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Research Paper

Isolation and Chemical Modification of White Sorghum (Sorghum Vulgare) Starch

Ahmed Salisu[1], Ibrahim Usman Gafai[2*], Saadatu Salisu Abdu[3]

[1,2,3]Dept. of Pure and Industrial Chemistry, Faculty of Natural and Applied Sciences, Umaru Musa Yar'adua University, P.M.B. 2218 Dutsinma Road Katsina, Nigeria

**Corresponding Author: chm171782@students.umyu.edu.ng | +234(0)8143232622*

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Abstract—Physical, chemical, thermal, morphological and functional properties of native starches differ greatly from one another. Modification of native starch is widely used to enhance its functional properties. In this study, native starch was isolated from white sorghum using wet-milling method and subjected to chemical modifications via oxidation, acetylation and acid-thinning. The isolated native starch and the modified starches were characterized using FTIR technique in order to confirmed the chemical modification by using the following agents; hydrochloric acid (HCl), sodium hypochlorite (NaOCl) and acetic anhydride ($(CH_3CO)_2O$) for acid-thinning, oxidation and acetylation, respectively. After the reactions, FTIR spectra revealed some changes in the absorption bands which confirmed the success of the modifications. The absorption peaks at around 1640.7cm^{-1} was an evidence that the hydroxyl groups (-OH) of native starch have been chemically transformed into carbonyl (-C=O) via oxidation and acetylation reactions. Physicochemical properties determined showed that acetylation of the native starch improved swelling capacity with the highest value of 69g/g at 90^oC while oxidation and acid-thinning have the values of 33g/g and 30g/g, respectively. Oxidation and acid-thinning both significantly increased solubility with values 157% and 110% respectively, whereas acetylated derivative was the least. After oxidation and acetylation reactions, the starch's hydrophilic inclination enhanced, thus oxidized and acetylated starches have more water absorption capacity having the highest value of 56% and 83% respectively, however, acid-thinning decreased water absorption having the least value of 34%. Following oxidation and acetylation, oil absorption capacity increased with 91% for the oxidized and 95% for acetylated starch, however, for acid-thinned starch it reduced to 67%. The ability of native starch to gel was diminished by oxidation and acetylation having the least gelation concentration (LGC) of 9 and 10 respectively.

Keywords— White sorghum, Starch, Oxidation, Acetylation, Acid-thinning, Physicochemical properties.

1. Introduction

White Sorghum belongs to the genus of flowering plants in the grass family. It is a crop that originated in Africa and has numerous farmed varieties today. White Sorghum has wide applications such as; Food, the manufacture of beverages that are alcoholic, and biofuels [1]. White sorghum is rich in several essential elements, including protein, fiber, the B-vitamins, niacin, thiamin, vitamin B6, and various dietary minerals, it is an ideal substrate for gluten-free. Additionally, it is a sustainable old grain that requires fewer natural resources to grow. This crop is perfect for anyone with celiac disease, gluten intolerance, or gluten sensitivity because it is naturally gluten free and Genetically Modified Organisms (GMOs) free. White sorghum is among the most important weaning meals in both high- and low-income countries [2]. It is also one of the most important food crops in Egypt, India and China, as well as the parched plains of tropical Africa. Egypt's sorghum farming takes up roughly 158,000 hectares and produces an average of 880,000 tons of grains. Nigeria, which grows sorghum on around 5.9 million hectares and produces an estimated 6.7 million tons annually, is the world's second-largest producer of the sorghum grain [3].

Figure 1. White sorghum

Alcohol, cold water or any other solvent do not dissolve the tasteless, soft, white powder known as starch. The chemical formula of starch is $(C_6H_{10}O_5)n$, it is a polysaccharide composed of 1,4-linked glucose monomers connected by glycosidic linkages. The majority of people on earth use starch as their main source of energy, making it a vital part of human diet since it gives the body the metabolic energy it needs to perform all of its various duties [4]. In both the culinary and nonfood industries, starch is a widely used biopolymer. Native starches, however, have a restricted range of applications since they retrograde, have poor paste clarity, and are sensitive to pH and heat [5]. Because of this, starches are routinely changed physically, chemically or both in order to improve their inherent functional properties and hence increase the range of products they can be used for in the food industry. Acetylated, oxidized, acid thinned, cross-linked and hydroxypropylated starches are the modified starches that are most frequently used. The most often utilized modified starches are oxidized, acid thinned, cross-linked and hydroxypropylated starches [6].

