

Effect of Steeping Treatment on Pasting and Thermal Properties of Sorghum Starches

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ABSTRACT

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Chemical treatments in wet milling could improve the physico-chemical properties of starch isolated from high-tannin sorghums. Sorghums Chirimaugute (medium-tannin), DC-75 (high-tannin), and SV2 (tannin-free) were steeped in water, dilute HCl (0.9%, v/v), formaldehyde (0.05%, v/v), and NaOH (0.3%, w/v) solutions before wet milling and starch separation. Pasting, textural, and thermal properties of starch were determined. Steeping in NaOH resulted in starches with higher peak viscosity (PV), cool paste viscosity (CPV), and setback than when water, HCl, and formaldehyde were used. The time to PV (P_{time}) and PV temperature (P_{temp}) were markedly reduced by treatment with NaOH. NaOH could have caused a degree of pregelatinization. HCl treatment gave

starches with higher P_{temp} and P_{time} , presumably due to delayed granule swelling. Gel hardness was largely determined by the starch amylose content. The low hardness of DC-75 starch gels was slightly improved in NaOH-treated grains. Gelatinization temperatures of sorghum starches were generally low, regardless of steeping treatment. Starch from NaOH-treated grain generally had slightly higher gelatinization temperatures than when water, HCl, or HCHO was used. Chemical treatments during steeping of sorghum grains greatly affected starch properties. Dilute alkali steeping during wet milling could be used to improve properties of starch isolated from tannin-containing sorghums.

Tannin-containing sorghum grain poses problems to the food processor from appearance and the antinutritional effects of condensed tannins (Butler 1982). Milling sorghum grains by decortication, as practiced in southern Africa, removes most of the tannins located in the outer layers of the grain (Chibber et al 1978). However, most high-tannin sorghums have a soft, floury endosperm that makes decortication inefficient (Chibber et al 1980; Mwasaru et al 1988). Chemical treatments using water, NaOH, or HCl (Reichert et al 1980; Beta et al 2000) and formaldehyde (Daiber 1975) have reduced or deactivated tannins in sorghum grain. NaOH also improves water uptake of sorghum grains (Dewar et al 1997). Yang and Seib (1995) used NaOH to improve the brightness of sorghum starch. However, there is no information on the effect of chemical treatment on starch properties of tannin-containing and tannin-free sorghums.

The possible adsorption and retention of tannins by starch if extracted from tannin-containing sorghum cultivars has been indicated (Davis and Hosney 1979). The pink color of sorghum starch has been associated with pigments in the pericarp and endosperm of the grain (Freeman and Watson 1971; Norris 1971). Subramanian et al (1994) implicated alcohol-soluble components in causing the dullness of sorghum starch. Sorghum starches also exhibit high gelatinization temperature ranges (71–81°C) (Akingbala et al 1982). The objective of this investigation was to determine the effect of chemical treatment during steeping on pasting, textural, and thermal properties of starch extracted from a tannin-free, medium-tannin, and tannin-rich sorghum.

MATERIALS AND METHODS

Samples

Three sorghum cultivars grown under uniform field conditions in the 1996–97 season at Matopos, Zimbabwe, were used: Chiri-

maugute (landrace, medium-tannin), DC-75 (hybrid, high-tannin), and SV2 (cultivar, tannin-free) (Beta et al 1999).

Starch Extraction

Starch was extracted following a combination of the methods used by Watson et al (1955), Perez et al (1993), and Zhao and Whistler (1994). Sorghum grain (100 g) was steeped in 200 mL of water, HCl (0.9%, v/v), formaldehyde (HCHO) (0.05%, v/v), or NaOH (0.3%, w/v) at 5°C for 24 hr. The steeped grain was washed and ground with an equal volume of water using a Waring blender. The slurry was filtered through a 200-mesh sieve (75- μ m opening). The material remaining on the sieve was rinsed with water. Grinding and filtering was repeated on this material. The material still remaining on the sieve was discarded. The filtrate was centrifuged at 760 \times g for 10 min. The gray-colored top protein layer was removed. Excess water was added to resuspend the sample and centrifugation (760 \times g) was done for 3 min. Washing and recentrifugation was repeated until the top starch layer was white. The starch was dried for 24 hr at 40°C.

