Full Length Research Paper

Effect of heat moisture treatment and annealing on physicochemical properties of red sorghum starch

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Accepted 14 June, 2005

Red sorghum starch was physically modified by annealing and heat moisture treatment. The swelling power and solubility increased with increasing temperature range (60-90°), while annealing and heatmoisture treatment decreased swelling power and solubility of starch. Solubility and swelling were pH dependent with higher values obtained at pH 12 in both native and modified starches. Water absorption capacities of both annealed and heat-moisture treated starches increased with increasing levels of moisture treatment while highest value was observed in annealed starch. Oil absorption capacity of annealed starch was increased which was contrast to heat-moisture treated starches which decreased from 160 glg in native starch to 140 glg in HMR₁₈ and HMR₂₇. Pasting analysis in the Rapid Visco Analyser (RVA) revealed that both annealing and heat-moisture treatment increased pasting temperature, while alkaline water retention improved after physical modification.

Key words: Red sorghum starch, heat moisture treatments, annealing, functional properties.

INTRODUCTION

Starches are the principal food reserve polysaccharides in the plant kingdom. They form the major source of carbohydrates in human diet and are therefore of great economic importance. Starches obtained from grains, tubers and roots have been consumed as food for many centuries (Jones, 1983). Starch is a very versatile raw material with a wide field of applications. The growing demand of starches for the modern food industry has created interest for new sources of this polysaccharide. It occurs in granular form and the shapes of the granules are characteristic of the source of the starch. Starch granule can be separated into two distinctly different components, amylose and amylopectin (Hoover et al., 1991).

Sorghum is cultivated in the arid regions of the world. It has a high agronomic potential even under adverse tropical conditions, with 49.8% produced in the Western

Hemisphere. It contains a high percentage of starch (65–76%) and protein (11.6%). However, it contains some antinutritional components that could limit its direct consumption in foods and feeds. Hence, the need to process it very well (D'mello and Walker, 1991). Depending on the botanical source, starches present specific physicochemical and functional properties. The main functional properties of native starches are their good thickening and gelling properties, which makes them excellent ingredients for the manufacture of foods such as custards, porridges, puddings, cookies and sausages (Pomeranz, 1991).

The molecular arrangement in a starch granule can be altered by various physical treatments. Annealing and heat-moisture treatments (HMT) are two common physical means by which the treated starch can acquire modified properties without rupturing the granule. Annealing is generally carried out by heating granule starch with a large quantity of water at a temperature below the starch melting point, whereas HMT is carried out at limited moisture contents (18, 21, 24, and 27%) but at an elevated temperature (Eliasson and Gudmundsson, 1996). These physical treatments can change certain

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starch properties using simple and environmentally safe processes. The physical properties of a heat-moisture treated starch depend on the starch origin and treatment conditions used.

In previous works, heat-moisture treated starches displayed an increased paste stability and gelatinisation temperature, regardless of origin (Abraham, 1993; Collado and Corke, 1999; Donovan et al., 1983; Hoover and Vasanthan, 1994; Lorenz and Kulp, 1982; Stute, 1992). Collado and Corke (1999) treated a sweet potato starch, and found that the starch paste became short and sheer-stable and the starch gel exhibited marked increases in hardness and adhesiveness, whereas annealing increases susceptibility to amylase (Wang et al., 1997) and changes pasting curves (Jacobs et al., 1995; Stute, 1992), Chung et al. (2000), reported that annealing increased the surface hardness of mung bean starch gels, and the hardness.

The objective of the present research was to determine the impact of HMT and annealing on physicochemical properties of red sorghum. The studies involve isolation of starch, and determination of physicochemical properties, such as swelling, solubility, alkaline water retention, water and oil absorption, gelation and pasting characteristics.

MATERIALS AND METHODS

Sample

Red sorghum grains were collected from Institute of Agriculture Research, Samaru, Zaria, Nigeria. The grains were cleaned and freed of mold or weathering. All chemicals were reagent grade.

Starch isolation

The method of Watson et al. (1955) was employed, with modifications, for the starch isolation.

Modifications of red sorghum starch

Heat-moisture treatment: HMT was carried out using the method of France et al. (1995). The moisture levels of the starch samples were increased to 18, 21, 24, and 27% by adding the appropriate amount of distilled water. The mixtures were stirred; the sealed samples in glass jars were heated in an air oven at $100\,^{\circ}\text{C}$ for 16 h. After cooling, the jars were opened and the starch samples were air dried to a moisture content of 10%.

Annealing: The method of Knutson (1990) was adopted in preparation of annealed red sorghum starch. The starch was annealed by heating 100 g of starch in excess water at a temperature of 50 ℃ slightly above gelatinization temperature for 24 h Sample was centrifuged to remove excess water and air-dried.

