

Studies on Isolation, Modification, Characterization and Evaluation of Some Physicochemical Parameters of Potato Starch

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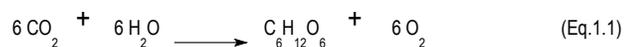
Abstract

Objectives: To isolate and modify starch using new and non-commonly used commercially available, cost-effective reagents and study the changes in functionality and physicochemical properties. **Methods/Statistical Analysis:** An outline and modification of the method: Addition of 100 mL of a 500 mL solution of 3.5 % hypochlorite (household bleach commonly known as hypo) in 2 L of water at interval of 1 min during grinding. Hypo substituted sodium metabisulphite, prevented browning and enhanced rasping and acted as bleach. Mucilage obtained by the modified method was non-sticky to starch cake. FT-IR results confirmed the direct formation of oxidized starch. **Findings:** Acetyl content (0.01-0.89 %) and DS (0.011-0.2) obtained by the modified method was in agreement with the approved DS by the Food and Drug Administration for food use. Proximate results showed that the isolated starch was rich in mineral content, fibre, fat and energy. Thermoplasticity of high temperature mercerized starch was revealed by SEM images. These properties will influence their use in composites and other applications where strength needs to be improved as documented. Mercerized starches as flocculants in water cleaning as ion changers or retention agents in the paper industry. The C=O absorption bands were observed at 1634, 1650, 1647 and 1646 cm^{-1} for mercerized starch. Bands observed at 1640, 1641, 1640, 1640 and 1642 cm^{-1} and 2932, 2926, 2920 and 2929 cm^{-1} and 1358, 1389, and 1385 cm^{-1} are assigned CO, C-H of methylene and $-\text{CH}_2$ stretching vibrations in ester group due to acetylation. Results of these findings showed the application of hypo and vinegar for isolation and acetylation of starch respectively. **Application/Improvements:** The feasibility of the modified method for starch isolation and modification using readily available, cost effective and eco-friendly chemicals for obtainment of food and pharmaceutical grade starch.

Keywords: Characterization, Modification, Potato, Starch, FT-IR, SEM

1. Introduction

Starch exists as the major stored carbohydrate in all plants containing the green pigment called chlorophyll^{L2}. Most of the glucose units are linked through C1 to C4 bonds, as in cellulose, but a C6 to C1 crosslink joins chains every 24 to 30 units.



These glucose links can be easily hydrolysed using a mineral acid or an alkali. Starch is readily available and cheap and commonly used in many facets of life for the manufacture of industrial products. The unique properties of starch which enhance its use basically include biocompatibility, biodegradability, and gelation and modification ability to suit potential usage. The two major reactive components of starch are the linear amylose and the highly branched amylopectin present as semi crystal-

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line granules³. The linear amylose component of starch can be structurally represented as shown in **Figure 1**.

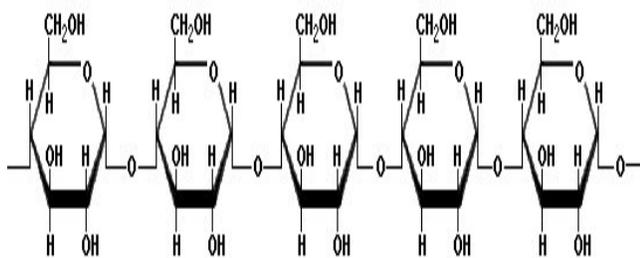


Figure 1. Structure of amylose component of a starch.

The amylopectin molecule differs from the amylose portion due the presence of a branch chain that alternates between two adjacent glucose units through $\alpha 1 \rightarrow 6$ glycosidic bonds³. The similarities between these two components can be seen from the linear arrangement of glucose units bonded via $\alpha 1 \rightarrow 4$ glycosidic linkages (**Figure 2**).

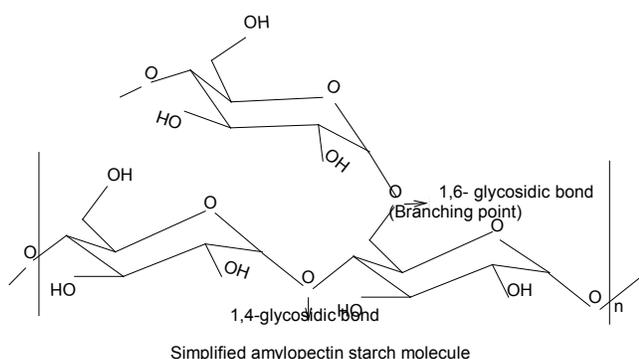


Figure 2. Structure of Amylopectin.

Starch has several uses in many industrial applications such as paper, paint, textile, adhesive beverages, confectionaries, pharmaceuticals and plastics^{4,5}. Consequently, it is of special interest to researchers in diverse disciplines such as in agriculture, forestry, science, engineering and technology⁶. It is non-toxic, renewable, and biodegradable⁷⁻⁹. The amylose constitutes (20-30 %) and amylopectin (80-70 %) which can be used to create high performance biocomposites/nanocomposites with unique and outstanding properties¹⁰. Starch is a versatile and useful raw material not only because it is cost effective but also the ease with which its physicochemical properties can be boosted through chemical modification¹¹. In order to increase the industrial use and to fulfil the various demands for functionality of different

starch products, they are often modified⁴. Starch has been extracted from different sources e.g. potatoes, corn, cassava, rice, wheat, tiger nut, maize, yam etc. using different conventional methods and can be preserved for a long period^{1,12}. 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 by several authors^{1,11-14}. Therefore, the aim of this work was to isolate and modify starch using cheap chemicals and study their effects on the morphological and physicochemical properties under different treatment conditions.

2. Materials and Methods

2.1 Reagents and Solvents

The potato tubers were obtained from a Local farm, Lapai, Nigeria. All reagents used were of analytical grade. These include: ethanol, methanol, acetone, sodium chloride, sodium hydroxide, potassium hydroxide. Heinz Vinegar **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.