Pasting Properties

Pasting properties of sorghum starches were determined using a Rapid Visco Analyser model 3D (RVA) (Newport Scientific, Warriewood, Australia). Sorghum starch (3 g, 14% moisture basis) was mixed with 25 g of accurately weighed water (10.32% dry solid content) in the aluminum canister. Peak viscosity (PV), temperature at PV (P_{temp}), time to PV (P_{time}), holding or hot paste viscosity (HPV), final or cool paste viscosity (CPV), and setback (CPV-HPV) were recorded. Two replicates per sample were analyzed.

Textural Properties

The sample from RVA testing was allowed to stand for 24 hr at room temperature for gelation to take place (Bhattacharya et al 1997). Hardness or firmness of the starch gel was measured using an SMS model TA-TX2i texture analyzer (Stable Micro Systems, Godalming, England). A standard two-cycle program was used to compress the gels for a distance of 10 mm at a crosshead speed of 30 mm/min using a 7-mm cylindrical probe with a flat end. Hardness was recorded as maximum force on cycle one in grams (g). Four repeat measurements were taken of each of the two gel replicates per sample.

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Thermal Properties

A Mettler DSC-20 differential scanning calorimeter (Mettler-Toledo AG Instruments, Naenikon-Uster, Switzerland) was used to measure thermal properties of the starch. Starch (2 mg, dwb) was weighed directly into a 40- μ L aluminum standard pan and water was added to give a final weight of 6.5 mg. The pan was covered with the lid and hermetically sealed. After equilibration at room temperature, the sample was heated from 30 to 120°C at 10°C/min. The gelatinization temperature ($^{\circ}$ C), parameters of onset temperature (T_o), peak (T_p), and conclusion (T_c) were determined. Gelatinization enthalpy (ΔH) in J/g was also recorded. Two replicates per sample were analyzed.

Statistical Analysis

Data was analyzed using ANOVA procedures of the Statistical Analysis System (version 6.10, SAS Institute, Cary, NC). Means were compared at the 5% significance level using Duncan's multiple range test.

RESULTS AND DISCUSSION

Starch Color

The color of starch from NaOH-treated grain was brighter than that treated with water, HCl, or HCHO during steeping. The effect of NaOH on brightness of sorghum starch color has been reported earlier (Yang and Seib 1995). SV2 gave a white starch with all treatments. SV2 is a tannin-free cultivar with white pericarp and tan glumes. However, DC-75 and Chirimaugute gave pink-colored starches, presumably due to the polyphenols present in the pigmented testa layer (Beta et al 1999).

Pasting and Swelling Properties

Pasting properties of sorghum starches are arranged in Table I according to treatment and cultivar. Starch pasting and swelling properties were affected by treatment and cultivar at $P < 0.05$. The peak viscosity (PV) was increased by the NaOH treatment. PV is an indication of the water binding capacity of the starch (Anonymous

1998). Treatment with NaOH apparently enhanced starch swelling, causing an increase in viscosity. Molecules containing ionic groups have intensified water-binding ability at the ionic location and, in addition, their repulsive charges cause the starch molecules to repel each other (Whistler and BeMiller 1997). Thus, NaOH presumably hydrated the starch molecules and also caused some partial pregelatinization. HCl and HCHO treatment gave relatively lower PV. HCl-treated sorghum could have undergone mild, acid-catalyzed hydrolysis resulting in starch depolymerization and, hence, lower viscosity products (Whistler and BeMiller 1997). HCHO presumably cross-linked the polymers, particularly protein and polyphenols, present as minor constituents in the starch, causing a reduction in swelling power. Starch from DC-75 had the highest PV regardless of treatment, probably because its amylose content was relatively lower than the other starches (Table II). The ability of starch to withstand heating and shear stress was indicated by hot paste viscosity (HPV). Subjecting a starch sample to a constant high temperature (95°C) and mechanical shear causes more granules to disintegrate. Amylose molecules will generally leach out into the solution and undergo alignment, resulting in a greater decrease in viscosity (Whistler and BeMiller 1997). NaOH and HCl treatments gave markedly higher HPV than water and HCHO for SV2 and Chirimaugute starches. Starch from NaOH-treated grain, apparently underwent excessive shear-thinning because the highly swollen granules were broken up easily. Acid-modified starches also break up easily and dissolve when heated in water (Whistler and BeMiller 1997). The tannin-rich cultivar, DC-75, gave starch with the lowest HPV, presumably due to the low starch amylose content. Researchers have surmised that the degree of shear thinning may also be related to the morphology and rigidity of the swollen granules (Williams and Bowler 1982; Steeneken 1987). Cool paste viscosity (CPV) and setback were generally higher in starch from NaOH-treated grain (Table I). Mistry and Eckhoff (1992) reported that an alkali extraction process results in maize starch with higher viscosity and higher hydration capacity in the commercial maize starch extraction process.