Effect of temperature on solubility and swelling

A starch sample 1.0 g was accurately weighed and quantitatively transferred into a clear dried test tube and re-weighed (w₁). The

starch was then dispersed in $50~\rm cm^3$ of distilled water using a blender. The resultant slurry was heated at the desired temperature (60, 70, 80, 90° C) for 30 min in a water bath. The mixture was cooled to $30\pm2^{\circ}$ C and centrifuged ($500~\rm rpm$, $15~\rm min$). Aliquots ($5~\rm ml$) 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 $g/100~\rm g$ of starch on a dry weight basis. The residue obtained from the above experiment (after centrifugation) with the water it retained was quantitatively transferred to the clean dried test tube used earlier and weighed (w_2).

Swelling of starch = $w_2 - w_1$ /weight of starch.

Effect of pH on swelling and solubility

To determine the effect of pH on swelling and solubility of the starch, slurries (1%, w/v) were prepared in distilled water and the pH adjusted to the desired values with 0.1 M HCl or NaOH. The slurries were then allowed to stand at $30\pm2\,^{\circ}\mathrm{C}$ for an additional 30 min, centrifuged (5000 rpm, 15 min) and the swelling (1%) and solubility determined as described above.

Oil and water absorption capacities

The method of Beuchat (1977) was employ and to determine the oil and water absorption capacities of the starch.

Gelation studies

The gelation properties of the starch were determined as described by Sathe and Salunkhe (1981a).

Alkaline water retention

1.0 g of each sample was quantitatively transferred into a test tube and weighed (w_1) . 5.0 ml of 0.1 M NaHCO₃ was added and mixed for 30 s (Fisher Vortex Genie 2^{TM} Mixers). The sample was then allowed to stand at 30 ± 2 °C for 20 min, centrifuged (200 rpm, 15 min) and drained for 10 min at an angle 10-15 ° to the horizontal. Test tube with the content was then weighed (w_2) and the alkaline water retention calculated as follows alkaline water retention capacity (g/g) of sample $w_2 - w_1$.

Rapid visco analysis measurement

The paste viscosity of red sorghum starch was evaluated by RVA. In the RVA, the short temperature profile (13 min) was used and the mixture was stirred at 960 rpm for I0 s and then at 160 rpm for the remainder of the test. A mixture of 3.5 g starch and 25.0 ml water was held at $50\,^{\circ}$ C for 1 min and subsequently, heated to $95\,^{\circ}$ at $12.2\,^{\circ}$ C/min.

Holding time at 95 ℃ was 2.5 min, subsequently the sample was cooled to 50 ℃ at 1.2 ℃/min, where it was kept for 2.1 min.

RESULTS AND DISCUSSION

The effect of temperature on swelling power of red sorghum starch (Table 1) revealed that each type of starch swells differently, indicating differences in the

Table 1. Effect of temperature on swelling of native and modified red sorghum starches.

Swelling Power	RNS (%)	RSAN (%)	RHMT ₁₈	RHMT ₂₁	RHMT ₂₄	RHMT ₂₇
60℃	3.24±0.04	1.72±0.03	2.96±0.03	3.24±0.02	2.29±0.02	3.34±0.02
70℃	4.94±002	5.92±0.02	4.13±0.03	4.63±0.03	3.74±0.04	3.93±0.03
80℃	6.60±0.04	7.32±0.02	6.23±0.03	6.60±0.02	6.61±0.02	5.20±0.01
90℃	9.93±003	9.24±0.04	7.85±0.03	7.10±0.01	7.46±0.02	5.91±0.02

All values are means of triplicate determination \pm S.D.

RNS: Red sorghum native starch. RSAN: Red sorghum annealed starch.

RHMT₁₈₋₂₇: Red sorghum heat moisture treated starches.

Table 2. Effect of temperature on solubility of native and modified red sorghum starches.

Swelling Power	RNS (%)	RSAN (%)	RHMT ₁₈	RHMT ₂₁	RHMT ₂₄	RHMT ₂₇
60°C	1.98±0.04	0.64±0.02	0.14±0.01	0.46±0.02	0.83±0.03	0.50±0.02
70°C	2.08±002	0.70±0.01	0.61±0.03	0.70±0.01	1.34±0.02	0.60±0.01
80℃	2.34±0.03	1.90±0.04	1.03±0.03	1.21±0.04	2.06±0.02	1.54±0.04
90℃	3.03±003	4.20±0.02	2.24±0.04	3.24±0.02	3.25±0.02	4.41±0.07

All values are means of triplicate determination \pm S.D.

RNS: Red sorghum native starch. RSAN: Red sorghum annealed starch.

RHMT₁₈₋₂₇: Red sorghum heat moisture treated starches.

Table 3. The effect of ph on the swelling power of red sorghum starches (native and modified).