2.2 Removal of Gums, Lignin and Waxy Substances

Removal of gums, lignin and waxy substances was carried out using the method of¹⁵. Potato tubers were washed to remove dirt, peeled and chopped into smaller pieces using a steel knife. The chopped potato pieces were soaked in sodium hypochlorite solution (3.5 % w/v of hypo). The solution was prepared by transferring 1000 mL of hypo into 4 L of distilled water separately and allowed to stand overnight to remove gums, lignin, waxes and decolouration of samples. Afterwards, it was washed and extensively rinsed several times with distilled water.

2.3 Starch Isolation from Potato Tubers

Starch isolation in the present study was a modification of the conventional method^{1,2,5,11}. The washed smaller pieces of potato tubers were ground with 750 watts mascot mixer grinder equipped with razor blades with the addition of 100 mL of a 500 mL solution of hypo in 2 L of

water at interval of 1 min during grinding. The slurry was filtered using a fourfold muslin cloth to remove debris. The filtrate was allowed to stand for 24 h for sedimentation to take place and then decanted. The mucilage was unusually not sticking to starch milk and so was decanted off the surface of starch milk. Starch milk was repeatedly washed with distilled water until the supernatant was neutral with pH paper. 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.

2.4 Starch Mercerization

Starch mercerization was a modification of the method described by⁴. It was carried out by treating 10 g each of oven dried isolated starch granules using 20 mL of 20 % KOH in a beaker at time intervals of 5, 10, 15, and 20 min at ambient temperature while stirring was done manually. After stirring each sample for the stipulated time, the brown viscous slurry obtained was treated with acetone to precipitate out the mercerized starch as thick rubber-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.

2.4.1 Starch Acetylation with Commercial Vinegar at Variable Temperature

Ten gram (10 g) native potato starch sample was placed in a 400 mL beaker and 50 mL of vinegar was added and stirred for 5 min. using a magnetic stirrer^{4,16}. Afterwards, 20 mL 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 respectively. A white homogeneous rubbery mass was obtained. The acetylation product was recovered using methanol as precipitants. The precipitate was filtered out and air dried at room temperature for three days. Acetylated samples obtained were store in sample bottles for further analysis.

2.4.2 Swelling Power/Water Absorption Test of Acetylated Starches

The starch sample (0.1 g) was weighed into a test tube and 10 mL of distilled water was added. The mixture was heated in a water bath at a temperature of 50 °C for 30 min with continuous shaking. The test tube was centrifuged at 1500 rpm for 20 min in order to facilitate the removal of the supernatant which was carefully decanted and weight

of the starch paste taken⁶. The swelling power was calculated as follows:

$$\text{Swelling Power} = \frac{\text{Weight of Paste}}{\text{Weight of Dry Starch Sample}} \times 100$$

This was carried out over a temperature range of 50 °C - 100 °C

2.4.3 Solubility Test of Acetylated Starches

Starch sample (2.0 g) was subjected to solubility test at 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. 2.0 g of each sample was placed in a boiling tube and 20 mL of distilled water was added. This was subjected to heating in a water bath with a starting temperature of 50 °C for 30 min. It was then centrifuged at 1500 rpm for 30 min. 10 mL of the supernatant was decanted and dried to constant weight. The solubility was expressed as the percentage (%) by weight of dissolved starch from heated solution⁶.

2.4.4 Acetyl Percentage and Degree of Substitution

The percentage of acetylation (% acetyl) and degree of substitution (DS) were determined titrimetrically, following the method described by¹⁷. Acetylated starch (1.0 g) was placed in a 250 mL flask and 50 mL of 75 mL/100 mL ethanol in distilled water were added. The loosely stoppered flask was agitated, warmed to 50 °C for 30 min, cooled and 40 mL of 0.5 mol/L KOH were added. The excess alkali was back-titrated with 0.5 mol/L HCl using phenolphthalein as an indicator. A blank, using the original unmodified starch, was also used.

$$\text{Acetyl \%} = \frac{\text{Blank (mL)} - \text{Sample (mL)} \times \text{Molarity of HCl} \times 0.043 \times 100}{\text{Sample weight (g)}}$$

Degree of substitution is defined as the average number of sites per glucose unit that possesses a substituent group.

$$\text{DS} = \frac{162 \times \text{Acetyl (\%)}}{4300 - (42 \times \text{Acetyl (\%)})}$$

2.5 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, Nigeria. Samples were run as (KBr) pellets, FTIR-8400S Fourier Transform Infrared Spectrophotometer in the spectra range of 4000-400 cm^{-1} .

2.6 Scanning Electron Microscopy

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

3. Results and Discussion

3.1 Determination of Certain Physicochemical Properties

It can be seen from (Table 1) that increase in mercerization reaction time led to little swelling and increase in water sorption capacity and solubility of starch granules which has been attributed to the breakdown of starch polymer chains due to hydrolysis. It was observed that solubility of acetylated starch samples increased with increase in acetylation time and temperature. The trend in solubility of acetylated potato starch increased with acetylation reaction time and temperature. This trend had a positive effect on the water sorption capacity and swelling of potato granules/fibres. The alkali treatment changed the colour of starch granules from white to brown and dark brown according to different mercerization grades, indicating the removal of residual wax, fatty substances and lignin.

3.2 Percent Acetyl and Degree of Substitution

Acetyl content, as shown in Table 2, of the acetylated starch studied ranged from 0.01-0.89 %. The DS, which ranged from 0.011 to 0.21 was in agreement with the approved DS (0.01-0.2) by the Food and Drug Administration for food use¹⁸. Thus, very low levels of acetylation of potato starch are safe for use in food industries and the cost of producing acetylated potato starch is minimized using commercial vinegar. It was observed that higher level of acetylation resulted in higher DS and acetyl content. The only exception was the sample acetylated for 120 min at 75 °C, where the percent acetyl content for the sample was

high but had low degree of substitution. This observation was attributed to deacetylation of acetyl group after equilibrium for the reaction had been reached due to prolong reaction time.

