

Isolation of Cassava Starch and Synthesis of Acetyl Derivatives Using Vinegar

Azeh Y., Paiko Y.B., Elele U.U., Adesina G.O., Mohammad M.A., Mohammed D.Z., Gimba A.A.

Department of Chemistry, Ibrahim Badamasi Babangida University, Lapai, Nigeria

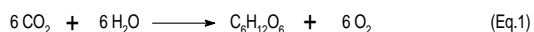
ABSTRACT

This study was carried out to assess and establish the changes in physicochemical parameters of cassava starch (CS) after modification using mercerization and acetylation. Substituted starch acetate was prepared by reaction of native CS with commercial vinegar and NaOH. The modification was confirmed by the titrimetric analysis and Fourier Transformed Infrared Spectroscopy. The presence of absorption band in FT-IR Spectra for acetylated samples confirmed the success of modification. The scanning electron microscopy (SEM) of samples suggested that acetylation at low temperature gave rise to smooth surfaces of CS granules, while at high temperature; the smooth surfaces of starch granules were changed into fibrous morphology after acetylation. Mercerization at long time also gave rise to fibrous surfaces of starch granules. Acetylated samples gave high solubility index more than both mercerized and native samples. Acetylation products at higher temperature showed high swelling power than native samples. Samples that were acetylated for 150 min. had a decrease in swelling power while the water absorbing capacity of the acetylated samples was also high compared to native starch samples.

Keywords: Cassava, starch, mercerization, acetylation, FT-IR, SEM

INTRODUCTION

Starch is the major by-product of the reaction between water and carbon (IV) oxide in the presence of sun light as catalyst and is stored as carbohydrate in all chlorophyll containing plants (Mistry, Schmidt, Eckholl & Sutherland, 1992).



Each chain is made up of series of six membered ring sugars commonly known as glucose units link together through a covalently bonded Carbon–Oxygen (C–O) of the anomeric carbon, C1 of one glucose ring and C4 of the adjoining ring called the $\alpha 1 \rightarrow 4$ glycosidic bond which can easily be degraded by mineral acid or alkali hydrolysis (Mistry et al., 1992; Adrina, 2004; Gunorubon & Kerpugile, 2012). The two major reactive components of starch are the linear amylose and the highly branched amylopectin present as semi crystalline granules in all higher plants (Adrina, 2004).

The linear amylose component of starch can be structurally represented as shown in Figure 1.1.

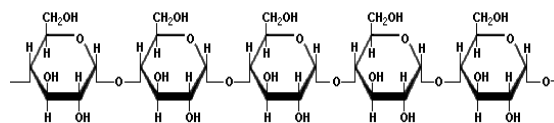


Fig.1.1 Structure of Amylose component of starch

The amylopectin molecule is different from the amylose portion due the presence of a branching chain that alternates between two adjacent glucose units through $\alpha 1 \rightarrow 6$ glycosidic bonds (Adrina, 2004; Gunorubon & Kerpugile, 2012). The similarities between these two components can be seen from the linear arrangement of glucose units bonded via $\alpha 1 \rightarrow 4$ glycosidic linkages.

Received 26 October, 2016
Accepted 25 November, 2016
Address Correspondence to:
yakubuazeh@gmail.com

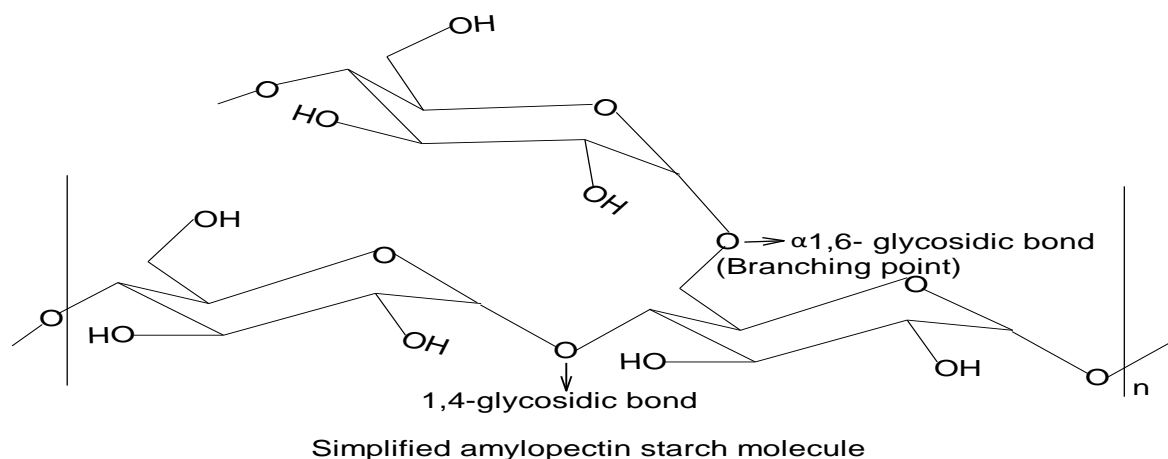


Fig. 1.2 Structure of Amylopectin

As a natural and the most abundant renewable and biodegradable re-source available to man, starch serves as the main energy re-serve and constitutes a major energy source in human and animal diets. In addition, it is widely used as a raw material in many industrial applications, e.g. in the paper, paint, textile, food and pharmaceutical industries (Sara & Gorton, 2003). Consequently it is of special interest to researchers in diverse disciplines such as agriculture, Forestry, Science, Engineering and Technology (Robin, Rose, Omi, Forry, Durall, & Bigg, 2012). It has great potentials for providing a broad range of important functional properties and possesses several advantages that make it essential for industrial application. It is non-toxic, renewable, and biodegradable and can be modified (Sara & Gorton, 2003; Wurzburg, 1986; Brandt, 1986; Van der Burgt, Bergsma, Bleeker, Mijland, Van der Kerk-Van Hoof, Kamerling & Vliegthart, 2000). The amylose constitutes (20 - 30 %) and amylopectin (80 - 70 %) can be used to create high performance biocomposites /nanocomposites with unique outstanding properties (Bente, Tina, Ole, Andreas, Niall, Lotte & Lars, 2007). Starch is a versatile and useful raw material not only because it is cost effective but also of the ease with which its physicochemical properties can be boosted through chemical modification (Dzogbefia, Ofosu, & Oldham, 2008). As environmental requirements have become of great importance in today's society, there is an increasing interest in industrial use of renewable resources, and considerable efforts are now being made in the

research and development of starch as the basic material in new applications. In order to increase the industrial use and to fulfil the various demands for functionality of different starch products, they are often modified (Sara & Gorton, 2003). An important source of starch is from cassava (*Manihot esculenta Cranz*) which is a widely cultivated starchy root crop in many developing countries, especially in Africa, Latin America and Asia (Nandan, Umashankar & Sankar, 2011). Starch has been extracted from different sources e.g. potatoes, corn, cassava, rice, wheat, tiger nut, maize, yam using different conventional methods and can be preserved for a long period (Benesi, 2004). The functional properties of starch such as viscosity, gelatinization-temperature, and solubility, amylose content, average granule diameter, swelling power, pasting characteristics, water binding capacity, oil absorption capacity, lipid, ash, moisture, fibre, enthalpy of gelatinization (ΔH_G) and profile texture have been reported (Adrina, 2004; Benesi, 2004; Dzogbefia, 2008; Izuagie, Hassan, Uba, Achor, Sahabi, & Sadiq, 2012; Lim, Lee, Shin, Lim, 1999; Shimelis, Meaza, & Rakshit, 2006). Starch modification should be investigated to meet the needs of the more specialized technology. Nanocomposites materials have been obtained using glycerol plasticized starch as the matrix and a colloidal suspension of cellulose nanowiskers as the reinforcing phase (Bent *et al.*, 2007). This study focuses on the assessment and evaluation of starch after modification by Fourier Transform Infrared Spectroscopy and Scanning Electron Microscope.