Starch from NaOH-treated grain took less time to reach PV presumably due to partial gelatinization (Table I). However, HCl treat-

TABLE I
Effect of Steeping Treatments^a on Pasting Properties^b
of Starch from Three Sorghum Cultivars

Cultivar	Control	HCl	HCHO	NaOH
SV2				
PV	373b ^c	360d	368bc	396a
HPV	112c	151a	125b	151a
CPV	257d	299b	272c	319a
SB	145bc	149b	148b	168a
P _{time}	7.27b	7.93a	7.34b	6.44c
P _{temp}	87.6b	91.6a	87.9b	82.6c
Chirimaugute				
PV	373b	368bc	361cd	410a
HPV	124c	162b	127c	177a
CPV	270d	306b	281c	356a
SB	146c	145c	153b	179a
P _{time}	7.10b	7.90a	7.18b	6.27c
P _{temp}	86.5c	91.3a	87.1b	81.5d
DC-75				
PV	463b	443c	424d	495a
HPV	116bc	126a	116bc	118b
CPV	239b	245b	239b	255a
SB	124b	119b	123b	136a
P _{time}	6.27ab	6.37a	6.40a	6.14b
P _{temp}	81.5b	82.1a	82.3a	80.7c

^a SV2, Chirimaugute, and DC-75, in HCl (0.9%, v/v), HCHO (0.05%, v/v), NaOH (0.3%, w/v).

^b PV = peak viscosity, HPV = hot peak viscosity, CPV = final or cool paste viscosity, and SB = setback (CPV-HPV) measured in Rapid Visco Analyser units (RVU). P_{time} = time (min) to PV and P_{temp} = temperature ($^{\circ}$ C) at PV.

^c Values followed by the same letter in the same row are not significantly different ($P < 0.05$).

TABLE II
Effect of Steeping Treatments^a on Gel Hardness and Thermal
Properties^b of Starch from Three Sorghum Cultivars

Cultivar ^c	Control	HCl	HCHO	NaOH
SV2				
Hard	73.6b ^d	81.5a	81.5a	80.6a
T_o	59.7c	60.6b	62.7a	62.9a
T_p	67.0c	68.3b	69.0a	69.3a
T_c	75.9b	78.5a	78.1a	78.3a
ΔH	9.4c	10.8a	9.8bc	10.1b
Chirimaugute				
Hard	82.9a	82.9a	79.2b	77.4c
T_o	60.6a	60.3a	60.6a	60.7a
T_p	66.8b	66.5b	66.8b	67.5a
T_c	75.8b	76.1ab	76.2ab	76.9a
ΔH	9.1ab	9.0b	9.1ab	9.6a
DC-75				
Hard	31.0c	31.5c	33.9b	36.8a
T_o	61.2a	60.6b	60.7b	61.2a
T_p	67.5a	67.0b	67.5a	67.5a
T_c	77.9b	78.3b	78.6ab	79.4a
ΔH	9.7b	9.7b	10.6a	9.7b

^a SV2, Chirimaugute, and DC-75, in HCl (0.9%, v/v), HCHO (0.05%, v/v), NaOH (0.3%, w/v).

^b Hard = starch gel hardness, T_o = onset temperature, T_p = peak temperature, T_c = conclusion temperature, ΔH = gelatinization enthalpy.

^c Amylose contents for SV2, Chirimaugute, and DC-75 are 27.4, 28.7, and 21.5%, respectively. Determined on starch from NaOH-treated grain using an iodine-spectrophotometric method of Juliano et al (1981).