3.3 Proximate Analysis

The proximate analysis of native PS (Table 3) was that the isolated starch was rich in mineral contents, crude fibre, protein and fat. The moisture content was attributed to the high water/moisture holding capacity of potato starch in its cell wall. The moisture content of native potato starch in the present study was higher than the value reported in our previous study⁴, but was within the range reported for cassava starch. The ash content was also within the range obtained for cassava starch¹⁹.

3.4 FT-IR of Acetylated and Mercerized PS Starch

3.4.1 FT-IR of Mercerized Starch Samples

In native starch (control sample) spectral absorption bands were observed at 3461 cm^{-1} but bonded -OH absorptions in NaOH treated samples were found around 3500-3400 cm^{-1} with sharp narrower peaks (Figure 3-5). This is an evidence that alkali treatment breakdown some hydrogen bonded network and this trend increased with increasing treatment time. It was observed that the intensity of the -OH group first increased and then diminished with increasing time. This implied that prolong treatment time increased the hydrolysis of the starch polymer chains which was observed in spectral peaks due to gradual disappearance of the starch finger print region for every unit increase in treatment time. Important peaks at 1182 and 1160 cm^{-1} assigned to C-O-C and C-O stretching vibrations²⁰ in starch greatly diminished to 1030, 1028 and 1021 cm^{-1} (Figures 3-5). This trend suggests the hydrolysis of the glycosidic linkages in starch molecules. It increased with time up to the 20 min maximum reaction time used (Figures 3-5). The peak intensity of the -OH groups also decreased, indicating the breakdown of hydrogen networks in starch to yield starch monomers. Starch gelation was first observed for the first 5-10 min time. This property was observed to increase as the reaction time increased up to 20 min. This was 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

Table 1. Swelling Power, Water Sorption Capacity and Solubility Index of Acetylation Product

Sample Identity	Swelling	Water Sorption Capacity	Solubility Index
Control/PS	1 x 10 ² ± 0.01	17.20 ± 0.00	2.60 ± 0.02
Acet01/30min/27 °C/PS	3 x 10 ² ± 0.00	20.90 ± 0.01	5.21 ± 0.00
Acet02/60min/45 °C/PS	4 x 10 ² ± 0.00	20.80 ± 0.01	5.23 ± 0.01
Acet03/90min/60 °C/PS	3 x 10 ² ± 0.01	19.80 ± 0.01	4.91 ± 0.00
Acet04/120min/75 °C/PS	4 x 10 ² ± 0.02	06.50 ± 0.00	6.40 ± 0.01
MPS/5 min	2 x 10 ² ± 0.01	08.00 ± 0.02	3.10 ± 0.01
MPS/10 min	1.2 x 10 ² ± 0.00	13.00 ± 0.02	3.25 ± 0.00
MPS/15 min	2.1 x 10 ² ± 0.02	18.60 ± 0.02	4.70 ± 0.00
MPS/20min	1.6 x 10 ² ± 0.02	29.50 ± 0.00	7.40 ± 0.01

Table 2. Acetyl content and degree of substitution (DS) of acetylated and native potato starch

Starch Sample	Acetyl Content (%)	Degree of Substitution (DS)
Native potato	0.001	0.001
Acet01/30min/27 °C/PS	0.01	0.011
Acet02/60min/45 °C/PS	0.28	0.11
Acet03/90min/60 °C/PS	0.56	0.21
Acet04/120min/75 °C/PS	0.89	0.034

Table 3. Proximate Analysis of Potato Starch (PS)

Sample	Moisture (%)	Protein (%)	Fat (%)	Crude Fibre (%)	Ash (%)	HCO (%)	Energy (Kcal)
Potato	11.62	0.27	0.18	0.95	0.24	83.74	1350.6

important aspect of starch technology²¹. 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 with literature reports^{21,22}. The increased surface area is implicated to the adsorption of Na⁺ ions onto the crystalline surface of starch granule as Na⁺ ion substituted Hydrogen atom of the hydroxyl group which then promotes granule swelling, surface modification and increase in surface area for improved fiber-matrix surface adhesion. This property can be utilized for high mechanical strength mercerized starch composite formulation with anionic polymers/removal of heavy metals in water system. 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 documented²³. Mercerized starch commonly known as cationic starch has been used as a sustainable product, serving as flocculants in water cleaning as ion exchangers and/or retention agents in the paper industry. Starch/cellulose and cellulose derivatives composites prepared under different conditions have been reported to exhibit high mechanical properties^{24,25}. The C-O 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 (Figures 3-5) while this band was missing in control sample (Figure 6). An important observation was the gradual decreased of this band with increasing reaction time which was indicative of an increased hydrolysis of starch macromolecules. Another important clue for the decrease in the CO absorption was due to reaction involving CO with NaOH which resulted to -OH groups whose extent of formation depends on the

extent of the conversion of CO by NaOH and prolong reaction time²⁶. This trend was evidenced by the reduction in CO absorption band with increased reaction time.

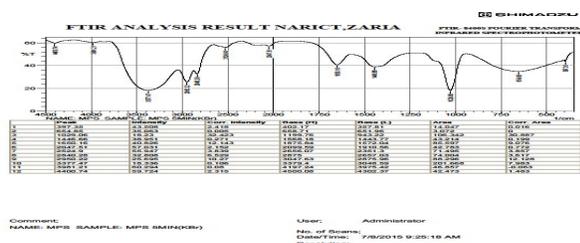


Figure 3. FT-IR Mercerized Potato Starch/5 min.

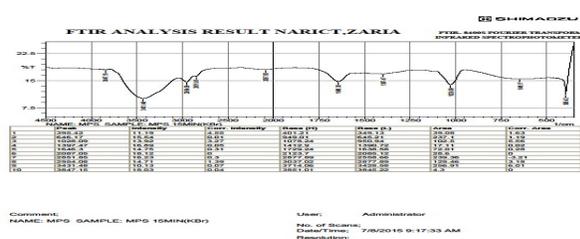


Figure 4. FT-IR Mercerized Potato Starch/15 min.



Figure 5. FT-IR Mercerized Potato Starch/20 min.