D-glucose units are used to make the straight chain polymer of the starch known as “amylose”. It is composed of monosaccharide molecules. D-glucose is the monosaccharide that causes the formation of amylose. As a result, amylose is classified as a polymer. Amylose makes roughly 20–35% of starch. The term "1-4 glycosidic linkage" refers to the specific type of chemical bonding that occurs between glucose monomers (usually for amylose). This is due to the fact that the removal of the OH group from one glucose molecule's first carbon and the H atom from another glucose molecule is necessary for the formation of amylose. This process is known as a condensation reaction because the removed OH group and H atom combine to form a water molecule [7].

A branching chain polymer made of D-glucose units’ structure is known as “amylopectin”. It is a polymer made of monosaccharides. Glucose units in amylopectin are joined together by 1-4 glycosidic linkages in line with 1-6 glycosidic bondings. These 1-6 glycosidic bondings are the basis for the branching structure of amylopectin. The glucose molecules' fourth and sixth carbon atoms are joined to one another in this configuration. Having Amylase and Amylase enzymes around, 1-4 glycosidic connections can be broken down, but 1-6 glycosidic linkages cannot. Amylopectin as a biopolymer in starch promotes swelling power despite being less water soluble and more soluble in hot water [7].

The aim of this research work was to isolate a starch from white sorghum using wet-milling, subject the isolated native starch to chemical modifications through oxidation, acetylation and acid-thinning, characterize the isolated native starch and modified starches using FTIR analysis to identify the actions of the chemical reagents employed for the modification processes and determine the physicochemical properties (solubility and swelling power, oil and water absorption capacity and gelation properties) of the isolated native starch and chemically modified starches in order to study the effects upon chemical modifications.

2. Related Work

From the report of [8], Celiac disease is a dangerous disorder that affects millions of people worldwide. Those suffering with this ailment must avoid substances containing the prolamin proteins present in cereal grains (which include wheat, rye and barley) for the rest of their lives. Because many food products are based on these grains, particularly wheat, celiac patients have very few dietary options, and those that are available to them are often of poor quality, nutritionally inadequate and expensive. However, the primary sorghum proteins, kafirins, are resistant to digestion. They are extremely difficult to extract and modify on an industrial scale and using food-compatible chemicals, this restricts their usage in foods. This review describes studies on kafirin extraction and strategies for altering sorghum proteins for increased nutrition and functionality as well as food applications. [9] Studied the effect of succinylation, acid-thinning and the combination of the two on the functional, textural and storage properties of starch extracted from white sorghum (Sorghum bicolor) grains. Prior to succinylation, native sorghum starch was acid-thinned individually with 0.1M, 0.5M and 1.0M HCl solutions. Succinylation of both native sorghum starch and acid-thinned starches lowered percent retrogradation in starches while dramatically increasing peak, cold paste and setback viscosities. On cold storage of starch gels, the amount of alterations in several textural qualities such as gumminess, hardness, and chewiness was greatly reduced. Similarly, the reduction in paste clarity was less significant in dual modified and single modified succinylated starches after cold storage. [10] oxidized corn starch with sodium hypochlorite in concentrations corresponding to 10, 20, and 40gCl/kg starch (oxidation levels I, II, and III) and then acetylated with acetic anhydride. The carboxyl and carbonyl groups as well as the acetyl groups were determined in modified starches to evaluate the efficacy of the oxidation and acetylation processes. The starches were also tested for water-binding ability and solubility at 50, 60, 70, and 80 degrees Celsius as well as their susceptibility to retrogradation in 2% starch pastes. Furthermore, the thermodynamic properties of gelatinisation were established. Rheological research included determining inherent viscosity, pasting qualities using RVA and mechanical spectra of starch gels. The results demonstrated that the oxidation level affects the efficacy of starch acetylation as well as the physicochemical and rheological aspects of starch studied in their research. [11] extracted starch from Musa AAB (poovan banana) and treated to acetylation, acid-thinning and oxidation. The treatments' effects on the molecular structure and functional characteristics of starch were investigated. Non-starch components were reduced after chemical treatment, according to chemical composition amylose concentration of starch reduced from 24.16% to 20.90% after acetylation, but increased to 24.50% and 25.5% after oxidation and acid-thinning, respectively. The X-ray diffraction pattern of modified starches revealed a B-type crystalline structure with peaks at 2 = 5.5, 15.0, 17.1, and 23.5; this pattern was similar to that of native starch. [12] modified Taro (Colocasia esculenta) starch using a variety of physical and chemical treatments. The effects of pH and