MATERIALS AND METHODS

Reagents and Solvents

Cassava used in this work was obtained from a Local farm in Lapai, Niger State. All reagents used were of analytical grade. These include; ethanol, methanol, acetone, sodium chloride, sodium hydroxide, potassium hydroxide. Vinegar [(Heinz) made in England by H. J. Co. Ltd] was used for acetylation of samples while commercial hypo (3.5 % sodium hypochlorite) was used for starch extraction and bleaching to obtain oxidized starch.

General Experimental Procedure for the Preparation of Samples

Removal of Gums, Lignin and Waxy substances

Macerated Cassava tubers were soaked into a solution of sodium hypochlorite (3.5 % w/v of hypo). The solution was prepared by transferring 1000 cm³ of hypo into 4 L of distilled water separately and allowed to stand for overnight to remove gums, lignin, waxes and discoloration of samples. Afterwards it was washed and extensively rinsed 3 times with distilled water.

Starch Isolation from Cassava tubers

Starch isolation in the present study was a modification of the conventional method. Cassava tubers were carefully and thoroughly washed with tap water. They were then peeled and macerated using a steel knife and then ground with a 750 watts mascot mixer grinder equipped with razor blades with the addition of 100 cm³ of a 500 cm³ solution of hypo in 2 L of water at interval of 1 min during grinding and then filtered using a four-fold muslin cloth. The filtrate was washed extensively with distilled water to separate the starch granules from cassava debris. The filtrate was allowed to stand for 24 h for sedimentation to take place and then decanted. The mucilage was unusually not sticky to starch milk and so was decanted off the surface of starch milk. Starch milk was repeatedly washed with de-ionized water until the supernatant (water) was neutral. The water was decanted and the starch milk was air dried overnight at room temperature and then placed in an oven at 105 °C for 60 min to obtain a white starch cake which was pulverized and stored in clean plastic containers for further analysis

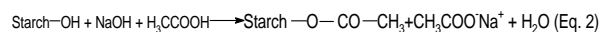
(Izuagie, Hassan, Uba, Achor, Sahabi, & Sadiq, 2012; Azeh, Olatunij, Mohammed & Mamza, 2013; Mistry, Schmidtd, Eckholl & Sutherland, 1992).

Starch Mercerization

Starch mercerization was carried out by treating 10 g each of oven dried isolated starch granules using 20 cm³ of 20 % KOH in a beaker at different time intervals of 5, 10, 15, and 20 min at ambient temperature and was stirred manually. After stirring each sample for the stipulated time, brown viscous slurry obtained was treated with acetone to precipitate out the mercerized starch as thick rubbery-like mass which was air-dried for one week followed by oven drying for 60 min at 45 °C. A dark-brown gel was obtained (Azeh, Abubakar, & Umar, 2014).

Starch Acetylation with Commercial Vinegar at Variable Temperature

10 g of Cassava starch sample was placed in a 400 cm³ beaker and 50 cm³ of commercial vinegar was added and a magnetic stirring bar was placed and the content was placed on a magnetic stirrer and stirred mechanically for five minutes. After which 20 cm³ of 4 % NaOH (1.6 g) was added and stirred for 30, 60, 90, 120, and 150 min at 37, 45, 60, 75, and 90 °C which gave white homogeneous slurry. The acetylation product was recovered using acetone. The precipitate was filtered out and air dried at room temperature for three days. The samples obtained were stored in sample bottles and were used for further analysis (Luis, Edith, Paul, Guadalupe, & Sandra, 2010; Azeh *et al.*, 2014).



Swelling Power / Water Absorption Test of Acetylated Starches

1.0 g of the acetylated cassava starch sample was subjected to water absorption and swelling power test. The samples were soaked in distilled water for 30 and 60 minutes. After each round of immersion, the sample was removed, wiped off, then re-weighed and the final weights were noted (Azeh *et al.*, 2014).

Using the expression = $\frac{H_2 - H_1}{H_1} \times 100$

Where, $H2$ = Final weight of acetylated starch sample and $H1$ = Initial weight of acetylated starch sample (Azeh *et al.*, 2014).

Solubility Test of Acetylated Starches

2.0 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 (Azeh *et al.*, 2014).

$$\text{Using an expression} = \frac{S1 - S2}{S1} \times 100$$

Where, $S2$ = Final weight of acetylated starch sample and $S1$ = Initial weight of acetylated starch sample.

FT-IR of Mercerized and Acetylated Starch

The FT-IR spectra of both mercerized and acetylated starch samples were recorded at the Chemical Engineering Department, Ahmadu Bello University, Zaria, Kaduna State. Samples were run as (KBr) pellets, FTIR-8400S Fourier Transform Infrared Spectrophotometer in the spectra range of 4000-400 cm^{-1} (Luis *et al.*, 2010; Azeh *et al.*, 2014).

Scanning Electron Microscopy

The surface morphology of the samples was carried out at Ahmadu Bello University, Zaria, Kaduna State. The PhenomWorld ProX desktop scanning electron microscope with fully integrated and specifically designed EDS detector made in Eindhoven Netherlands was used.

The alkali treatment changed the colour of the starch granules from white to brown and dark brown according to different mercerization grades, indicating that the removal of residual wax, fatty substances and lignin had been achieved (Luis *et al.*, 2010).

RESULTS AND DISCUSSION

FT-IR of Mercerized Starch Samples

In native starch spectral absorption bands were observed at 3461 cm^{-1} , but bonded -OH absorptions in NaOH treated samples were found around 4400-3377 cm^{-1} with broad peaks shown in Figure 1.3.

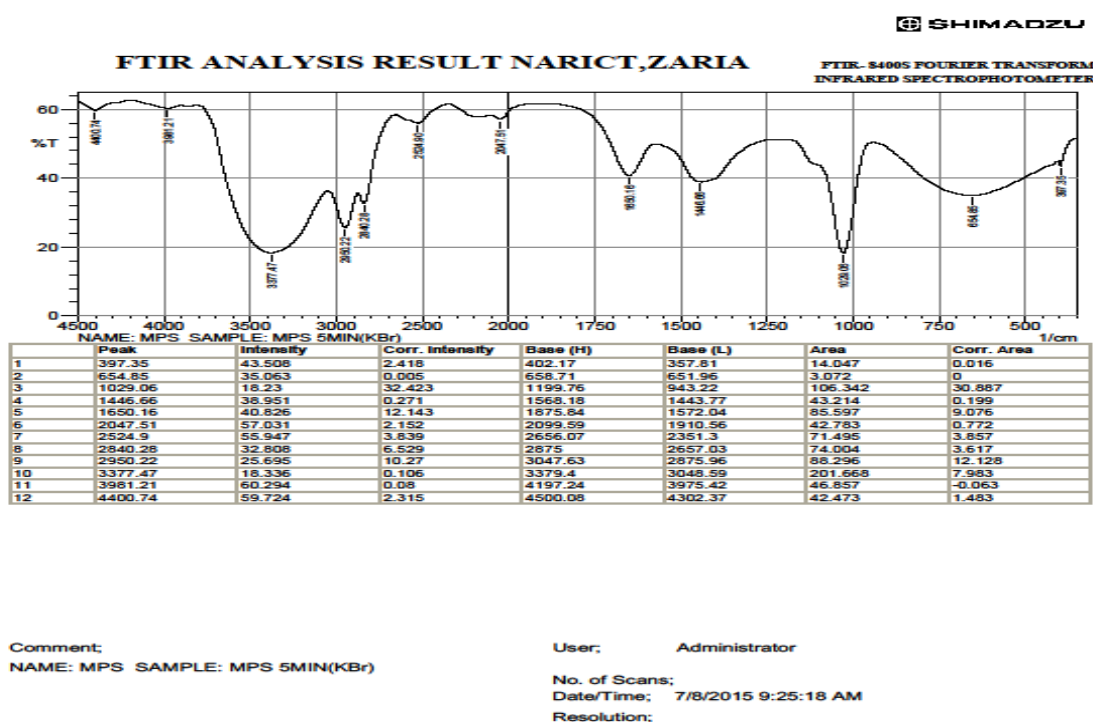


Fig. 1.3: FTIR of Mercerized Cassava Starch

This is evidence that alkali treatment breakdown some hydrogen bonded network and this trend increased with increasing reaction time. It was observed that the intensity of the –OH group first increased and then diminished with increasing time.

