was used to recover acetylated potato starch taking advantage of their insolubility in excess of these solvents. Other workers have reported the use of ice chips to precipitate out acetylated starch samples. This proved why the resultant acetylated cassava and potato starch samples were not fully recovered and hence accounted for low weight percentage products recovered (Ohwoarworhua *et al*., 2010). Acetylated cassava and potato starch samples recovered with acetone and methanol showed remarkably improved changes in physical appearance, compaction and disintegration properties. The powdery flow properties, hydration and swelling capacities of acetylated starches were also improved as outlined by (Ohwoarworhua *et al*., 2010).

4. Conclusion

Acetylated cassava and potato starch have been synthesized using commercial vinegar as acetylating agent in the presence of 17 % NaOH as catalyst. It was observed that acetylation via commercial vinegar changed both the physical and chemical properties of native cassava and potato starches as observed in this work. This is an indication that vinegar is a viable acetylating agent for biopolymers and can replace other acetylating agents such as acetic anhydride that are not eco-friendly due to the release of noxious by products. We successfully prepared starch acetates with low water swelleability and solubility.

These properties shown by starch acetates synthesized make them good candidates for application in food such as stickening agents, thickeners and stabilizers in ice screams yoghurts etc. Native starch was isolated using a modified method and the properties of these starches were comparable to those of laboratory grade reagent starch and pharmaceutical grade starch as indicated by the proximate analysis composition.

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