heating temperature on swelling and solubility were investigated. Heat-moisture treated oxidized and acetylated starches were more soluble at 95^{o}C whereas cross-linked starch was less soluble. At 95^{o}C, heat-moisture treated and chemically modified starches had lower swelling capacity than isolated starch. Swelling capacity and solubility were found to be pH dependent with all of these modified starches having increased swelling capacity and solubility at pH 2.0 and 10.0. [13] extracted starch from water yam and chemically modified it by acetylation, oxidation, and acid thinning. Standard procedures were used to determine the chemical composition, functional qualities and pasting characteristics of native and modified starches. Chemical modifications decreased the fat, protein, sugar, and amylose content. Amylose content in native and modified starches ranged from 9.42 to 12.53%. Acetylation and oxidation decreased the ash content, whereas acid thinning increased it. Pasting qualities revealed that commercial cassava flour was the best overalls while acid thinned was the best for native and modified water yam starches. Sensory study found that the best yoghurt was made from acetylated starch. While water yam had good starch characteristics in general, acid-thinned water yam provided the best overall outcome that could be used in industrial applications.

3. Methodology

3.1 Sample Preparation

White sorghum grain (one kilogram) was purchased at katsina state Central market, Katsina Local Government, Katsina State, Nigeria.

3.2 Isolation of Starch

The starch was isolated using wet milling as reported by [14] with little modifications. The purchased white sorghum grain was washed off three (3) times using distilled water to remove the impurities such as sand and other unwanted materials, the washed grain was soaked into distilled water for twelve (12) hours to be soft with regular stirring, after twelve (12) hours of soaking, the grain was washed again twice and blended using Home electric blender. The blended pulp obtained was filtered using cloth-sieve which has the ability to retain the fiber. The fiber was rewashed again to remove the adhering starch on it. The isolated starch was allowed to sediment for two (2) hours, after the two (2) hours, the supernatant was decanted off. The sedimented starch obtained was washed with 1Litre of distilled water three (3) times until a white and odorless starch was obtained. The starch obtained was exposed to air-dry for 24hrs after which it was ground to fine powder using Home electric blender and packaged in a sealed polyethylene bag for chemical modification. The starch percentage yield was calculated using the relationship:

$$\%\text{yield} = \frac{Mass\ of\ dried\ Isolated\ starch\ (g)}{Mass\ of\ white\ Sorghum\ sample\ (g)} \times 100$$

3.3 Acetylation

Starch acetylation was carried out as described by [15] with little modification. Slurry was made by dispersing 100g of isolated white Sorghum starch in a beaker containing 500ml of distilled water, heating the mixture (container) on a hot plate and stirring the contents (mixed) using magnetic stirrer for 30minutes. The resulting slurry's pH was brought up to 8.0 by the addition of 1M NaOH. After one hour, pH was stabilized between 8.0 and 8.5, 10ml of acetic anhydride was added to the slurry. The slurry's pH was brought down to 4.5 with 0.5M HCl after the addition of acetic anhydride and a 10-minute reaction time. The sludge was filtered through a cloth-sieve, washed four times with distilled water and then dried in the air for 24 hours at room temperature. Powdered acetylated starch was then placed in a sealed polyethylene bag.

3.4 Oxidation

The method reported by [16] was used to carry out the oxidation reaction and was slightly modified. 50% starch slurry was made by combining 100g of isolated white Sorghum starch with 500ml of distilled water in a beaker. The slurry's pH was brought up to 9.5 with 2M NaOH. After 35 minutes with the pH kept between 9 and 9.5 and steady stirring at 28^{o}C, 10grams of Sodium hypochlorite (NaOCl) were added to the slurry. After adding the NaOCl, the reaction was allowed to proceed for 15 minutes. After the reaction was completed, 1M H_2SO_4 was added to the slurry to bring the pH level back to 7.0. The slurry was filtered using cloth-sieve and washed off with distilled water before leaving the residue out to dry in the air for 24 hours. After being dehydrated and oxidized, the starch was powdered and stored in a hermetically sealed polyethylene bag.

3.5 Acid-thinning

White Sorghum starch slurry was made by dispersing 100g of the starch into a beaker containing 500ml of 0.15M HCl, as described by [17] for acid thinning. The depolymerization reaction was stopped after 9 hours of stirring the produced slurry magnetically at 50 degrees Celsius on a hot plate. Cloth sieve filtration and three washes in distilled water were used to remove impurities from acid-modified white sorghum starch. After air drying the residue for 24 hours at room temperature, the acid-modified starch was pulverized and stored in a vacuum-sealed polyethylene bag.

3.6 Determination of solubility and swelling power

Swelling power and solubility were determined at temperatures ranging from 50 to 90^{o}C using the method reported by [18] with little modification.

3.7 Determination of Capacity to absorb oil and water

To measure the oil and water absorption capacity of the starch, the procedure reported by [19] was employed with little modification.

