Physicochemical properties, morphological and X-ray pattern of chemically modified white sorghum starch. (Bicolor-Moench)

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Abstract Starch isolated from white sorghum was subjected to chemical modifications like oxidation, acetylation and acid thinning. Proximate composition of these, such as crude protein, crude fat, moisture content and ash content were studied. Wide angle X-ray diffractograms showed typical ‘A’ pattern characteristic of cereal starches, but significant differences were observed between the X-ray pattern of native and modified starches. Scanning electron microscopy revealed round and polygonal shapes for the starch granules with heterogeneous sizes and chemical modifications altered the starch granules morphology. Swelling power and solubility increased with increasing in temperature. Swelling power increased upon acetylation but decreased during acid thinning and oxidation. Solubility increased in these three modifications compared to the native starch.

Keywords White sorghum · Acetylation · Acid thinning · Oxidation · Morphology · X-ray crystallinity

Introduction

Starch is currently enjoying increased attention owing to its usefulness in different food products. Starch contrib-

utes greatly to the textural properties of many foods and is widely used in food and industrial applications as a thickener, colloidal, stabilizer, gelling agent, bulking agent and water retention agent etc. However, a large percentage of starch that serves this purpose is from crops that equally serve as a source of staple foods. This has led to finding an alternative source for starch in underutilized crops, cereal grains, Field pea (Ratnayake et al. 2001, Lentil: Hoover and Manuel 1996, Sago: Cui and Oates 1999) and Bambara groundnut: Adebawale et al. 2002). Starch is the principal food reserve polysaccharides in the plant kingdom. It forms the major source of carbohydrates in the human diet and is therefore of great economic importance being isolated on an industrial scale from many sources (Carioca et al. 1996). Large scale industrial production of starch has been focused on cassava, potato, maize and rice which are of commercial importance (Gebre-Mariam and Schmidt 1996). An underutilized plant sources that could serve as an alternative use are cereal grains such as white sorghum. It is vital food crops for millions of people in parts of Africa & Asia. It's high carbohydrate content (70%) makes it an invaluable source of starch for both domestic and industrial uses. Native starch is a good texture stabilizer and regulator in food systems (cousidine 1982) but limitations such as low shear resistance, thermal resistance, thermal decomposition and high tendency towards retrogradation limit its use in some industrial food applications. Chemical modifications which alter the physical and chemical characteristics, of native starch to improve its functional properties have been used to tailor starch to specific food applications. Chemical modification is generally achieved through derivatization such as etherification, esterification, cross-linking and acid hydro-

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lysis (Santacruz et al. 2002). In acetylation, hydrophilic hydroxyl groups are substituted with hydrophobic acetyl groups. It makes starch more hydrophobic and prevents the formation of hydrogen bonding between hydroxyl groups and water molecules. Since an aqueous starch dispersion has the tendency to increase in viscosity on cooling and finally to gel is related to the association of amylose molecules. The acetylation treatment retards or eliminates retrogradation will effect stabilization of the starch sol.

In acid modification, the hydroxonium ion attacks the glycosidic oxygen atom and hydrolyses the glycosidic linkage. An acid acts on the surface of the starch granule first before it gradually enters the inner region. It changes the physicochemical properties of starch without destroying its granule structure and the properties of acid –thinned starches differ according to their origin (Betancur et al. 1997). Effect of different acids (HCl, HNO₃, H₂SO₄, and H₃PO₄) used in the preparation under similar conditions of treatment on molecular weight, alkali fluidity number, iodine binding capacity and intrinsic viscosity of various starches has also been studied (Singh and Ali 2000). Oxidized starch is produced by reacting starch with a specified amount of oxidizing reagent under controlled conditions of temperature and pH (Kuakpeton and Wang 2001; Wurzburg 1986). Oxidation causes depolymerization of starch granules, which results in lower gel viscosity and minimizes retrogradation of amylose by introducing carbonyl and carboxyl groups (Rutenberg and Solarek 1984). The objective of this study was therefore, two fold: (i) investigate the effect of acetylation, acid thinning and oxidation on physicochemical properties of a starch isolated from white sorghum. (ii) To investigate the effect of acetylation, acid thinning and oxidation on granule morphology and X-ray crystallinity.

Materials & methods

Materials

White sorghum grains were collected from Agricultural Institute Samaru, Zaria. Sorghum is the most drought-tolerant cereal grain and requires little input during growth, but as with other crops yield well with good husbandry and it was harvested in December and stored in silo. All chemicals used were of Analar grade.