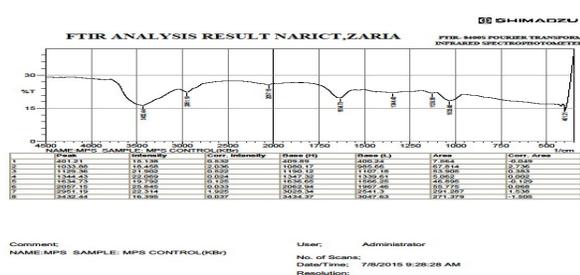


Figure 6. FT-IR Mercerized Potato Starch Control Sample.

3.4.2 FT-IR of Acetylated Starch Samples

FTIR absorption peaks for native, mercerized and acetylated potato starch samples obtained at different reaction time and temperature are shown as Figures 5-8. The CO absorption bands at different reaction conditions are 1640, 1641, 1640, 1640 and 1642 cm^{-1} (Figures 7-10). 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 (Figures 7-10). 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 dialdehyde functional group formed due to hypochlorite oxidation (Figure 6). The band which appeared at 4467 - 3774 cm^{-1} are due to bonded -OH groups in starch. The absorption band at 3344 - 3322 cm^{-1} is assigned to free bound H_2O ²⁶. The observation of the band at 3400 - 3344 cm^{-1} was attributed to the shift in -OH group stretching vibration due to the weakening of -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 starch²⁷. The crystallinity band at 930 - 600 cm^{-1} is due to out-of-plane bonded -OH deformation and C-H deformation vibrations²⁷. The band at 3400 - 3344 cm^{-1} appeared sharp for the 90 min acetylation products and was present in all acetylated samples (Figures 7-10). This band suggests the weakening of intermolecular hydrogen bonding network in starch due to masking of accessible -OH groups by acetyls according to literature reports²⁸. 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 -OH groups in native starch. The success of acetylation using commercial vinegar was clear due to decreased in intensity of the absorption peaks of bonded hydrogen network of -OH groups in acetylated samples. This was due to reduction in the number of free and accessible -OH groups implicated by substitution of -OH by acetyl groups¹⁷. The band observed at 1282 cm^{-1} , has been assigned to C-O stretching vibration of acetyls due to acetylation^{17,29}.

3.5 Scanning Electron Microscopy Morphological Studies of Samples

3.5.1 Acetylated Potato Starch Samples

The morphology of starch granules was studied using Scanning Electron Microscopy (SEM). Samples were

viewed at various magnifications in order to provide clear pictures of the nature of the morphology of the granule and size of native and modified starch. Acetylated potato starch samples had large granules as revealed at 4400 x magnification. Samples exhibited different morphologies such as; oval, round and flattened shapes with smooth surface. Clusters of various sizes were observed due to agglomeration resulting from 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 (Figure 11).

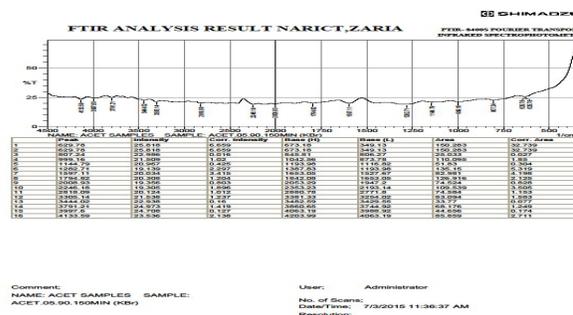


Figure 10. FT-IR of Acetylated Potato Starch/90 °C/150 min.

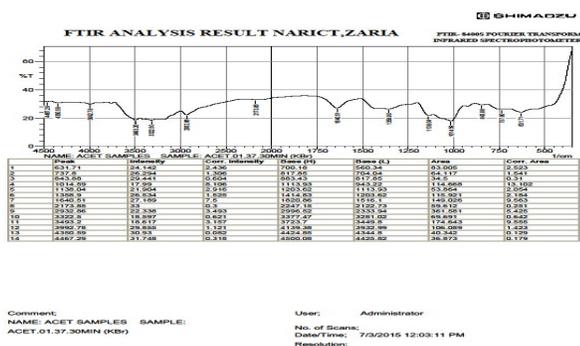


Figure 7. FT-IR of Acetylated Potato Starch/37 °C/30 min.

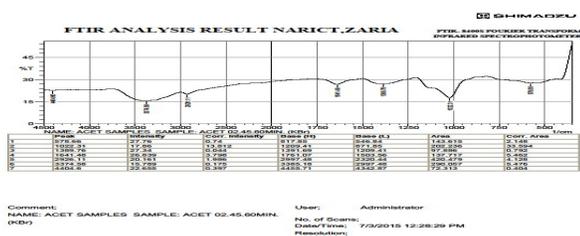


Figure 8. FT-IR of Acetylated Potato Starch/45 °C/45 min.

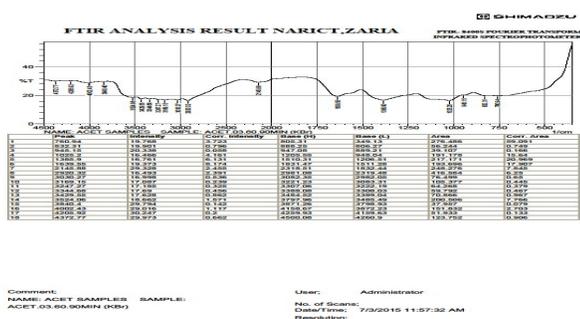


Figure 9. FT-IR of Acetylated Potato Starch/60 °C/90 min.

At 37°C modification, granule morphology was intact similar to literature reports on Sago and methylated Sago starch²⁷. Acetylated starch granules obtained after a 30 min reaction at 37 °C, had smooth surface which was attributed to low degree of acetylation. This observation was in agreement with other reported work¹⁷. Agglomeration of acetylated PS granules was observed. The presence of granules with smooth surface and different sizes of clusters due to agglomeration were observed. Additionally, various sizes and shape ranging from oval to octagonal structures were observed for the 45 °C/60 min. PS reaction conditions (Figure 12).