^d Values followed by the same letter in the same row are not significantly different ($P < 0.05$).

ment gave starches that took longer to reach PV, presumably because of delayed starch swelling, as evidenced by the comparatively low viscosity. P_{time} was lowest for DC-75 because of its higher amylopectin content, which accelerated granule swelling more than in other starches. P_{temp} was markedly lowered in starches from NaOH-treated grain, as the partially gelatinized starch granules easily produced high viscosity pastes. Treatment with HCl gave starches with higher P_{temp} because more energy was required to produce viscous pastes from some of the relatively shortened starch chains. P_{temp} range under different treatments (80.8–82.3°C) was lower for DC-75 starch compared with other starches that had higher amylose content.

Textural Properties

Hardness or firmness of the starch gels was significantly affected by both treatment and cultivar (Table II). All treatments resulted in very soft gels for DC-75 starches. This was due to low amylose content of DC-75 as retrogradation of cooked starch involves both starch polymers. Amylose underwent retrogradation at a much more rapid rate than did amylopectin (Whistler and BeMiller 1997). A firmer gel can also be prepared with starch from corneous rather than the flourey endosperm of sorghum (Cagampang and Kirleis 1984). However, a firm starch gel was still obtained from Chirimaugute, a cultivar with a flourey endosperm texture largely due to its relatively high amylose content. With the exception of Chirimaugute, NaOH generally gave starches with firmer gels than other treatments. Thus treatment with NaOH enhanced retrogradation, as evidenced by the high setback values of the starch pastes (Table I). The control (water) resulted in a gel that was less firm and significantly different from all the other treatments for SV2 starch. Gel firmness was largely affected by the amount of amylose present in the starches.

Thermal Properties

Starch from NaOH-treated grain generally had slightly higher gelatinization temperatures than the water, HCl, and HCHO treatments (Table II). The effect of NaOH on lowering P_{temp} during pasting could not be compared directly with the effect on starch thermal properties. Gelatinization refers to the disruption of molecular order within starch granules, while PV is reached when some of the highly swollen granules have ruptured and fragmented due to shearing forces (Whistler and BeMiller 1997). Steeping SV2 and DC-75 in HCHO or NaOH gave starches with similar T_p values. T_p values for starches isolated from Zimbabwean cultivars were lower, regardless of treatment, than values reported by Akingbala et al (1982), which ranged from 74 to 76°C for normal sorghum starches. T_p values for sorghum starches from NaOH-treated grain were also lower than those reported for eight maize starches (72–75°C) extracted in alkali (Mistry and Eckhoff 1992). T_c was lowest when water was used for steeping. Mean values of T_o , T_p , and T_c for starches isolated from 35 tropical maize germ plasm accessions were 63.0, 71.0, and 77.8°C, respectively (Li et al 1994), values similar or slightly higher than those of the sorghum starches studied. These findings confirm the view of Taylor et al (1997) that southern African sorghums may have a relatively low gelatinization temperature range. The enthalpy for gelatinization (ΔH) was quite narrow at 9.0–10.8 J/g. ΔH was significantly higher in HCHO-treated DC-75 starch than with other steeping solutions. HCHO could have largely reacted with tannins (Daiber 1975) or proteins and had little effect on the molecular order of the starch granule. However, starches of SV2 and Chirimaugute, from water- and HCl-treated grain, respectively, had lower ΔH values than other treatments, an indication of less ordered granules.

CONCLUSIONS

Sorghum starch pastes had higher peak viscosity, cool paste viscosity, and setback when grain was steeped in NaOH than in water, HCl, or formaldehyde. NaOH also reduced the time to reach peak viscosity and temperature at peak viscosity. NaOH appears to

improve sorghum starch properties for certain applications by causing partial pregelatinization. The low hardness of DC-75 starch gels was slightly improved by the NaOH treatment of grain. Gelatinization temperatures of Zimbabwean sorghum starches were generally low, regardless of treatment. It is surprising how much soaking treatments affected sorghum starch properties. Dilute alkali solution, if used during steeping of sorghum grains, could enhance the starch properties of tannin-containing and tannin-free sorghums.

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