Important peaks at 1182 and 1160 cm^{-1} assigned to C-O-C and C-O stretching vibrations in starch greatly diminished to 1030, 1028 and 1021 cm^{-1} (Hongwei, Yuan, Qun & Zhikun, 2015). This trend suggests the hydrolysis of the glycosidic linkages in starch molecules. This trend increased with time up to the 20 min maximum reaction time used. The peak intensity of the –OH groups also decreased, indicating the breakdown of hydrogen networks in starch to yield starch monomers. Starch gelatinization was first observed for the first 5-10 min time. This property was observed to increase as the reaction time increased up to the maximum reaction time used. This is an important observation in that; it will allow for applications in food, pharmaceutical and plastic industry where functional properties of gels are required as an important aspect of starch technology (Omar, Haq & Elizabeth, 2013).

The SEM images of the different mercerized starch grades clearly showed that, the amorphous portion that is randomly distributed among the amylopectin clusters was degraded as a result of loss of the natural organization of the chains to yield thermoplastic films. The breakdown of hydrogen network and the glycosidic linkages in starch molecules led to the increased swelling observed in starch molecules. The evidence can be observed by the disruption of granule morphology leading to increased surface area as reaction time increased in accordance to literature reports (Omar, Haq & Elizabeth, 2013; Rachtanapun, Simasatitkul, Chaiwan & Watthanawojasakun, 2012). The increased surface area is implicated to the adsorption of Na^+ ions unto the crystalline surface of starch which then promotes granule swelling and surface

modification for improved fiber-matrix surface adhesion. This property can be utilized for high mechanical strength mercerized starch composite formulation with anionic polymers. It was evident that starch samples mercerized at high NaOH concentration and high temperature were more elastic and showed thermo plasticity as revealed by SEM images. These properties will influence their used in composites and other applications where strength needs to be improved as documented (Modibbo & Nkafamiya, 2009).

Mercerized starch is commonly known as cationic starch and can be used as a sustainable product, serving as flocculants and retention agents in the paper industry. Mercerized starch products offer also large potential as ion changers in water treatment processes. Starch/cellulose and cellulose derivatives composites prepared under different conditions have been reported to exhibit high mechanical properties (Koh, 2013; Sherif & Abdullah, 2013; Morsyleide, Bor-sen, Eliton, Delilah, Tina, Luiz, William & Syed, 2009). The CO absorption bands were observed at 1634, 1650, 1647 and 1646 cm^{-1} for NaOH treated samples at 5, 10, 15 and 20 min reaction time respectively. This bands are absent in control sample. An important observation was the gradual decrease of these bands with increasing reaction time which is indicative of an increased hydrolysis of starch macromolecules. Another important clue for the decrease in the CO absorption is due to reactions involving CO with NaOH to form –OH groups and the extent of conversion of CO by NaOH depends on the reaction time (Salisu, Musa, Abbas, & Kogo, 2013). This trend was evidenced by the reduction in CO absorption bands from 10-20 min hydrolysis.

FT-IR of Acetylated Starch Samples

FT-IR absorption peaks for acetylated samples obtained at various reaction time and temperature and the control sample are as indicated in Figure 1.4.

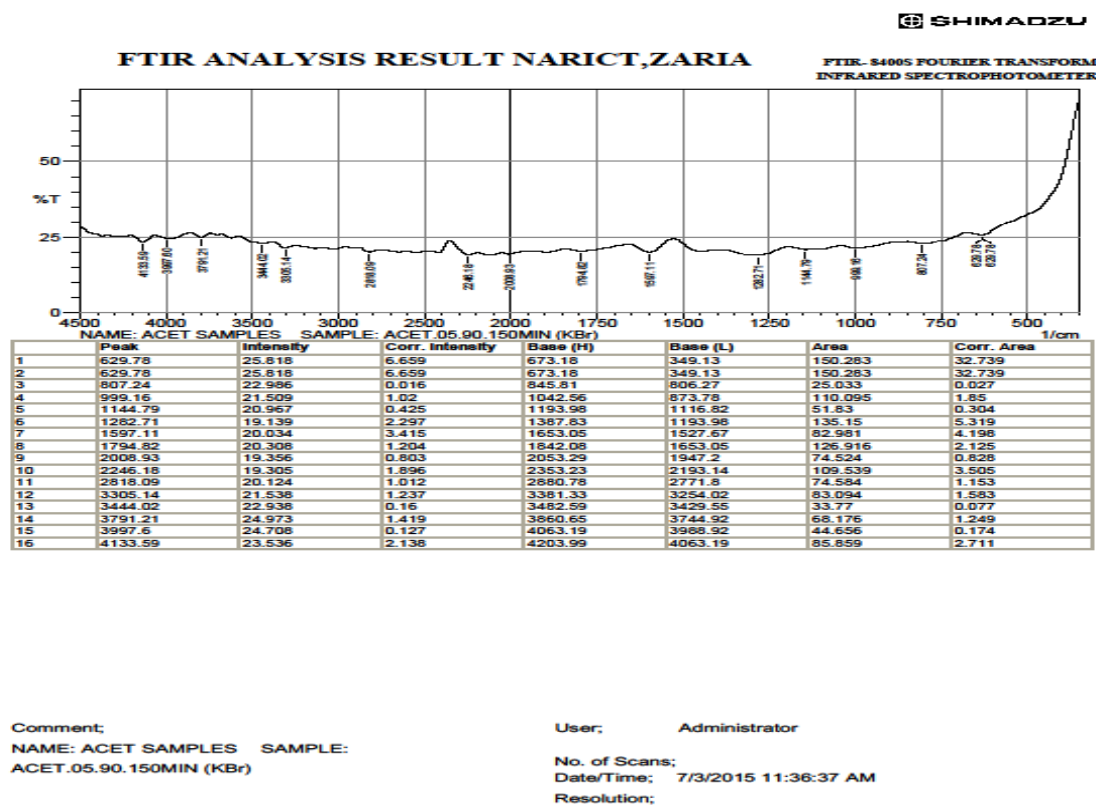


Fig. 1.4: FTIR of acetylated Cassava Starch

The CO absorption bands at different reaction conditions are 1640, 1641, 1640, 1640 and 1642 cm^{-1} . Other important bands indicative of the success of acetylation are bands observed at 2932, 2926, 2920 and 2929 cm^{-1} , assigned to symmetry stretching vibrations of CH of methylene group. The bands at 1358, 1389, and 1385 cm^{-1} have been attributed to $-\text{CH}_2$ deformation bending vibrations in acetate ester group due to acetylation. The implications for this is that the presence of hydrophobic acetyl groups in starch will allow for decrease in surface energy of starch and increased surface compatibility with hydrophobic polymers for construction of composite with high strength. The absorption band at 1642 cm^{-1} in native oxidized starch is due to CO of aldehyde group formed during hypochlorite treatment. The band which appeared at 4467 – 3774 cm^{-1} are due to bonded $-\text{OH}$ groups in starch (Rachtanapun et al., 2012; Salisu et al., 2013; Yu et al., 2015). The absorption band at 3344 - 3322 cm^{-1} is assigned to free bonded H_2O (Salisu et al., 2013). Another supportive reason for the observation of the band at 3400 – 3344 cm^{-1} was attributed to the shift in $-\text{OH}$ group