рН	RNS (%)	RSAN (%)	RHMT ₁₈	RHMT ₂₁	RHMT ₂₄	RHMT ₂₇
2	2.6±0.4	0.72±0.07	0.53±0.06	0.38±0.07	0.34±0.06	0.21±0.06
4	3.2±0.4	0.28±0.06	0.43±0.05	0.47±0.06	0.37±0.06	0.23±0.04
6	3.5±0.6	0.41±0.06	0.37±0.06	0.44±0.05	0.43±0.06	0.36±0.08
8	4.0±0.6	0.44±0.04	0.42±0.06	0.53±0.05	0.43±0.06	0.46±0.05
10	5.6±0.6	0.47±0.04	0.48±0.06	0.60±0.07	0.49±0.06	0.53±0.05
12	7.8±0.6	0.48±0.06	0.65±0.06	0.61±0.06	0.51±0.07	0.55±0.07

All values are means of triplicate determination \pm S.D.

RNS: Red sorghum native starch. RSAN: Red sorghum annealed starch.

RHMT₁₈₋₂₇: Red sorghum heat moisture treated starches.

molecular organization within the granules. However, the swelling power of starch increased with temperature. The degree of swelling and the amount soluble components depends on the starch species (Schoch, 1964). There was a decrease in swelling power and solubility of the annealed starch compared to the native starch due to the ordering rearrangement of starch molecules in the granules. Eerlingen et al. (1997) proposed that the decrease in swelling powers and the increase in gelatinization temperature were caused by transformation of amorphous amylose into a helical form, increase in interactions between amylose chains, and alteration in the interaction between crystallites and the amorphous matrix during annealing.

The solubility of all the starches increased with temperature (Table 2). HMT_{27} showed the highest

solubility. This is probably due to the weathering of the starch granules during HMT leading to improved solubility (Shieldneck and Smith, 1971). HMT allowed the amylose molecules located in the bulk amorphous regions to interact with the branched segments of amylopectin in the crystalline regions (Hoover et al., 1993; Hoover and Manuel, 1994).

The effect of pH on the swelling power of red sorghum starches (Table 3) showed that increase in pH leads to increase in the swelling power for all starches in the alkaline region (pH 8–12) while there were very little increase in the acidic region (pH 2–6). Shieldneck and Smith (1971) reported similar findings at alkaline pH. Native starch exhibited a higher solubility than the modified starches (Table 4). RSAN exhibited a maximum at pH 2, which indicated good applications in acidic food

Table 4. Effect of pH on solubility of native and modified red sorghum starches.

рН	RNS (%)	RSAN (%)	RHMT ₁₈	RHMT ₂₁	RHMT ₂₄	RHMT ₂₇
2	3.4±0.6	0.71±0.07	0.11±0.05	0.23±0.05	0.38±0.07	0.25±0.05
4	2.2±0.5	0.46±0.05	0.18±0.05	0.04±0.03	0.44±0.05	0.38±0.05
6	4.6±0.6	0.42±0.06	0.63±0.07	0.17±0.05	0.53±0.06	0.41±0.05
8	7.3±0.6	0.28±0.06	0.45±0.04	0.41±0.05	0.35±0.05	0.39±0.06
10	10.2±0.5	0.41±0.06	0.40±0.05	0.27±0.05	0.39±0.07	0.48±0.06
12	12.2±0.6	0.47±0.07	0.98±0.05	1.34±0.06	0.50±0.05	0.53±0.05

All values are means of triplicate determination \pm S.D.

RNS: Red sorghum native starch. RSAN: Red sorghum annealed starch.

RHMT₁₈₋₂₇: Red sorghum heat moisture treated starches.

Table 5. Gelation capacity of native and modified red sorghum starches.

Sample concentration	Native RNS	Annealed RSAN	HMTR ₁₈	HMTR ₂₁	HMTR ₂₄	HMTR ₂₇
3	Viscous	Viscous	Viscous	Viscous	Viscous	Viscous
6	Viscous	Viscous	Viscous	Viscous	Viscous	Viscous
9	Viscous	Viscous	Viscous	Viscous	Viscous	Viscous
12	Viscous	Viscous	Viscous	Viscous	Viscous	Viscous
15	+ Gel	+ Gel	Viscous	Viscous	Viscous	Viscous
18	+ Gel	+ Gel	+ Gel	Viscous	+ Gel	+ Gel
21	Firmgel	Firmgel	+ Gel	+ Gel	+ Gel	+ Firmgel
LGC	15	15	18	21	18	18

Determinations carried out in triplicates.

(-) No gelation, (+) gelation

LGC - Least gelation concentration.