Isolation and purification of starch

About 1 kg of the sorghum grains was suspended as water in the ratio 1:5 differently. The pH of each solution was adjusted to 8 with 0.2% w/v of NaOH solution at 4°C for

12 h. The grains were screened and washed with distilled water until they were unpigmented. The steeping and wet milling procedure (The steeped sorghum grains was grinded in a small volume of water for 30 mins using a Warring type blender.” (Dynamic corp. of America, New Hartford City, CT) of Watson et al. (1955) with minor modifications was employed. The grains were blended with distilled water for 45 min. The slurry obtained after blending was re-suspended in 50 ml of distilled water and the pH was adjusted to 8.0 using 0.5M NaOH solution.

The pH was maintained between 8.0 and 8.5 and the dispersion was stirred manually for 30 min. The suspension obtained was screened through mesh size i.e 75 µm and an 80 µm (mesh size) and centrifuged for 30 min and was repeatedly washed for four times before drying in air for 48 h at 30±2.0°C. Starch lumps were powdered before it was stored in polythene bag prior before use.

Chemical composition

Standard Association of Official Analytical Chemistry method, AOAC (1996) was adopted for estimating moisture content, ash content, crude protein and crude fat.

Starch acetylation

Starch acetylation was followed as per the method of Sathe and Salunkhe (1981). 100 g of starch were dispersed in 500 ml of distilled water; it was magnetically stirred for 20 min. The pH of the slurry obtained was adjusted to 8.0 using 1 M of NaOH. 10.2 g acetic anhydride was added over a period of one hour while maintaining a pH range of 8.0–8.5. The reaction proceeded for 5 min after the addition of acetic anhydride. The pH of the slurry was reduced to 4.5 using 0.5 M HCl. It was filtered, washed for four times with distilled water and air-dried of 30±2.0°C for 48 h. Acetylated starch was reduced to 85 g.

Starch oxidation

Starch oxidation was prepared according to the method of Forssel et al. (1995) with modifications. 50% slurry of starch was prepared by dispersing 100 g of starch in 200 ml of distilled water. The pH was adjusted to 9.5 with 2 M NaOH. 10 g of NaOCl is of analar grade from the chemical store (6% active chlorine, 0.6 g Cl/100 g) was added drop-wise to the slurry over a period of 30 min, while maintaining pH range 9.0–9.5, with constant stirring 30±2°C. The reaction proceeded for 10 min after addition of NaOCl. After the reaction the pH was adjusted to 7 with 1 M H₂SO₄ and the oxidized starch was filtered, washed four times with distilled water and air-dried at 30±2.0°C for 48 h and the powdered oxidized starch was kept in a polythene bag.

Acid thinning

Starch acid thinning was performed according the method of Singh and Ali (2000). 200 g (dry basis) of the starch sample was hydrolyzed by suspension in 600 ml of 6% (w/v) HCl. Solution at 50°C for 24 h in water bath.

The slurry was stirred frequently during the treatment period. At the end of the time the reaction was stopped by neutralization with 10% (w/v) NaOH solution. The suspension was then washed three times with distilled water repeatedly until the filtrate was free from respective anions. The wet acid modified starch was air-dried in the air for 48 h at 30±2.0°C. The dried powder was finally sieved through a 100-mesh sifter to obtain acid-modified starch powder.

Determination of degree substitution of acetylated starch

The determination of the degree of substitution (D.S) of the acetylated starch was carried out by the procedure of Smith (1967). 5 g of the acetylated starch was dispersed in 75% aqueous ethanol and warmed for 30 min in water bath at 50°C. This was cooled to room temperatures and 25 ml of 1.0 M NaOH solution was added. Using the purified starch instead of the acetylated starch, a blank determination was carried out alongside that of the acetylated starch. The two flasks were Stoppard and allowed to stand for 72 h at room temperature and occasionally swirled. Excess NaOH was then back titrated

with 2.0 M HCl using methyl orange as indicator and the flask were allowed to stand at room temperature for 2 h, and the titration completed.

$$\% \text{ Acetyl} = \frac{(\text{Blank} - \text{sample}) \text{ ml} \times M_{\text{HCl}} \times 0.43 \times 100}{\text{Weight of sample}}$$