3.8 Gelation Determination

Starch samples ranging from 4 to 20% (w/v) were prepared and poured into various test tubes and 8mL of distilled water were added. The starch suspensions were mixed for 7 minutes with a Vari-Whirl mixer. The test tubes were heated in a water bath for 25 minutes at 70 degrees Celsius, then rapidly cooled under flowing cold tap water. The test tubes were then chilled for 2.5 hours at 30^{o}C. The gelation properties were determined.

3.9 Fourier Transform Infrared Spectroscopy (FTIR) Characterization

FT-IR analysis was conducted using spectrophotometer (FTIR-630, Shimadzu Scientific instrument). Native starch, acid thinned, acetylated and oxidised starches were milled separately into fine powdered and small amount of KBr was added, the mixture was then pressed using a die that formed pellet which was placed in the sample holder. Thereafter the samples were scanned between 400-4000 cm^{-1} (wavenumber).

4. Results and Discussion

4.1 Starch Yield in Percentage

Table 1: Starch percentage yield of white sorghum

Weight of sorghum sample	Weight of isolated starch	%yield
1000g	350g	35%

The white sorghum used in this study has a starch yield of 35% as shown from Table 1 above. White sorghum's high carbohydrate content makes it an ideal food and industrial ingredient in Nigeria and the rest of tropical Africa. [20] listed gelation, gelatinization, pasting, solubility, swelling, color and digestibility as the primary properties of starch that determine its applications in the food industry. Depending on the application, one or more of the aforementioned parameters may undergo a series of chemical transformations, including degradation, substitution and cross-bonding [21].

4.2 Oxidized Starch Derivative

As a type of chemical modification, oxidation employs the addition of carboxyl (R-COOH) and carbonyl (-C=O) functional groups via starch depolymerization. The oxidized starches have been shown to be whiter and more resistant to retrogradation [22]. Similar to the odorless, whiter colour oxidized starch obtained in this research. In this study, sodium hypochlorite (NaOCl) was utilized as the oxidizing agent during the oxidation of white sorghum starch and it was found to act mostly on the amorphous areas of the starch granule. Thereby, oxidizing the hydroxyl groups of the native starch to carboxyl and carbonyl groups.

This was accomplished by depolymerizing the starch molecule; this resulted in the development of carboxyl and carbonyl groups that prevented crystallization. Compared to unprocessed starch, oxidized starch obtained was whiter in colour and exhibited less viscosity. Because of its flavorlessness and low viscosity, oxidized white sorghum starch has several potential applications in the food industry, including the production of mayonnaise, salad creams, and lemon curd. Typically, starch is oxidized to lessen its viscosity in solution or in dispersion. Starch molecules are broken down during the oxidation reaction to produce molecules with a lower molecular weight From the figure 2, the peaked absorption around 1640.7 cm^{-1} was an evidence that the hydroxyl groups (-OH) of starch have been chemically modified into carbonyl (-C=O) and carboxyl (R-COOH) groups. Thus oxidation was achieved.

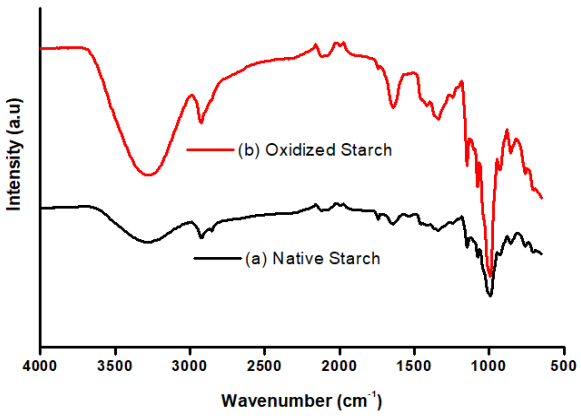

Figure 2. FTIR Spectra (a) Native starch and (b) Oxidized starch

4.3 Acetylated Starch Derivative

In this research work, the white sorghum starch molecules were acetylated by being exposed to 10ml of acetic anhydride ($C_4H_6O_3$), in the reaction process, the hydrophilic hydroxyl (OH^-) groups of the starch molecules are replaced with hydrophobic acetyl

[-C(=O)-CH_3] groups during the acetylation process, thereby increasing the hydrophobicity, thus preventing the formation of hydrogen bonds between the hydroxyl (OH^-) groups of the starch molecules and water molecules. This results in the elimination of retrogradation, which have a negative impact on the stabilization of the starch solution. Because the oxygen atom in the hydroxyl (OH-) group has stronger electronegativity, the electron pair from the hydrogen atom in water is drawn to it, making the hydroxyl (OH-) group negatively charged. This polar group also strengthens hydrogen bonds in organic molecules. Acetic anhydride incorporated new functional groups into the starch molecules. The addition of acetyl groups widens the gap between the molecules of starch, which lessens retrogradation and preventing the formation of hydrogen bonds.