At 4500 x magnification, fissures attributed to fractured surfaces started to manifest on the granular structure of acetylated PS starch. This has been attributed to increasing reaction time and temperature²⁷. The smoothness of the surfaces of PS starch was a consequence of the modifying agent which was an indication that the granular starch particles will be homogeneously dispersed in aqueous solutions. Modification at 60 °C/90 min/PS had granules that exhibited rough surface, indicative of disruption of granules due to increase in temperature and time. The rupturing of granule morphology was as a result of disorientation of amylose and amylopectin hydrogen bonds network and the subsequent re-organization of the network to initiate gelation. The SEM image at higher magnification 4500x, revealed the presence of pith in acetylated starch granules. The gelation process can be clearly seen at 1000x magnification, where granules with ruptured surfaces were evident at this temperature. The SEM images of 60 °C/90 min PS clearly showed that PS granules were less susceptible to heat and reaction time (Figure 13) compared to SEM images of cassava starch obtained under similar reaction condition. This may be

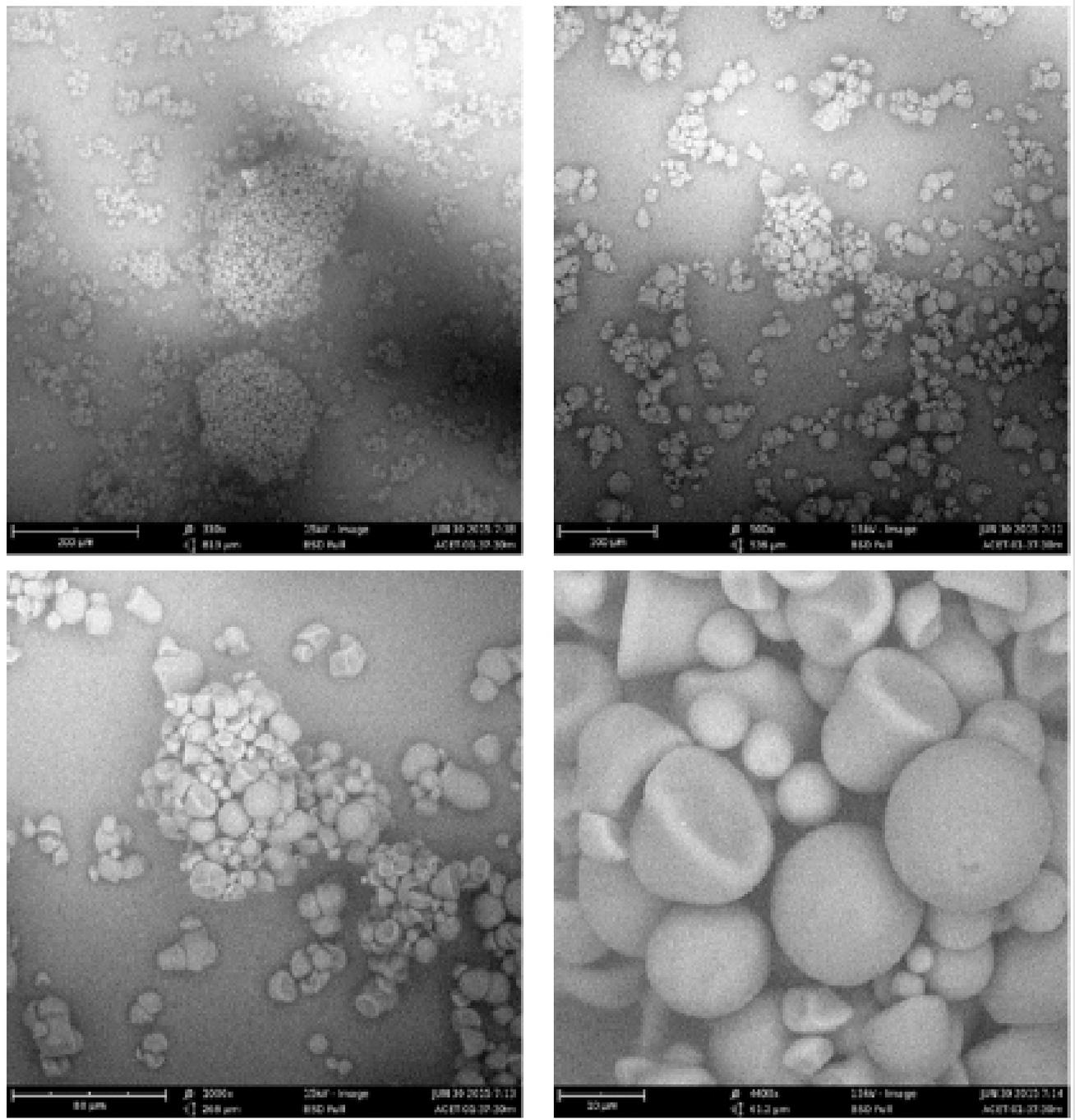


Figure 11. SEM images of acetylated starch at different mag. prepared at 37 °C/30 min.