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

Determination of degree of substitution of oxidized starch

The degree of substitution of oxidized starch (carboxyl and carbonyl content) was determined using the procedure of Forssell et al. (1995). 5 g of starch was slurried in 25 ml of 0.1 M HCl and the solution was stirred occasionally over a period of 30 min. The slurry was then filtered through a medium-porosity fritted-glass funnel and residue was washed with distilled water until it was chloride free (by testing with AgNO₃). The sample was transferred to a beaker and suspended in 300 ml of distilled water. The suspension was heated in boiling water with continuous stirring for about 10 min to ensure complete gelatinization. The hot sample was titrated to pH 8.3 with 0.025 M NaOH solution.

$$\% \text{ Carboxyl} = \frac{(\text{Sample titre} - \text{Blank titre}) \text{ ml} \times \text{Alkali Molarity} \times 0.045 \times 100}{\text{Sample weight (g)}}$$

X-ray diffraction

The X-ray diffraction patterns of native white sorghum starch and its derivatives were recorded with an X'Pert pro X-ray diffractometer equipped with X'celerator as detector (Panalytical, Kassel, Germany). The diffractograms were registered at Bragg angle (2θ)=5–45° at a scan rate of 5°/min.

Granule morphology

Granule morphology of the starches was studied by scanning electron microscopy (SEM). Sample was sputter-coated with Au/pd using a vacuum evaporator (Edwards, Milano, Italy) and examined using a scanning electron microscope (model 500, Philips, Eindhoven, The Netherlands) at 10 kV accelerating voltage using the secondary electron technique.

Physicochemical properties

Swelling power and solubility

The effect of temperature on swelling and solubility was carried out according to the method of Waliszewski et al. (2003). 1 g of the starch sample was accurately weighed and quantitatively transferred into a clean dried test tube and weighed (W₁). The starch was then dispersed in 50 cm³ of distilled water using stirrer. The slurry obtained was heated for 30 min at various temperatures from 60°C to 90°C respectively. The mixture was cooled to room temperature and centrifuged for 15 min at 3000 g rpm. The residue obtained after centrifugation with the water it retained and the test tube was weighed (W₂). Aliquots (5 ml) of the supernatant were dried to a constant weight at 110°C. The residue obtained after drying the supernatant represented the amount of starch solubilized in water.

Solubility was calculated as g per 100 g of starch on dry weight basis.

Swelling power = $W_2 - W_1$ /weight of starch.

Effect of pH on swelling and solubility

The method of Adebawale et al. (2002) was used to determine the effect of pH on swelling and starch solubility. 1 g of the starch sample was accurately weighed and quantitatively transferred into a clean dried test tube and weighed (W_1). The slurries of (1% w/v) were prepared in distilled water and the pH adjusted to the desired values with 0.1 M HCl or 0.1 M NaOH.

The pH values for this analysis were 2, 4, 6, 8, 10, and 12. The slurries were then allowed to stand for 1 h at $30 \pm 2.0^\circ\text{C}$ for an additional 30 min, centrifuged (5000 rpm, 15 min). The residue obtained after centrifugation with the water it retained and the test tube was weighed (W_2). Aliquots (5 ml) of the supernatant were dried to a constant weight at 110°C to determine% solubility of the starch as mentioned above.

Statistical analysis

Analyses were done in triplicate. Analysis of variance was performed to calculate significant differences in treatment means, and LSD ($P < 0.05$) was used to separate means (SAS 1988).

Result and discussion

Chemical composition

The chemical composition of the white sorghum starch is presented in Table 1. The crude protein content of the native starch was 1.5%. The low value showed the purity of the starch as indicated by the low nitrogen and low ash levels. Gunaratue and Hoover (2002). The high carbohy-

drate contents (>80%) showed that the native starch was rich in starch. The percentage yield of white sorghum starch was 70 and agreed with Elevina et al. (1997) who reported percentage yields between 68% and 75% for white and dark sorghum starches.

The moisture contents ranged from 8.4% to 10.6%, these low values were advantageous in terms of shelf life and keeping the quality of the starches Olungwe et al. (1995). The values for moisture content were lower than value reported for sorghum starch 13% Davila and Camelo (2001). The slight difference between these values and those obtained by the author may be due to different method used in heating at different temperature and time.

Chemical modifications reduced the values for non-starch components such as protein, ash, fat and moisture content. The low non-starch components of the starch make them useful in some industrial applications and low protein content make them valuable in the production of syrups with high glucose content compared to the native starch. Reductions observed in fat, protein and% ash could also be attributed to various degradative processes during modifications of the starch and it might be due to washing of degraded starch molecule after modifications. Low moisture and fat contents in modified starch play a vital role in long storage but high moisture levels could be deleterious because it would favour microbial growth and cause the starch to become discoloured especially if moisture content level exceeds 18% Shipman (1967).