[-C(=O)-CH_3] group from the acetic anhydride blocked the electron pair from the hydrogen atom in water from bonding with the hydrophilic hydroxyl group in the starch, thereby acetylated starch was produced. [23] reported that during the acetylation of native starch, the acetic anhydride used in the acetylation process disrupted the potential hydrogen link between the hydrophilic hydroxyl group of the starch and the electron pair from the hydrogen atom in water.

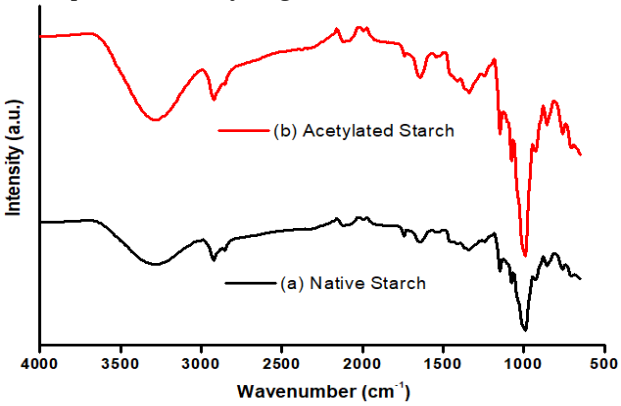

Figure 3. FTIR Spectra (a) Native starch and (b) Acetylated starch

From the figure 3 above, the band observed at 1543.1 cm^{-1} from the acetylated starch spectrum interprets the addition of acetyl moiety in to starch by replacing the hydrophilic hydroxyl (OH^-) groups of the starch molecules into hydrophobic acetyl [-C(=O)-CH_3] groups during the acetylation process. Thus acetic anhydride acted during the process, thereby acetylation was achieved.

4.4 Acid-thinned Starch Derivative

Chemical alteration via acid hydrolysis results in the production of thin boiled starch, which can be employed in a wide variety of food and non-food contexts [24]. This kind of modification uses low concentration mineral acid to hydrolyze starch while maintaining a temperature below the starch's gelatinization temperature. In this process, Acid predominantly affects the starch granule's easily accessible amorphous area, where hydroxonium (H_3O^+) ions hydrolyzed some of the glycosidic bonds and resulted to decreased in chain molecular weight. In this study, through the process of acid-thinning, the glycosidic linkage in white sorghum starch was altered by reacting the starch molecules with hydrochloric acid (HCl), which introduced the hydroxonium (H_3O^+) ion.

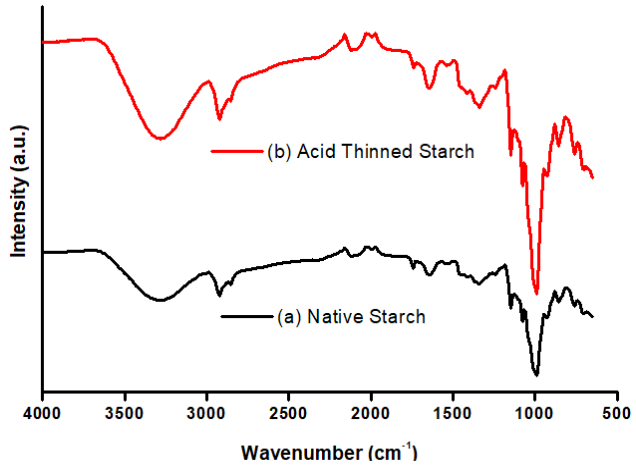

Figure 4. FTIR Spectra (a) native starch and (b) Acid thinned starch

From the figure 4 above, the band at 1341.6–1148.0 cm^{-1} from acid-thinned starch spectrum indicated the breakage of C-O-C bonds on starch molecule. Thus partial hydrolysis of the glycosidic bonds caused a decreased in chain molecular weight because of leaching of amorphous chain and enhanced bond formation between amylopectin molecules.

4.5 The Effect of Temperature on Starch Swelling power and Solubility

Table 2. Effect of temperature on solubility and swelling power of the native starch and modified starches

Starch	Temperature (°C)				
	50	**60**	**70**	**80**	**90**
Swelling power (%)					
Nwss	18.06±0.03	26.31±0.26	33.61±0.71	42.51±0.32	55.29±0.52
Owss	16.51±0.07	19.57±.72	23.12±0.04	30.04±0.51	33.01±0.33
Awss	25.72±0.04	40.33±0.17	50.06±0.51	55.17±0.31	69.31±0.07
AtWSS	11.83±0.09	14.91±0.87	23.62±0.79	24.78±0.07	30.71±0.63
Solubility (%)					
Nwss	29.45±0.71	57.31±0.07	87.41±0.54	145.37±0.19	163.53±0.21
Owss	37.21±0.36	62.81±0.32	95.21±0.39	157.81±0.36	177.43±0.62
Awss	19.78±0.31	33.91±0.73	47.88±0.73	96.51±0.71	106.44±0.63
AtWSS	38.71±0.01	60.31±0.81	91.52±0.42	110.87±0.34	129.21±0.04