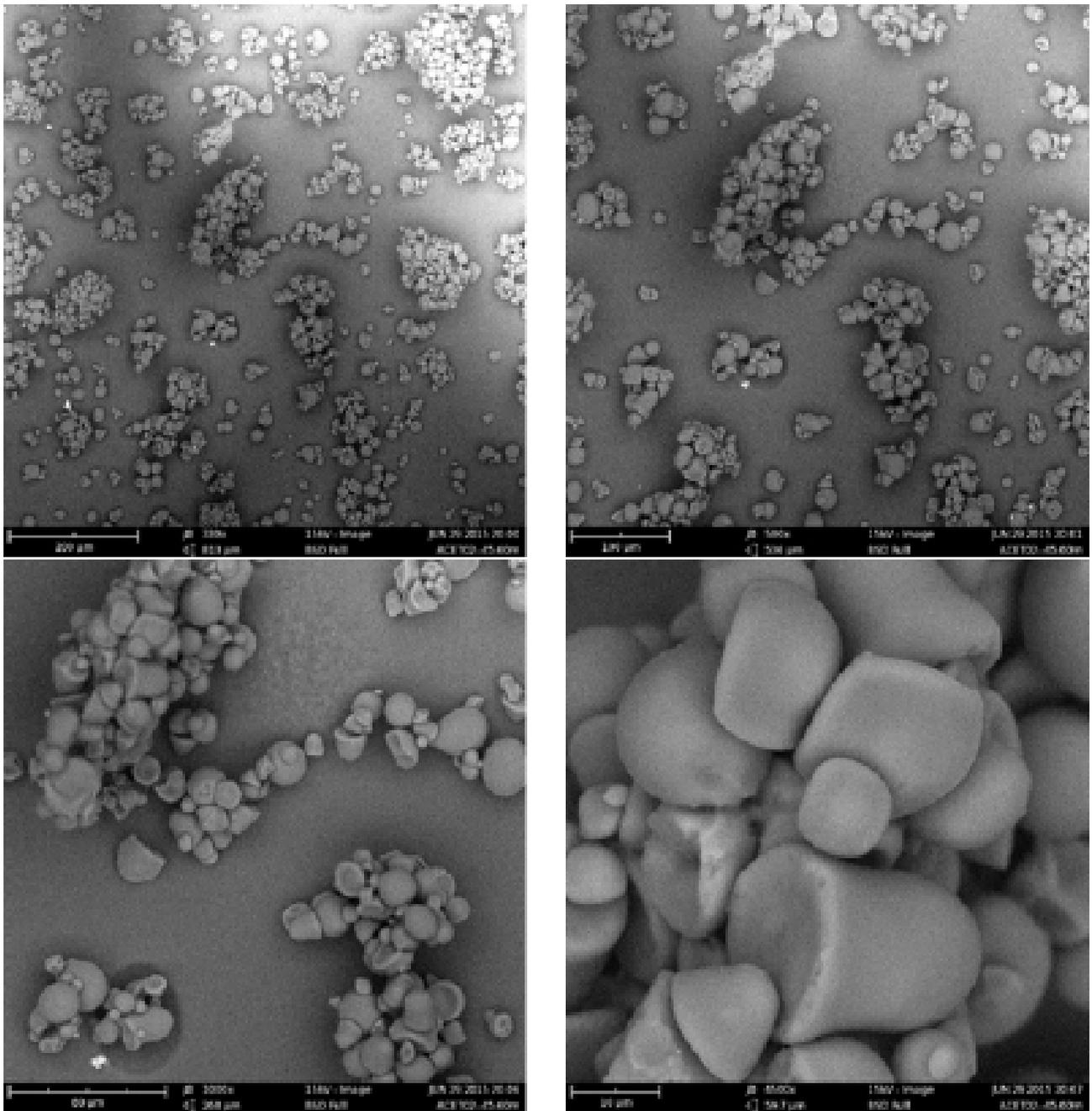


Figure 12. SEM image of Potato starch at different mag. Prepared at 45 °C/60 min.

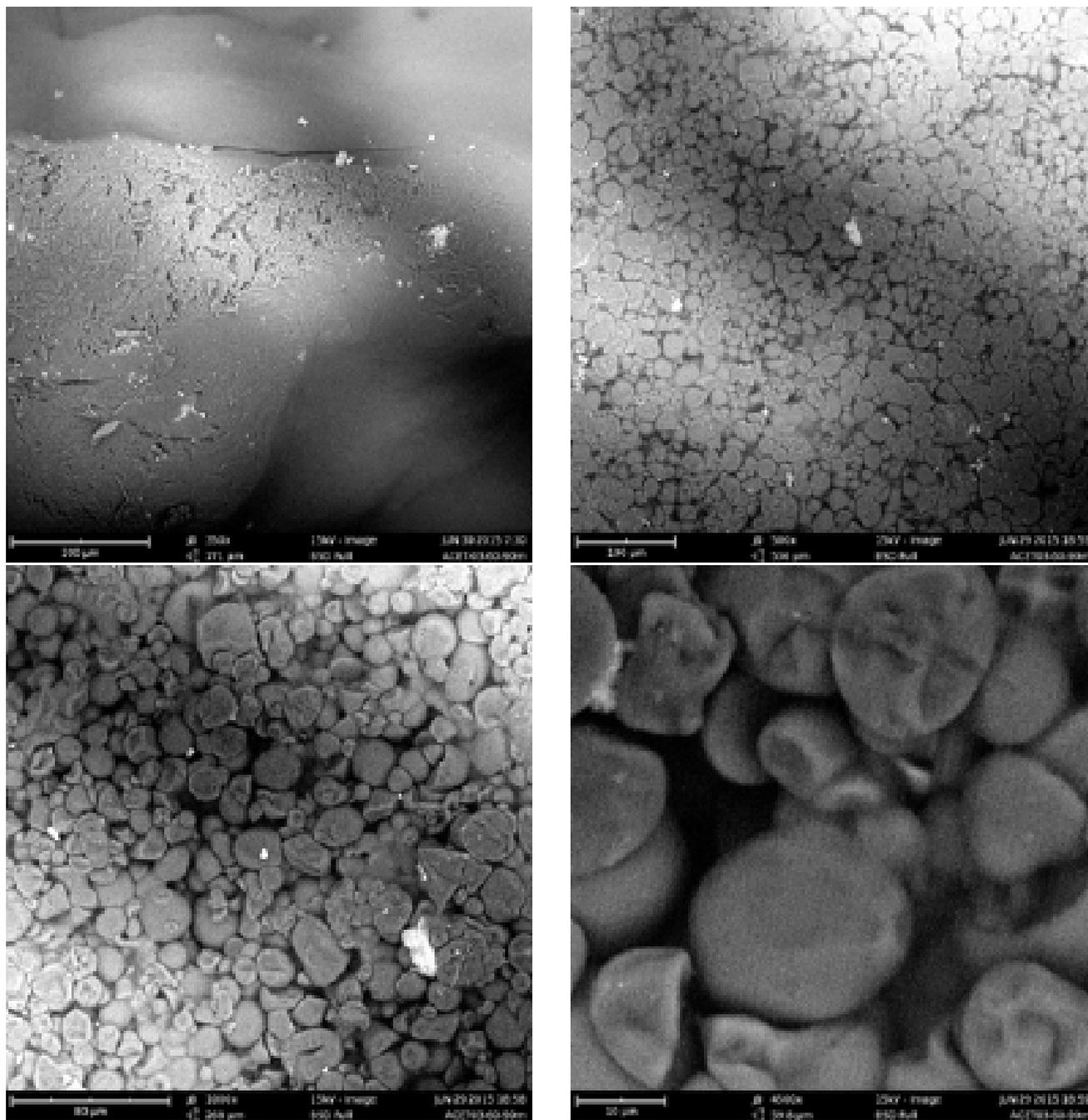


Figure 13. SEM images of acetylated PS starch at 60 °C/90 min.