The effect of temperature on swelling power and solubility of the native starch and chemically modified starches was temperature dependent and is presented in (Fig. 1a–b). Swelling and solubility of the starch increased with increasing in temperature from 60°C to 90°C . The swelling power increased considerably more between the temperature range 80°C – 90°C . The swelling power from 60°C to 90°C ranged from 3.3 to 8.8 and was less than the swelling powers reported for six varieties of defatted sorghum starches which are in the range of 20.6–25.4 (Subramanian et al. 1994) and those reported by Perez and Gonzalez (1997). The solubility values are within those

Table 1 Proximate analysis of native, oxidized, acetylated and acid thinned white sorghum starch^{a,b}

Sample	Moisture (%)	Protein (%)	Crude fat (%)	Ash (%)	Carhydr(%)
WNS	10.3±0.05 ^a	1.5±0.20 ^a	1.4±0.12 ^a	1.6±0.03 ^a	85.2±0.10
OXW	10.6±0.02 ^b	1.0±0.03 ^b	0.5±0.02 ^b	0.9±0.03 ^b	88.5±0.02
ACETW	8.4±0.07 ^a	1.1±0.05 ^b	0.3±0.06 ^a	1.1±0.06 ^a	89.2±0.50
ACW	8.7±0.10 ^a	1.4±0.01 ^a	0.3±0.03 ^a	0.9±0.20 ^b	88.8±0.07

^a Each value represents the mean of three determinations ±standard deviation

^b Samples followed by the same letter are not significantly different ($p < 0.05$)

WNS - White native sorghum starch
 OXW - Oxidized white sorghum starch
 ACW - Acidified white sorghum starch
 ACETW - Acetylated white sorghum starch

The mean of three determinations (n=3)

Fig. 1 Effect of temperature and pH on quality characteristics of native and chemically modified white sorghum starches

reported by Subramanian et al. (1994). Solubilization of the starches increased with increasing in swelling power. This should be expected because as starch granules swell, the intragranular bonds are weakened the more and the loosely held starch molecules mostly amylose leach out into the continuous medium (Oates 1990). When starch molecules are heated in excess water, as semi crystalline structure is disrupted and water molecules become linked by hydrogen bonding to the exposed hydroxyl groups of amylose and amylopectin, which causes an increase in granule swelling and solubility. The degree of swelling and the amount soluble depends on the starch species. It has been proposed that bonding forces within the granules of starch affect swelling power (Carcea et al. 1990). Consequently, highly associated starch granules, with an extensive and strongly bonded micellar structure should display relatively greater resistance to swelling, while starches with amorphous areas undergo more progressive hydration and consequent swelling. Increase in swelling power and solubility was observed in acetylated starches. The introduction of (bulky) acetyl groups into starch molecules by acetylation leads to structural reorganization owing to steric hindrance; this results in repulsion between starch molecules, thus facilitating an increase in water percolation within the amorphous regions of granules and a consequent increase in swelling capacity and the structural disintegration probably weakens the starch granules after acetylation, and this enhances amylose leaching from the granule, thus increasing starch solubility. Oxidation and acid thinning reduced the swelling power but increased solubility at all temperatures. Similar reductions in swelling power after acid thinning and oxidation have been reported by (Shieldneck and Smith 1971; Deshpande and Damodaran 1990). During the process of acid thinning, the hydroxonium ion (H_3O^+) breaks down the glycosidic oxygen atoms and hydrolyses the glycosidic linkages. Acid gradually degrades the surface of the starch granule first before entering the inner region. It preferentially breaks down the amorphous region because the crystalline area is not freely accessible to the acid and this makes it remain intact. As a result of this development, % relative crystallinity increases following acid thinning. Increase in crystallinity probably accounts for reduction in swelling capacity of the acid thinned starch since swelling is restricted by stiffness of entangled amylopectin network in the crystalline region of the starch (Cairns et al. 1990). Increase in solubility following acid thinning and oxidation is a result of depolymerization and structural weakening of the starch granule. The effect of pH on the swelling power and solubility of native and chemically modified starches was pH dependent (Fig. 1c–d). Swelling power progressively increased from 2 to 12 while solubility reduced as pH increased from 2 to 6, after which progressive increases were observed with increase in pH. It was observed that