stretching vibration due to the weakening of $-\text{OH}$ bond by intermolecular hydrogen bonding in the glycosidic region. The peaks at 1144 – 850 cm^{-1} are characteristic absorptions of C-O stretching in C-O-O and C-O-H in the glycosidic ring of starch (Bohari, Mohammed, Cairu, Kamaruddin & Bukhori, 2011). The crystallinity band at 930 – 600 cm^{-1} is due to out-of-plane bonded $-\text{OH}$ deformation and C-H deformation vibrations (Bohari et al., 2011). The band at 3400 - 3344 cm^{-1} appeared sharp for the 60 min acetylation products and was present in all grades of acetylated samples. This band suggests the weakening of intermolecular hydrogen bonding network in starch due to masking of accessible $-\text{OH}$ groups in starch by acetyls as reported by (Jiaying, Yan & Tie, 2012). The implication is that they can be used as drug carriers for the control release of active components. This band appeared broad in control sample indicating the extent of the free and accessible $-\text{OH}$ groups in native starch. The success of acetylation using commercial vinegar was clearly observed due to decreased intensity of the absorption peaks of bonded hydrogen network of $-\text{OH}$ groups in all

acetylated samples. This is due to reduction in the number of free and accessible –OH groups implicated by substitution of –OH by acetyl groups (Luis, Edith, Paul, Guadalupe & Sandra, 2010). The band observed at 1282 cm⁻¹, has been assigned to C-O stretching vibration of acetyls due to acetylation (Luis *et al.*, 2010; Adebajo & Frost, 2004).

Morphological Properties of Samples

The morphology of starch granules was studied using SEM. The technique produces high resolution as it allows closely spaced features in

a sample to be examined. Samples were viewed at various magnifications in order to provide clear pictures of the nature of the granule morphology and size. At 4400 x magnification, acetylated starch exhibited different morphologies such as; oval, round and flattened shapes with smooth surface. Clusters of various sizes were observed due to agglomeration as a result of physical interactions. At lower mag. 500 x large and small clusters of starch granules were observed. These varied in their sizes as evidenced at 4400 x and 1000 x magnifications Plate I.

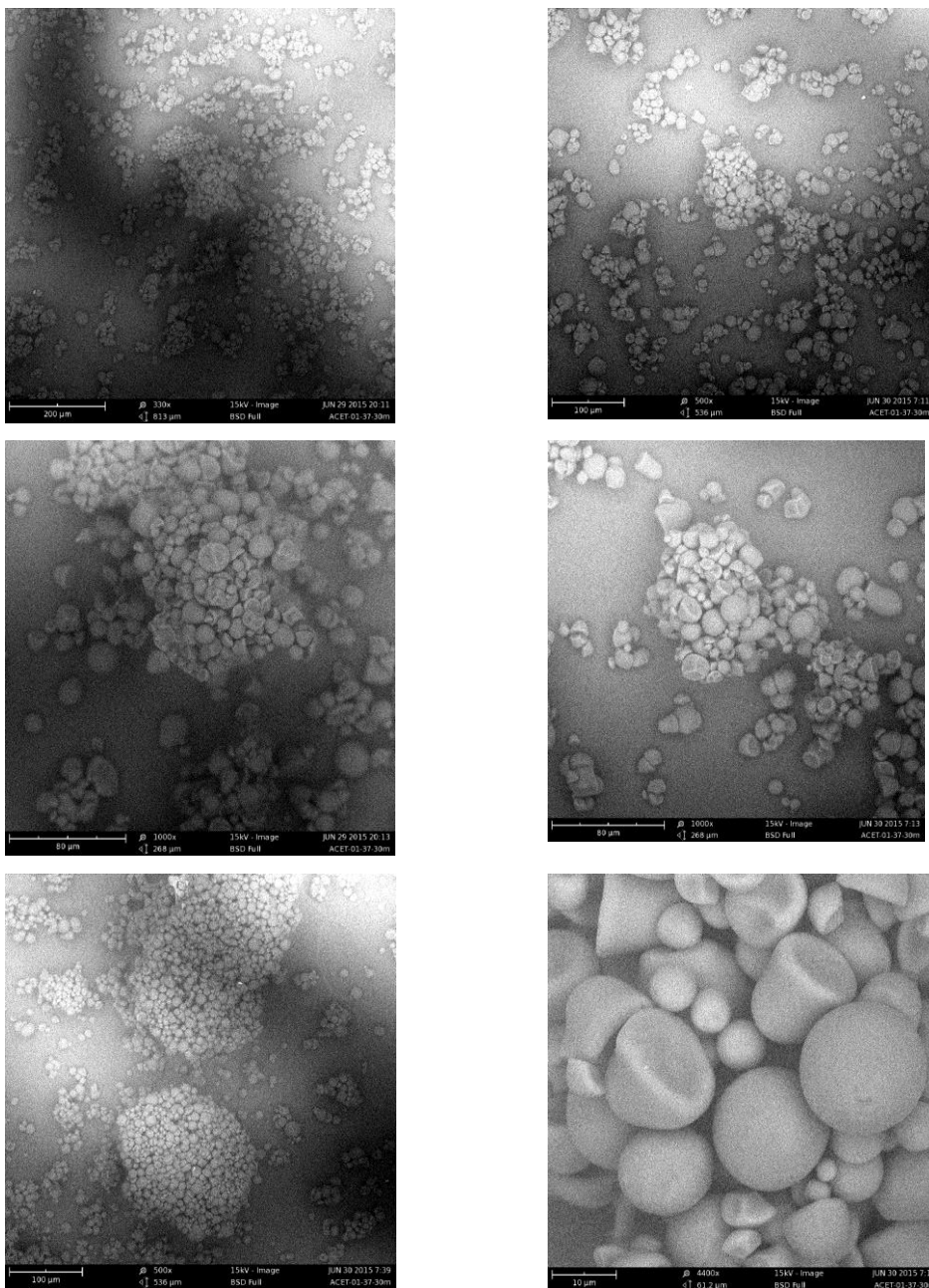


Plate I: SEM images of acetylated starch at 37 °C / 30 min

Starch modification at 37 °C, granule morphology was intact similar to literature reports on Sago and methylated Sago starch (Bohari *et al.*, 2011). Acetylated starch granules obtained at 37 °C for 30 min reaction time had smooth surface which is due to low degree of acetylation and were in agreement with other reported work (Luis *et al.*, 2010). The smoothness of the surfaces of CS starch granules is a consequence of the modifying agent and it is an indication that the granular starch particles will be homogeneously dispersed in aqueous solutions. Acetylated CS starch granules obtained at 60 °C / 90 min showed no presence of individual or agglomerated starch granules both at low and at high magnifications.

The granular shape was completely ruptured or destroyed forming stream-like shaped gel network of fibrous-like material. Some areas exhibited cracks while some had smooth surfaces. The implication is that the fibrous-jelly-like network features have potential applications in foods as thickeners, drugs and in agro-based industry for the controlled release of drug, fertilizers and for the control of moisture in storage foods and as gelling agents.

The SEM images of 60 °C / 90 min / CS clearly showed that acetylated CS were highly susceptible to heat and thus loss their granule morphology Plate II.