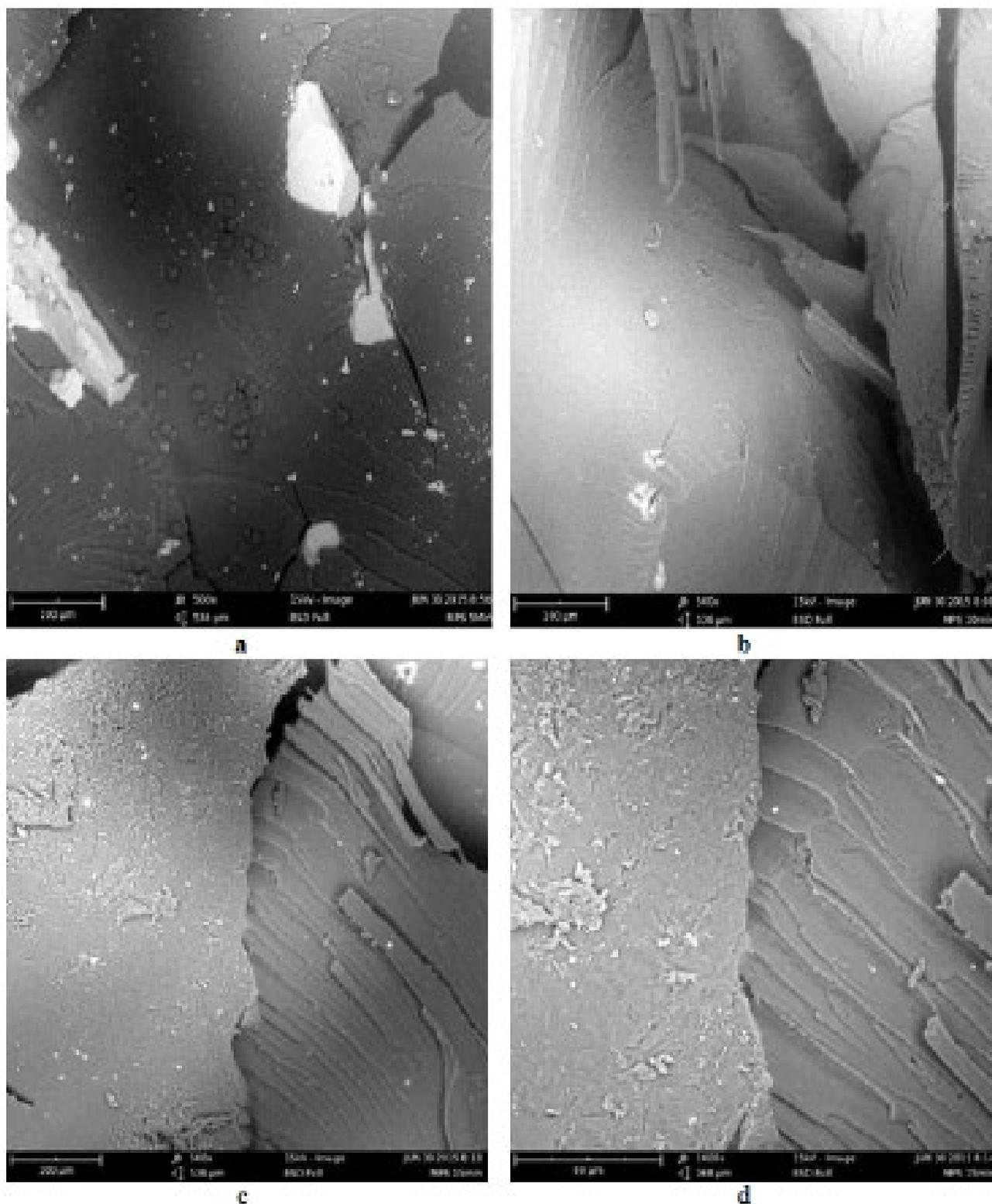


Figure 15. SEM images of mercerized PS starch at 80 oC at different time interval: a/5; b/10; c and d/15.