Key: Nwss = Native white-sorghum starch, Owss = Oxidized white-sorghum starch , Awss = Acetylated white-sorghum starch, Atwss = Acid-thinned white-sorghum starch

All the modified starches have shown greater capacity to swell as the temperature increases as shown in table 2. This is similar to the findings reported in [25]. Additionally, it was reported in another study that, mucuna bean starch swelling power increases with temperature [24]. The swelling power of nWSS at 90°C was lower than that of native maize starch at higher temperature of 95°C as reported by [26] but higher than that of potato at the same temperature of 90°C reported by [27]. It was also higher than waxy maize starch, which has a lower swelling power at 95°C according to [28].

In all the temperatures used, oxidation and acid thinning diminished the swelling power. More so than the impact of oxidation, acid-thinning caused a reduction in swelling power. In comparison to the values for oWSS (16g/g) and nWSS (18g/g) at the same temperature of 50°C, atWSS was found to have the lowest value of 11g/g. After acid thinning and oxidation, a similar decrease in swelling power has been documented by [29]. On the other hand, after the raw starch was acetylated, swelling power increased at all tested temperatures. The maximum result for aWSS was measured at 90°C and the value is 69 g/g, whereas nWSS recorded a value of 55 g/g at the same temperature. The solubility of native and all modified derivatives of white sorghum starch rose as the temperature climbed from 50 to 90 °C. Both oxidation and acid-thinning improved the native starch's solubility significantly. However, the effect of oxidation was more severe than the increase in solubility caused by acid-thinning. At 90°C, the greatest value of 177% was observed, compared to 163% and 129% for nWSS and atWSS, respectively. Acetylation reduced the native starch's solubility percentage. In a study of the solubility pattern of various starches, [18] reported that 60-fluidity acid-modified maize starch was roughly four times as soluble in water as its parent starch at 85°C; they also documented an increase in corn starch solubility at all temperatures following oxidation.

Cassava starch [30] and red bean starch [31] were also improved upon acid treatments. In acid modification, the hydroxonium ion (H_3O^+) attacks the glycosidic oxygen atom and hydrolyzes the glycosidic bond. Acid first acts on the surface of the starch granule before gradually entering the interior region. It is thought that the acid preferentially attacks the amorphous region because the crystalline region is not freely accessible to the acid, allowing it to remain intact. As a result, after acid-thinning, the percentage relative crystallinity

increases. Because swelling is constrained by the stiffness of the entangled amylopectin network in the crystalline area of the starch, an increase in crystallinity accounts for a reduction in swelling capacity of the acid-thinned starch [32]. The reduction in swelling following oxidation is ascribed to structural disintegration within the starch granules during the modification process.

According to [16], the oxidizing agent penetrates deeply into the granule, working mostly on the amorphous portions. Depolymerisation and structural weakening of the starch granule cause an increase in solubility after acid-thinning and oxidation. Earlier, similar logic was given by [33]. Acetylation lowers intermolecular connections in starch granules, resulting in fewer structural constraints against swelling.

4.6 Capacity to absorb water and oil

The results for water and oil absorption capabilities demonstrated that after oxidation and acetylation reactions, the hydrophilic propensity of the starches improved, however acid-thinning reduced the starch's ability to absorb water. However, acetylation outperformed oxidation in terms of improving water absorption capacity. Following a similar trend, aWSS and oWSS have higher oil absorption values than atWSS and nWSS. Although aWSS had the highest value of 95%, compared to 91% and 87% for oWSS and nWSS, respectively, atWSS still had a lower value of 67% of oil absorption capacity than nWSS. As a result, acid-thinning reduced the native starch's hydrophilic and hydrophobic capabilities. Contrary to the findings of [16], acetylation and oxidation improved the oil absorption capacity of black gram starch by nearly 2.5 times more than the control. The insertion of functional groups on the starch molecules allows for a higher binding capacity than native starch. Acid-thinning essentially reduced oil and water absorption capabilities by reducing the amorphous region of starch granules. This lowers the amount of accessible binding sites for water and oil in the starch granule.