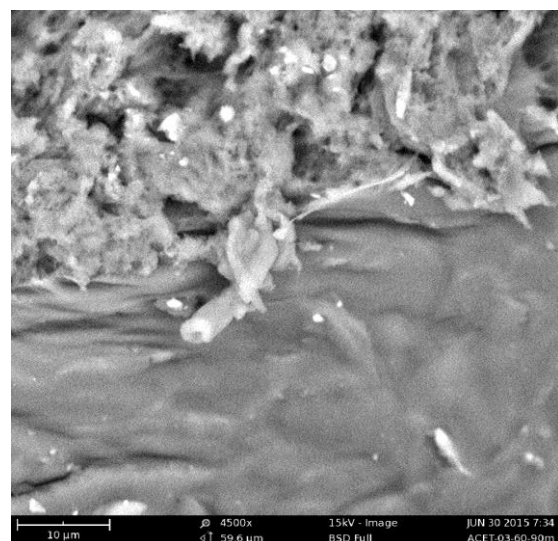
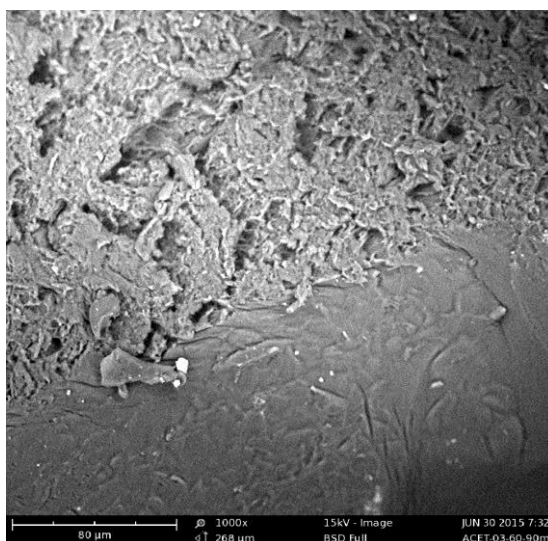
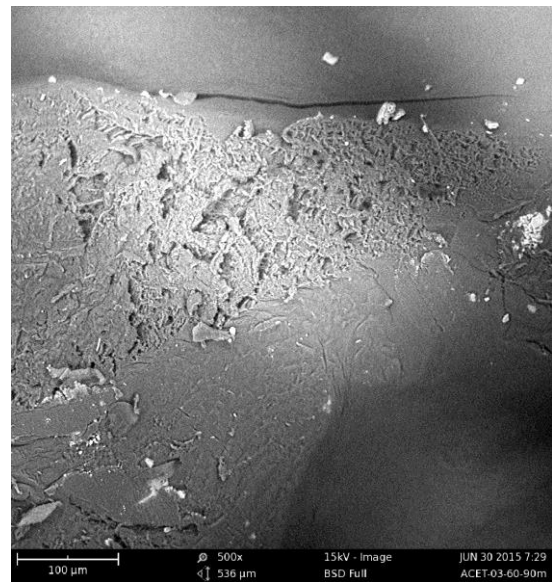
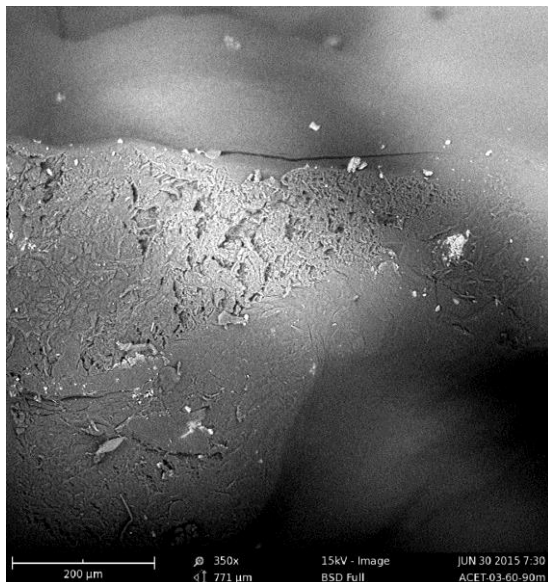


Plate II: SEM images of acetylated CS at 60 °C/90 min

This may be due to the fact that the alpha-amylase and glucoamylase in CS have less resistance at this temperature. It also implied that, modified CS granules had less intermolecular hydrogen bonding and therefore, the granular structure was completely lost (Hong Zhou Tan, Zai-Gui, Bin, 2009; Olurem & Onoja, 2013; Akpa & Dagde, 2012).

The Acetylation at 75 °C / 120 min CS SEM image showed that the structural morphology was transformed Plate III.

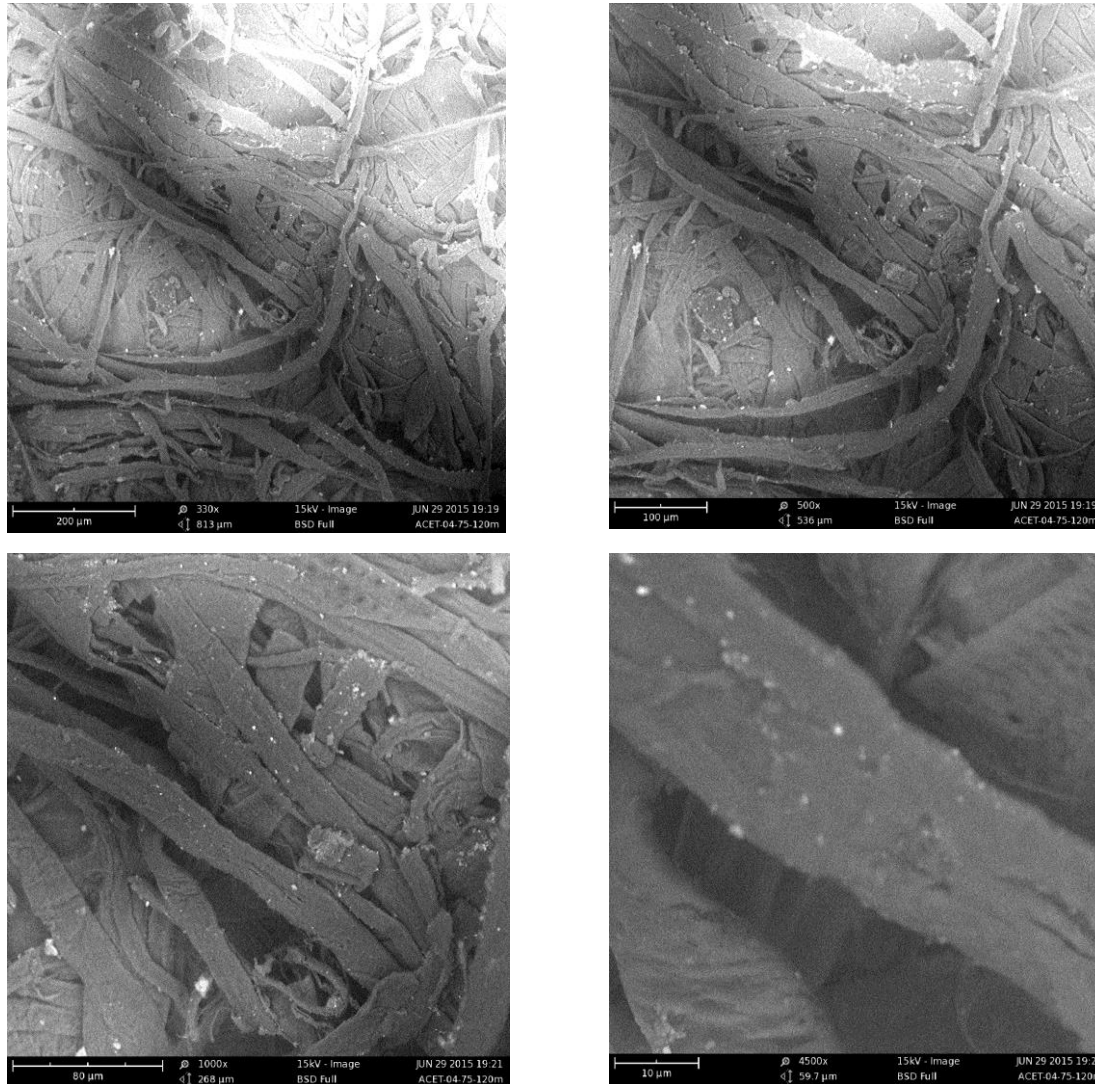


Plate III: SEM images of acetylated CS starch at 75 °C/120 min

Swollen and defibrillated strands of fiber bundles with rough surface were observed. The native structural order of crystalline granules was completely absent at 75 °C and 120 min duration. This is an indication that the presence of acetyls due to substitution of -OH reduced the gelling temperature and surface smoothness. This was not observed in control sample as the presence of granules with intact morphology observable in the fibrous strands

was seen. At this reaction time and temperature, there is clear evidence of the re-organization of gels fibrous networks and appearing as filamentous materials. Starch samples acetylated using Acetic Anhydride showed similar results. Though, the presence of granulated starch particle was visibly clear.