both native and modified starches had highest swelling power and solubility at pH 12. As the pH increased from 8 to 12 in the alkaline region the swelling power for all starches significantly increased, while little increase was observed in acidic region (pH 2–6). Shieldneck and Smith (1971) reported similar findings at alkaline pH. This behaviour could be due to interaction between the protein and starch at alkaline pH. Swelling is therefore expected to be high at alkaline pH and low at acidic pH, depending on the amount of protein associated with the starch. At alkaline pHs, partial gelatinization of starches may occur and this probably resulted in increased swelling power and solubility at these pHs (Deshpande and Damodaran 1990). At all pHs studied (2–12), both acid thinning, acetylation and oxidation reduced the swelling power. Minimum solubility of native starch was observed at pH 4, while modified derivatives had minimum solubility at pH 2. The increased solubility at alkaline pH may be due to increased hydrophilic character of the starch at these pH values. The x-ray diffraction patterns of native and modified starches are presented in Fig. 2. The results revealed that the acid-thinned starches showed similar x-ray patterns as their native starches and had slight sharper peaks at $2\theta=17.5^\circ$ and 23.5° . Acid thinned starches still remained typical A-type diffraction pattern. This result is related to other acid-thinned starches which exhibited the same crystalline type comparison with the unmodified starch (Atichokudomchai and Varavinit 2003; Wang et al. 2003). While oxidized and acetylated starches had their stronger peaks at $2\theta=17.5^\circ$, 23.5° and 27.5° , while at 27.5° were indicative of the A-type pattern. Scanning electron micrograph indicated round and polygonal shapes for the starch granules with heterogeneous sizes (Fig. 3a,b,c,d). At magnification of $\times 3000$, all the starches appeared in big granules with pores in a few of the granules, indicating real anatomical features of the native granule structure rather than artifacts of drying,

Fig. 2 X-ray diffraction spectra of native (unmodified), acid-thinned, acetylated and oxidized white sorghum starches

(a) native

(b) acidified.

(c) acetylated.

(d) oxidized.

Fig. 3 Scanning electron micrograph of (a) native, (b) acidified, (c) acetylated and (d) oxidised white sorghum starch ($\times 3000$ magnification)

specimen preparation (Fannon et al. 1992). Surface pores on granules of corn, sorghum and millet are openings to channels that penetrate in a radial direction through the granules (Baldwin et al. 1994; Huber and Bemiller 1997). This suggested that the concentration of H_3O^+ inside the granule interior may also be influenced by granule porosity. It was evident that hydrolysis does not occur uniformly as some areas are much more susceptible to attack than others. The acid acts by first attacking the surface and forming cracks on it. Acids cause surface alterations and degrade the external part of the granule by exo-corrosion. When exo-corrosion occurs, the internal part of the granule is corroded through small cracks through which acids could penetrate the granule. Jayakody and Hoover (2002) postulated that pores on the granule surface may allow direct access of H_3O^+ into the granule interior and thus should also be considered as a factor influencing the rate and extent of acid hydrolysis. In this study, it was found that small granules

are more rapidly hydrolyzed than big ones because of a larger and more reliable surface area. It appears that the starch granules which are readily or rapidly hydrolyzed with acid are those whose surfaces are readily attacked with the formation of canals. Similar observations have been reported by (Pang et al. 2007; Hoover and Manuel 1996; Vasanathan and Bhatta 1996). Acetylation treatment has also been found to alter the granule morphology, although to a lesser extent. In acetylated white starch, some granules surfaces were fused and deformed. This might also be the result of surface gelatinization upon addition of NaOH to maintain alkaline condition during acetic anhydride addition. This result agreed with (Singh et al. 2004; Gonzalez and Perez 2002; Sodhi and Singh 2005) who reported deformation of rice starch granules after acetylation. The micrograph of the oxidized starches showed that the granule surfaces were with more pores, indentation and cracks. Rutenberg and Solarek (1984) reported that the surfaces of regular corn and potato starch granules were affected with some apparent change at 8% active chlorine level.

Conclusion

The low non-starch components reduced after chemical modifications. Temperature exerted a change on the swelling power and solubility of the starches and swelling power increased after acetylation but reduced following acid thinning and oxidation. Solubility of these three types of modified starches increased. At alkaline regions high swelling power and solubility were observed for all the starches. The x-ray pattern of the chemical modified starches showed slight sharper peaks than the native starch and chemical modifications altered the starch granules morphology to a certain extent. The properties studied indicate that these three types of modified starches are well suited in various products of food industry.

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