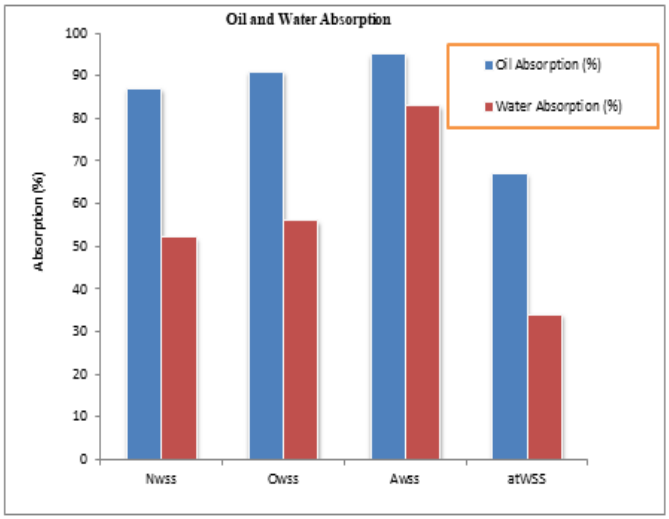

Figure 5. Oil and water absorption Capacity of native and modified white sorghum starches

4.7 Gelation characteristics

Table3. Gelation characteristics of native and chemically modified white sorghum starches

Temperature (^{0}C)	nWSS	oWSS	aWSS	atWSS
4	Liquid	Liquid	Liquid	Liquid
6	Viscous	Viscous	Liquid	Gel
8	Gel	Viscous	Liquid	Gel
10	Strong gel	Gel	Gel	Strong gel
12	Strong gel	Gel	Strong gel	Strong gel
14	Strong gel	Gel	Strong gel	Very strong gel
16	Very strong gel	Strong gel	Strong gel	Very strong gel
18	Very strong gel	Very strong gel	Strong gel	Very strong gel
20	Very strong gel	Very strong gel	Very strong gel	Very strong gel
LGC	7	9	10	5

Key: LGC = Least Gelation Concentration

Table 3 shows the gelation properties of native, oxidized, acetylated and acid-thinned white sorghum starches using the least gelation concentration as the index of gelation capacity. The least concentration of nWSS starch for gelation (LGC) is 7% (w/v). After oxidation, this value increased to 9% (w/v) and 10% (w/v), indicating that nWSS has greater gelation property that could be used as food additive than oWSS or aWSS. After acid-thinning, the least value found was 5% (w/v). Examining the physical appearnce of the starch gels as concentration increases reveals that a strong gel is generated at 14^{0}C when using aWSS as opposed to oWSS which formed a non-strong gel. After modification, the addition of carbonyl, carboxyl, and acetyl groups generated inter-molecular repulsion in the starch gel which accounts for the weaker gels in oWSS and aWSS. In contrast, acid-thinning improved gelation in the current study. The minimal concentration required for gelation is 5% (w/v), which is an improvement over the unmodified starch having lowest gelation concentration value of 7% (w/v). This observation is consistent with [21] earlier reported on the improvement of gelation ability of maize starch, potato starch, and rice starch after acid-thinning. It has also been shown that acid-modified red bean starch and cassava starch have higher gel strength than unmodified starch [31] and [30] respectively.

The organized arrangement of double helix amylopectin structures constitutes the crystalline area. Amylose has been attributed to disruption of the crystalline packing of amylopectin by being embedded in the amorphous area [34]. In this regard, acid hydrolysis may result in fewer impediments of double helical chains approaching each other, allowing for the formation of Van der Waals forces and hydrogen bonding, resulting in enhanced gelation qualities.

4.8 Fourier Transform Infrared Spectroscopy (FTIR)

From figure 6, there were shifts in the absorption bands from spectrum of acetylated, acid-thinned and oxidized starch when compared to the native starch spectrum. The absorption peak at 3265.5cm^{-1} and 2929.7cm^{-1} are attributed to the symmetric and asymmetric stretching vibration of O-H bonds and CH_2 of the glucose units, respectively. The absorption at 1640.7cm^{-1} was attributed to an O-H bending vibration. The

absorption peaks at 1740.7 and1640cm^{-1} indicated the conversion of hydroxyl groups into carbonyl and carboxyl groups in acetylated and oxidized, respectively.