At 4500x magnification, SEM image of this sample further exposed some spaced feature of

the nature of the fibrous strand as it revealed a basket-like material with even distribution of pore network with almost equal size and shape. This feature will find applications where these properties are desired. For instance, in trapping large organic molecules, medicine, water treatment, in composite etc. Acetylated products obtained at higher temperatures/time will make good candidates for application in bio-plastic and biodegradable films, blends and in pharmaceuticals due to low solubility in aqueous medium. In acetylated samples, the acetyls in vinegar gradually replaced the hydrogen of the –OH groups in starch macromolecules to produce acetylated starch and water. Being a reversible reaction, the process is slow and because water molecules are continuously generated from the condensation of acetic acid in vinegar, the process allows for even distribution of heat and penetration of acetyls into starch granules giving rise to clear gels with no traces of granular starch particles.

Increase in temperature and reaction time led to obtainment of acetylated starch with large surface area and porosity (Shogren & Biswas, 2006). This property is potentially viable for application of the material as flocculants in water and waste water treatment. Vinegar has imparted some very important pharmaceutical characteristics to cassava starch such as increased swelling, water solubility, thermoplasticity and film-formability. The acetylated products are potential materials for the sustain release of drug for better patient compliances. The mechanism of drug release from materials with such properties has been attributed to the controlled passage of drug molecules through the obstructive gel layer, gel structure and matrix (Herman & Remon, 1989; Michailova, Titeva, Kotsilkova, Krusteva & Minkov, 2001; Efentakis, Pagoni, Vlachou & Avgoustakis, 2007; Emeje & Asha, 2012). Acetylated starches have been implicated for use as plasma volume expanders mainly for the treatment of patients suffering from trauma, heavy blood loss and cancer. Research has shown that, chemically modified starches have more reactive sites to carry biologically active compounds; they become more effective biocompatible carriers and can easily be metabolized in the human body (Simi & Emilia, 2007; Prochaska, Konowal, Sulej-Chojnacka & Lewandowicz, 2009; Emeje & Asha, 2012).

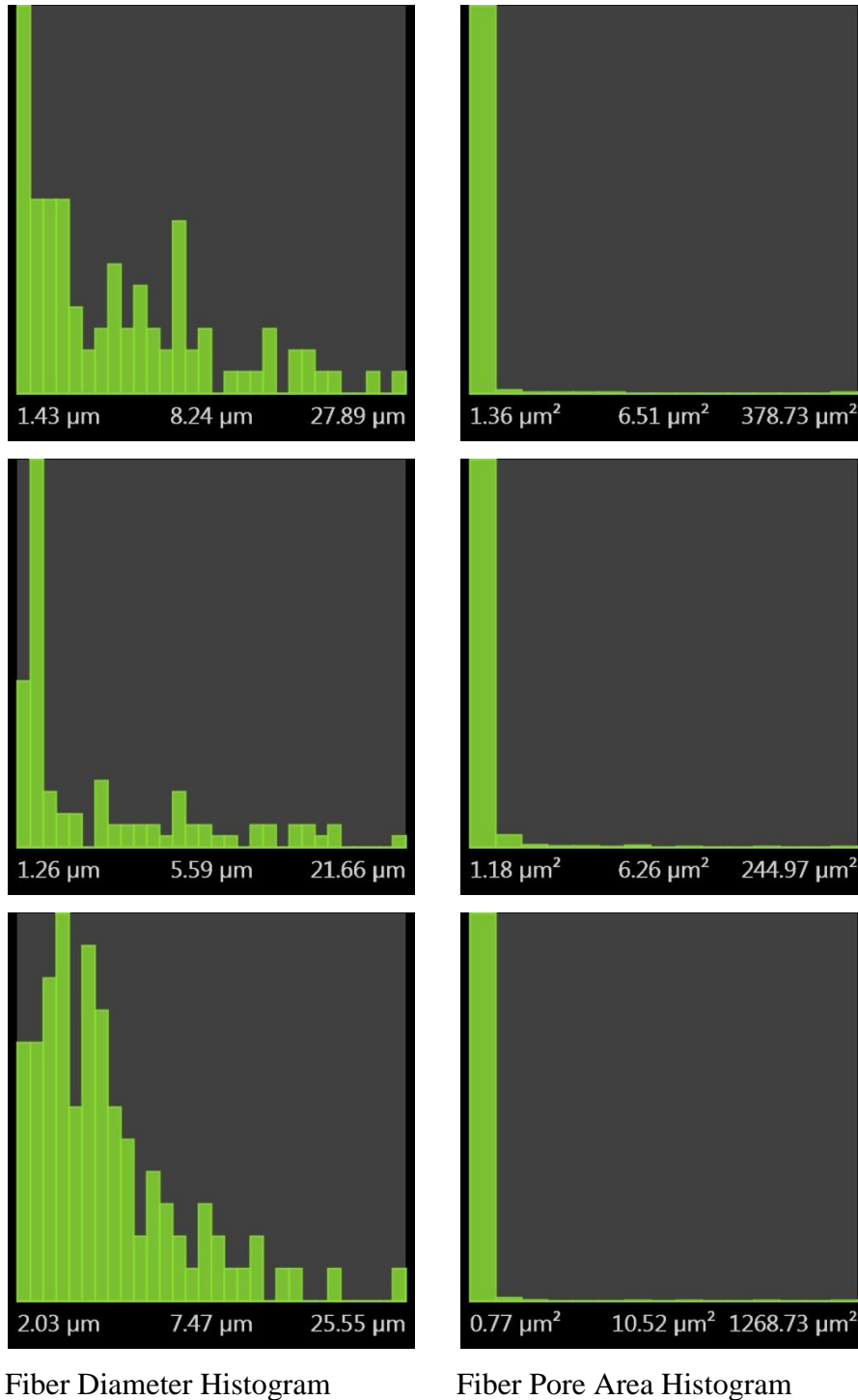
Acetylated starch samples showed improved properties over its native form from due to its stability and resistance to retrogradation as reported by (Singh, Chawla, & Singh, 2004). Increase in its viscosity, solubility, swelling factor, hardness, cohesiveness, adhesiveness and translucency of the gels were observed while it decrease in its initial gelatinization temperature (Leila, Mahdi, & Mohammad, 2009). Acetylated starches with acetyl contents of 0.5-2.5 %, are used in food to improve the resistance to shear and cold ageing stability during storage (Abbas, Khalil & Hussin, 2010). The concentration of NaOH was important for the progressive disruption of starch granule morphology. This changed the granule through a swollen mechanism of the amorphous region that weakens the granules through hydrolysis followed by their re-organization through formation of hydrogen bonding network in acetone as anti-solvent. The appearances of granular starch particles with intact morphology in control sample heated to 75 °C for 120 min has been attributed to interactions between water molecules and accessible –OH groups at C2, C3 and C6 positions. This reaction is so fast that a gel quickly formed on the surface of granules like a coat and prevents further access of water molecules from contacting starch granules. This process prevents complete gelation of starch granules.