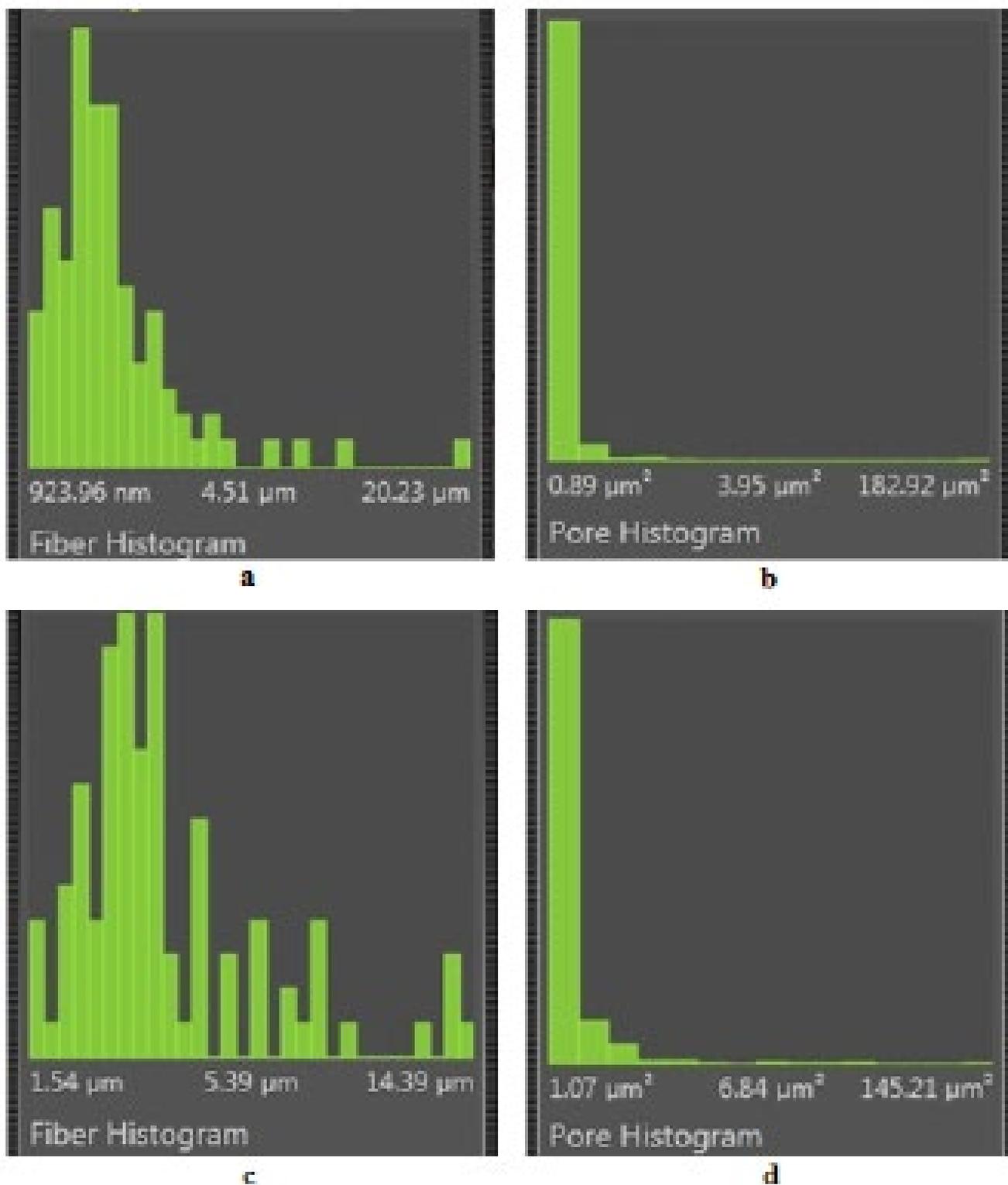


Figure 16. Fiber Diameter and Pore Area Histogram of Mercerized Potato Starch^{a,b} and Acetylated Potato Starch^{c,d}.

due to the fact that the alpha-amylose and glucoamylose in PS showed strong resistance at this reaction temperature. It also implied that, modified PS granules had strong intermolecular hydrogen bonding and therefore, the granular structure was not completely lost³⁰⁻³² (**Figure 13**).

Increase in temperature and reaction time led to obtainment of acetylated starch with large surface area and porosity³³. This property is potentially viable for the use of this synthesized acetylated starch as flocculants in water and waste water treatment. Acetylation has imparted some very important pharmaceutical characteristics to potato 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. 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^{34,35}. Acetylated starches with acetyl contents of 0.5-2.5 % have been used in food to improve the resistance to shear and cold ageing stability during storage³⁶. The acetyl content obtained in this study was within the range reported. A change in reaction conditions to 75 °C/120 min/90 °C/150 min. (**Figure 14**), led to total deterioration of granule morphology and resulted in smoother and even surface.

3.5.2 Mercerization of Potato Starch

The alkali treatment changed the colour of starch granules from white to brown and dark brown according to different mercerization grades, indicating the removal of residual wax, fatty substances and lignin. The concentration of NaOH was important for the progressive disruption of starch granule morphology. At constant reaction temperature and NaOH concentration, hydrolysis of the starch polymer chains and the rate at which NaOH diffused into the innermost part of starch granule was increased. This was clearly shown by the appreciable change in granule morphology observed as the treatment time increased. This implied that increase in reaction time had significant effect on the starch structure such that, granular shape gradually disappeared with time (**Figure 15**).

The surface of granule appeared eroded as the treatment time increased beyond 10 min. This may be due to deterioration of the granules due to degradative hydrolysis. The present results are in agreement with the work done on the effect of treatment time on kenaf fibre.

3.6 Fiber Diameter and Pore Frequency Distribution of Potato Starch

The fibre diameter and pore frequency distribution of mercerized and acetylated starch indicated a fibre diameter in the range 92.6 to 539 nm, with 92.6 nm fibre having the highest percentage frequency distribution intensity from 0.13-1.57 μm which was very interesting (**Figure 16**).

The average pore area distribution intensity was in the range 89 to 107 nm^2 (0.89 to 1.07 μm^2). A few fibres with large diameter were found around 451 to 539 nm. The information provided by fibre diameter and pore histograms was indicative of the presence of a majority of starch granules and/or fibre in nanometer attributed to degradation of amorphous domains within the polymer chains due to chemical treatment. This implied the synthesized potato starch materials have the potentials to perform just like their nano counterpart in medical, pharmaceutical etc³⁵. The frequency of occurrence of the fibres with small sizes has been attributed to removal of amorphous portion and high hydrolysis due to acetylation and mercerization reactions. Based on the DS and percent acetyl, acetylated 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. The observed trends are consistent with other modified starches that have found useful applications in pharmaceutical, food, confectionary and water treatment industries. The results also showed that long time mercerization at constant temperature and acetylation using vinegar, a low acetyl donor reagent at temperatures beyond 50 °C transformed potato starch into nano scale material.

4. Conclusion

In the present work, vinegar, a low acetyl donor successfully introduced acetyl groups unto accessible hydroxyl group 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/fila-

mentous and rough surfaces as revealed by SEM images. Acetylated samples showed high solubility than mercerized and native starch. High swelling was observed for acetylation products obtained at prolonged temperature. Prolonged chemical treatment time and temperature led to high hydrolysis and thus, decreased the granules/fibre size from micrometer to nanometer size.

5. References

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