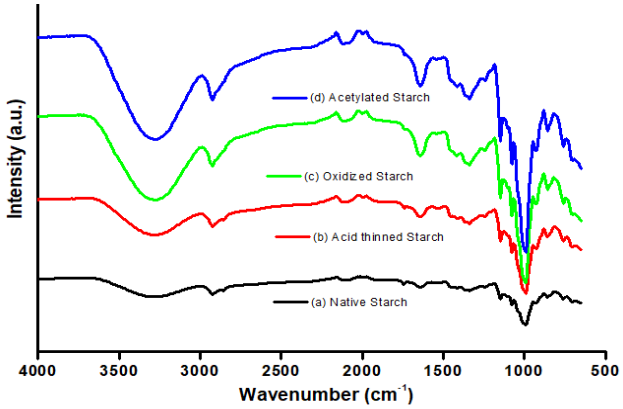

Figure 6. FTIR spectra (a) Native starch (b) acid thinned starch (c) oxidized starch (d) acetylated starch

5. Conclusion and Future Scope

White sorghum native starch was isolated using wet milling and subjected to chemical modifications such as oxidation, acetylation, and acid-thinning. Physicochemical properties (solubility and swelling power, oil and water absorption capacity and gelation properties) were determined. The results revealed that functional properties of white sorghum starch that have been improved after the chemical modifications, which indicated potential industrial applications including food products. Oxidized, acetylated and acid-thinned white sorghum starches may also find uses in foods with large solid contents that do not need for considerable thickening. Generally, the water-binding capacity and water solubility of acetylated starch were improved. Starch acetylation altered the gelatinization and intrinsic viscosity. These variables changed in response to the degree of starch oxidation. Oxidized and acetylated starches inhibited gel formation and decreased starch's susceptibility to retrogradation during storage. Starch solubility and water absorption capacity were both shown to increase with acetylation and oxidation while decreasing with acid thinning. Additional peaks that appeared in the FTIR spectra of the modified starches successfully confirmed chemical reactions on the native starch. In the future study, the rheological properties of chemically modified white sorghum starches shall be determined, so as to understand other physicochemical properties of Starches in response to applied forces or stresses. Furthermore, morphological properties of the native and modified starches such as shape, structure, pattern and size of the starch's granules by scanning electron microscope and X-ray diffractometer should be carried out.

Data Availability

Because of the technical and time limitations, the raw data required as part of an ongoing study cannot be shared.

Conflict of Interest

The authors have no any potential conflicts of interest to declare.

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Authors' Contributions

The author Saadatu Salisu Abdu isolated the starch from white sorghum and carried out the chemical modifications (oxidation, acetylation and acid-thinning), the author Ibrahim Usman Gafai carried out the determination of solubility and swelling power, capacity to absorb oil and water, gelation determination and also wrote the manuscript, the author Ahmed Salisu supervised the research. All authors reviewed and edited the manuscript and approved the final version of the manuscript.

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AUTHORS PROFILE

Dr. Ahmed Salisu received his first degree; Bachelor of Science (B.Sc.) in Chemistry from Bayero University Kano, Nigeria, in the year 2004, Master's degree (M.Sc) in Organic Chemistry from Bayero University Kano, Nigeria in the year 2011 and Doctor of Philosophy (Ph.D) in Chemistry from Universiti Teknologi Malaysia (UTM) in the year 2015. He has 18 years of working (teaching) experience and 15 years of research experience. He has about 32 research journal publications in both local and international academic journals. His highly esteemed research interests are in the field of natural products and Polymer Chemistry. He is currently working as a Senior Lecturer in the Department of Pure and Industrial Chemistry, Umaru Musa Yaradua University Katsina, Nigeria.

Mrs. Saadatu Salisu Abdu obtained Bachelor of Science (B.Sc.) in chemistry from Umaru Musa Yaradua University Katsina, Nigeria in the year 2021. During her undergraduate studies, she worked and gained experience with Al-Dusar Food and Beverages Company Limited in the year 2019 and Katsina State Water Board (Ajiwa Water Treatment Plant) in the year 2020, all as a part of Students Industrial Work Experience Scheme (SIWES). She is currently into National Youth Service Corps (NYSC) program, working with Katsina State Water Board (Ajiwa Water Treatment Plant) as her place of primary assignment. She has research interests in natural products chemistry, food chemistry, environmental chemistry and scientific water treatment process.

Mr. Ibrahim Usman Gafai is a first-class graduate in chemistry from Umaru Musa Yaradua University Katsina, Nigeria in the year 2021**,** During his undergraduate studies, he worked and gained experience with Al-Dusar Food and Beverages Company Limited in the year 2019 and Standard Organization of Nigeria (SON) in the year 2020, all as a part of Students Industrial Work Experience Scheme (SIWES). He is currently into National Youth Service Corps (NYSC) program, working with National Population Commission (NPC) as his place of primary assignment. He is a member of Chemical Society of Nigeria (CSN) and a member of professional bodies which include Chartered Institute of Loan and Risk Management (CILM), Chartered Institute of Human Resources Management (CIHRM), Chartered Institute of Project Contract and Facility Management (CIPCFM) and Nigerian Institute of Management (NIM). He has research interests in polymer chemistry, sustainable and renewable energy, innovative chemical sciences, materials science and food chemistry.

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