Fiber Length Diameter and Pore Frequency Distribution

The fiber diameter and pore frequency distribution of vinegar modified starch samples Figure 1.5. Showed that fiber length ranged from 0.10 - 1.26 μm (100 – 1260 nm) with average length and frequency distribution from 0.13 – 1.57 μm which was very interesting. The average pore area distribution intensity for most modified starches was 1.10 μm^2 . Very few starch fiber with length around 2.32 - 27.89 μm were revealed. This agreed with other literature reports on the granule size of native starch. However, the average fiber length of most fibers in the modified granules was about 0.13 μm (130 nm). These implied that most of the acetylated starch particles were in nanometer scale and therefore, are viable candidates for application in the construction of nanoscale sensors, tissues, mechanical devices, and drug delivery system (Le Corre, *et al.* 2010; Emeje & Asha, 2012). The frequency of occurrence of

the fibers with small sizes has been attributed to removal of amorphous portion due to acetylation coupled with reactions at high temperatures. The modified samples are viable candidates for applications in food and pharmaceutical industry as gelling agents,

stabilisers and for the sustain release of drug in the body etc. The observed trends are consistent with other modified starches that have found useful applications in pharmaceutical, food, confectionary and water treatment industries.



Fiber Diameter Histogram

Fiber Pore Area Histogram

Fig. 1.5: Fiber Diameter and Pore Area Histogram of Modified Starch

Determination of Certain Physicochemical Properties

Table 1.1: Swelling Power, Water Absorbing Capacity and Solubility Index of Acetylation and mercerized products

Sample Identity	Swelling	Water Absorbing Capacity	Solubility Index
Control/CS	$1 \times 10^2 \pm 0.01$	15.00 ± 0.01	1.50 ± 0.01
Acet01/30min/27 °C/CS	$0.8 \times 10^1 \pm 0.02$	21.20 ± 0.00	5.20 ± 0.00
Acet02/60min/45 °C/CS	$4 \times 10^2 \pm 0.02$	20.60 ± 0.02	5.15 ± 0.01
Acet03/90min/60 °C/CS	$2 \times 10^2 \pm 0.02$	22.00 ± 0.01	5.50 ± 0.02
Acet04/120min/75 °C/CS	$4 \times 10^2 \pm 0.01$	22.00 ± 0.02	6.50 ± 0.00
Acet05/150min/90 °C/CS	$1 \times 10^2 \pm 0.01$	22.00 ± 0.01	5.32 ± 0.01
AA/120 min/75 °C/CS	$6 \times 10^2 \pm 0.01$	22.60 ± 0.02	5.71 ± 0.00
MCS/5 min	$1 \times 10^2 \pm 0.02$	17.20 ± 0.00	4.30 ± 0.01
MCS/10 min	$3.6 \times 10^2 \pm 0.01$	25.50 ± 0.01	6.45 ± 0.00
MCS/15 min	$4 \times 10^2 \pm 0.02$	06.50 ± 0.00	3.20 ± 0.01
MCS/20min	$1.3 \times 10^2 \pm 0.02$	14.60 ± 0.02	3.70 ± 0.00

Increase in mercerization time led to small swelling and increasing water capacity and solubility of starch granules attributed to high hydrolysis of the starch polymer chains. Solubility of acetylated starch samples increases with increasing acetylation time and temperature. The trend in solubility of acetylated product increased with increasing water absorbing capacity for the samples.

temperature. The trend in solubility of acetylated product increased with increasing water absorbing capacity for the samples.

Table 1.2: Acetyl content and degree of substitution (DS) of acetylated cassava starch

Starch Sample	Acetyl Content (%)	Degree of Substitution (DS)
Acet01/30min/27 °C/CS	0.3	0.011
Acet02/60min/45 °C/CS	0.7	0.033
Acet03/90min/60 °C/CS	0.9	0.034
Acet04/120min/75 °C/CS	1.50	0.059
Acet05/150min/90 °C/CS	0.10	0.004
AA/120 min/75 °C/CS	1.66	0.064

Acetyl content and DS as shown in Table 1.2, of the acetylated starches examined ranged between 0.1 and 1.66 %, with DS which ranged between 0.004 and 0.064 respectively. It was observed that higher level of acetylation resulted in higher DS. The only exception was acetylation carried out for a period of 150 min. This sample gave low level of acetylation which corresponded to low value of DS. This is attributed to deacetylation of acetyl groups after equilibrium for the reaction had been reached. Since, esterification reaction is an equilibrium

reaction, long reaction duration will eventually lead to removal of the attached acetyl.

Conclusion

In the present work, vinegar successfully introduced acetyl groups into accessible hydroxyl groups on starch granules as indicated by FT-IR analysis. Smoother granule surfaces were observed for low temperature acetylation products while at higher temperature, granule morphologies were transformed into fibrous and filamentous structures. Acetylated samples showed high solubility than mercerized and

native starch granules. High swelling power was observed for acetylation products obtained at higher temperature. These properties are all essential for applications in food, synthetic polymer and pharmaceutical industry as rheology modifier in food industry, surface compatibility in polymer-plastic industry and for sustain/control release of drug active components in pharmaceuticals.

Acknowledgment

The authors wish to acknowledge TETFUND, IBBU Lapai, for providing financial support to carry out this work.

REFERENCES

- Adrina, T. P. L. (2004). Physico – chemical properties of starch in Sago Palm (Metroxylon sago) at different stages. Thesis submitted in fulfillment of the requirements for the degree of Master of Science, Universiti Sains Malaysia.
- Abbas, K.A. (2010). Modified Starches and Their Usages in Selected Food Products: A Review Study Journal of Agricultural Science, 2 (2), 90-100: ISSN: 1916-9752.
- Akpa, J. G. and Dagbe, K. K. (2012). Modification of Cassava Starch for Industrial Uses, International Journal of Engineering and Technology, 2 (6), 913 – 919.
- Azeh, Y., Olatunji, G. A., Mohammed, C. Mamza, P. A. (2013). Acetylation of wood flour from four wood species grown in Nigeria using vinegar and acetic anhydride. *International Journal of Carbohydrate Chemistry*, Vol., 2013, <http://dx.doi.org/10.1155/2013/141034>.
- Azeh, Y., Abubakar, R. M. and Umar, M. T. (2014). Isolation and acetylation of starch using ethanoic acid for industrial uses. *Ilorin journal of Science*, 1 (2), 301–318.
- Bello – Perez Luis A., Edith Agama – Acevedo, Paul B. Zamudio – Flores, Gaudalup Mendez – Montealvo and Sandra L. Rodriguez, (2010). Effect of low and high acetylation degree in the morphological, physicochemical and structural characteristics of barley starch, *LWT – Food Science and Technology*, 43, 1434 – 1440.
- Brandt, L.: Cellulose ethers, in: Campbell, F.T. Pfefferkorn, R., Rounsaville, J.F. (1986). (Eds.), *Ullmann’s Encyclopedia of Industrial Chemistry*, VCH Verlagsgesellschaft, Wein- heim, p. 461.
- Bente, W., Tina, A., Ole, B., Andreas, B., Niall, Y., Lotte, J. and Lars T., (2007). Testing properties of potato starch from different scales of isolations—A ring test. *Journal of Food Engineering*, 79, 970–978.
- Dzogbefia, V. P., Ofosu, G. A. Oldham, J. H. (2008). Physicochemical and pasting properties of cassava starch extracted with the aid of pectin enzymes produced from *Saccharomyces cerevisiae* ATCC52712. *Scientific Research and Essay*, 3 (9), 406-409.
- Dzogbefia, V. P., Ofosu, G. A. and Oldham J. H. (2008). Evaluation of Local Processed *Sacchanomyces cerevisiae* pectinase enzyme for industrial extraction of starch from cassava in Ghana. *Scientific Research and Essay*, 3(8) 365 – 369.
- Emeje, M. O. and Asha, R. (2012). Starch: From food to medicine, scientific, health and social aspects of the food industry, Dr. Benjamin Valdez (Ed.), ISBN: 978-953-307-916-5, InTech, Available from: <http://www.intechopen.com/books/scientific-health-and-social-aspects-of-the-food-industry/starch-fromfood-to-medicine>.
- Fabio, D. S., Larotonda, K. N. M., Valdir, S. and Joao, B. L. (2004). Biodegradable films made from raw and acetylated cassava starch. *Brazilian Archives of Biology and Technology International Journal*, 47 (3), 477 – 484.
- Gonzalez, Z. and Perez, E. (2002). Effect of acetylation on some properties of rice starch. *Starch/Starke*, 54, 148 – 154.
- Heny, H. (2012). Nano crystalline starch and it alternative implementation. *International Conference on Chemical and Material Engineering*, ISBN: 978 – 602 – 097 – 281 -7, SPE. 10 – 1.
- Hong-Zhuo, T., Zai-Gui, L. and Bin, T. (2009). Starch noodles: History, classification, materials, processing, structure, nutrition, quality evaluating and improving. *Food Research International*, 42, 551–576.