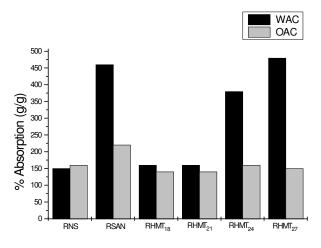


Figure 1. Oil and water absorption capacities of native and modified red sorghum starches. RNS, red sorghum native starch; RSAN, red sorghum annealed starch; RHMT $_{18-27}$, red sorghum heat moisture treated starches.

items. The increased solubility at alkaline pH may be due to increase hydrophilic characters of the starch at these pH values.

Water and oil absorption capacities of the native and modified are presented in Figure 1. Heat moisture treatment linearly increased water binding capacity of these starches, which implies that hydrophilic tendency increased with increasing level of moisture treatment. While there were decreases in oil absorption capacity from 160mg/g in native starch to 150 g/g in RHMT₂₇. This result compared favourably with those obtained by Kulp and Lorenz (1981) for potato and wheat starches. Annealed starch here increased in water absorption capacity indicating that the amorphous region may expand slightly and some hydrogen bonds between the amorphous and crystalline regions could be broken. There was increase in oil binding capacity, which shows the lipophilic nature of the outer covering formed in the granule surface during annealing (Morrison et al., 1993).

As the starch granules swell to form a gel by heating in water, the amorphous region became hydrated. Table 5 shows the effect of concentration on the gelation capacity of the native and modified starches. Native starch did not form a gel until it reached 15% concentration. Annealed starch had the same least gelation with the native starch while the heat moisture treated starches from HMTR₁₈, HMTR₂₄ and HMTR₂₇ had higher concentration than

Parameters	RNS Native	Annealed RSAN	HMR ₁₈	HMR ₂₁	HMR ₂₄	HMR ₂₇
Peak Viscosity	97.00	365.04	257.08	172.08	119.67	126.78
Hot Pasting Viscosity	44.67	208.07	170.75	61.83	42.75	46.35
Breakdown	52.33	150.04	86.33	110.17	75.92	82.15
Final Viscosity	59.50	167.08	207.08	95.58	59.25	60.12
Set Back	14.83	126.19	36.33	36.75	16.50	18.56
Pasting Temperature	63.75	64.55	64.70	65.20	64.20	64.05

Table 6. Pasting properties of native and modified red sorghum starches.

RNS: Red sorghum native starch. RSAN: Red sorghum annealed starch.

RHMT₁₈₋₂₇: Red sorghum heat moisture treated starches.

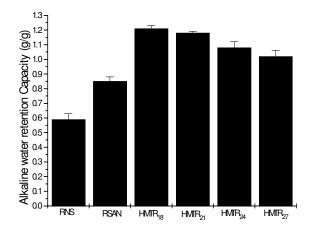


Figure 2. Alkaline water retention of native and modified red sorghum starches. RNS, red sorghum native starch; RSAN, red sorghum annealed starch; RHMT18-27, red sorghum heat moisture treated starches.

native starch. HMTR₂₁ has the highest gelation capacity and it might be due to the increased quantity of the amorphous phase, induced by transformation of the intercrystalline and crystalline regions by HMT might cause an increased readiness of the structural transformation (Lim et al., 2001).

All the modified starches showed increase in alkaline water retention compared to the native starch (Figure 2). This increase in water retention was attributed to the surface area of the starch phase (Yamazaki et al., 1997).

The peak viscosity (pv) at any concentration is an important distinguishing feature of a starch. Treated starches showed an increase in viscosity development on set temperature and a decrease in peak viscosity. The extent of the effects depended on the treatment. The annealed starch showed a peak viscosity higher than native and heat-moisture treated starches due to unrestricted swelling of the starch. The viscosity values obtained after the isothermal holding at 95 ℃ were generally lower than the peak viscosity value. There was

considerable increase in final viscosity from RSAN HMTR₁₈-HMTR₂₁, which indicated dissolved starch molecules into larger units as the solutions were cooled. Annealed starch had the highest set back value, because the tendency toward set back or gel formation has been minimized in the heat-moisture treated starches. According to Jacobs et al. (1995), both the formation of a tightly packed array of swollen and deformable granules and the leaching of amylose can contribute to viscosity development in starch paste during heating and rigidity of granule increases due to insufficient gelatinization. This should give higher viscosity to paste because the rigid granules are more resistant to shearing. The clarity of a starch gel directly influences the slime and colours of products that contain it as a thickner. Annealed starch had the highest breakdown compared with native starch and heat-moisture treated starches indicating that it had less stability during heating, whereas peak viscosity increased after HMT.

In conclusion, starch obtained from red sorghum grains can be modified physically by two common modifications such as annealing and HMT. Temperature exerted a change on the swelling capacity and solubility of the starch, and also the starches behaved differently towards acidic and alkaline regions. Both annealing and HMT increased the surface hardness of red sorghum starch gels and the hardness was inversely proportional to the swelling power. Therefore physical modifications would enhance gel formation, which is good for the food industries.

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