- Ibrahim R. M. Benesi (2012). Characterisation of Malawian cassava germ-plasm for diversity, starch extraction and its native and modified properties. A Thesis submitted to the Department of Plant Sciences: Plant Breeding, in the Faculty of Natural and Agricultural Sciences for the award of Ph.D. Degree at the University of the Free State Bloemfontein South Africa.
- Izuagie, T., Hassan, L. G., Uba, A., Achor, M., Sahabi, D. M. and Sadiq, I. S. (2012). Compaction properties of starch extracted from seeds of christ thorn (*Ziziphus spinachristi*). *International Journal of Food and Nutrition Science* 1(2), 120-135. 21.
- Koh, M. H. (2013). Preparation and characterization of carboxymethyl cellulose from sugarcane bagasse. A project report submitted to the Department of Chemical Science Faculty of Science Universiti Tunku Abdul Rahman In partial fulfilment of the requirement for the degree of Bachelor of Science (Hons.) Chemistry.
- Leila, M., Mahdi, K. and Mohammad, S. (2009). Effects of cross-linking and acetylation on oat starch properties. *Food Chemistry* 116, 709–713.
- Effect of low and high acetylation degree in the morphological, physicochemical and structural characteristics of barley starch
- Luis A. Bello-Pérez*, Edith Agama-Acevedo, Paul B. Zamudio-Flores, Guadalupe Mendez-Montecalvo,
- Sandra L. Rodriguez-Ambriz
- Mistry, A. H., Schmidt, S. J., Eckholl, S. R. and Sutherland, J. W. (1992). Alkali Extraction of Starch from Corn Flour, *Starch/ Starke*, 44, 284 – 288.
- Martin, K. (2012). Dissolution of cellulose for textile fibre applications. Karlstad University, Faculty of Technology and Science Chemical Engineering SE-651 88 Karlstad, Sweden ISBN 978-91-7063-420-3 Print: Universitetsstryckeriet, Karlstad 2012 ISSN 1403-8099. Karlstad University Studies, 16 Licentiate Thesis.
- Morsyleide, F. R., Borsen, C., Eliton, S. M., Delilah, F. W., Tina, G. W., Luiz, H.C. M., William, J. O. and Syed, H. I. (2009). Effect of fiber treatments on tensile and thermal properties of starch/ethylene vinyl alcohol copolymers/coir biocomposites. *Bioresource Technology* 100, 5196–5202.
- Modibbo, U. U., Aliyu, B. A. and Nkafamiya, I. I. (2009). The effect of mercerization media on the physical properties of local plant bast fibres. *International Journal of Physical Sciences* Vol. 4 (11), 698-704.
- Nandan, S., Umashankar, A. and Sankar, C. D. (2011). Effect of cellulase treatment on extraction of starch from potato *International Food Research Journal*, vol. 18, 337-346.
- Oluremi, I. A. and Onoja, P. O. (2013). Effect of starch granule morphology on production of bioethanol from cassava and sweet potato. *International Journal of Scientific Research in Knowledge (IJSRK)*, 1(9), 343-348, Available online at <http://www.ijsrpub.com/ijsrk>.
- Omar, A. E. S., Haq, N. and Elizabeth, P. G. A. (2013). Chemistry and applications of polysaccharide solutions in strong electrolytes/dipolar aprotic solvents: An Overview. *Molecules*, 18, 1270-1313.
- Rahman, S. M. M. and Rakshit, S.K. (2004). Effect of endogenous and commercial enzyme on improving extraction of sweet potato starch, paper no.047076, ASAE Annual Meeting 2004.
- Rachtanapun, P., Simasatikul, P., Chaiwan, W. and Watthanaworasakun, Y. (2012). Effect of sodium hydroxide concentration on properties of carboxymethyl rice starch (CMS). *International Food Research Journal*, 19 (3), 923 – 931.
- Ramazan, K., Joseph, I. and Koushik, S. (2002). Characterization of irradiated starches by using FT – Raman and FRIT Spectroscopy, Department of Agricultural and Biological Engineering and Department of Food Science, Pennsylvania State University.
- Robin, R., Cathy, L. R., Steven, K. O., Keith, R. F., Daniel, M. D. and William, L. B. (1991). Starch determination by perchloric

acid vs enzymes: Evaluating the accuracy and precision of six colorimetric methods. *J. Agric. Food Chem.* 39, 2-11.

Salwa, A. E. F., M., Hanan, A. S. M. A., Nessrien, N. M. A., (2010). Physicochemical properties of starch extracted from different sources and their application in pudding and white source. *World Journal of Dairy and Food Sciences.* 5 (2), 173-182.

Sara, R. and Lo, G. (2003). Review characterization of the substituent distribution in starch and cellulose derivatives. *Analytica Chimica Acta*, 497, 27–65.

Shimelis, E., Meaza, M. and Rakshit, S. (2006). Physico-chemical properties, pasting behavior and functional characteristics of flours and starches from improved bean (*Phaseolus vulgaris* L.) varieties grown in east africa. *Agricultural Engineering International: the CIGR Ejournal. Manuscript FP 05 015.*

Seung, T. L., Jong, H. L., Dong, H. S., Hyesook, S. L. (1999). Comparison of protein extraction solutions for rice starch isolation and effects of residual protein content on starch pasting properties. *Journal Paper No. CAFST 97010 of Korea University; Starch/Stärke* 51 (1999) Nr. 4, S. 120–125.

Sherif, M. A. S., Keshk, A. and Al-Sehemi, G. (2013). New Composite Based on Starch and Mercerized Cellulose. *American Journal of Polymer Science* 2013, 3(3): 46-51 DOI: 10.5923/j.ajps.20130303.02.

Takeshi, M., Dipak, R.: Recent advances in membrane science and technology in seawater desalination – with technology development in the Middle East and Singapore. *Water and Waste Water Treatment Technologies–Multi-Effect Distillation (MED) – Raphael Semiat Encyclopedia of Life Support Systems (EOLSS);*<http://www.desware.net/DESWARE>

Wurzburg, O.B. (1986). *Modified Starches: Properties and Uses*, CRC Press, Boca Raton, p. 277.