Shear Thinning Properties of Sorghum Starch

S. N. SUBRAHMANYAM[2,3] and R. C. HOSENEY[2]

Cereal Chem. 72(1):7-10

ABSTRACT

This study was made to determine the causes of variations in shear thinning properties of sorghum starches. Shear thinning was measured as loss of viscosity with stirring at 95°C for 1 hr in the Brabender viscoamylograph. Certain cultivars of sorghum gave starches that shear thinned less than other sorghum starches. Removal of starch lipids by exhaustive extraction with methanol did not affect shear thinning. However, propanol-water defatting of sorghum starches at 100°C gave starch pastes that either did not shear thin or shear thinned less. This appeared to be the result of a change in the starch, because adding the extracted lipid back did not result in a system with its original properties. Other factors examined in an effort to explain shear thinning were swelling, solubilization, gelatinization characteristics, iodine binding capacity, and phosphorus content. Relatively high correlations were found between shear thinning and swelling after 1 hr of stirring at 95°C ($r = 0.91$) and solubility after 1 hr of stirring at 95°C ($r = 0.96$).

Many uses of starch involve heating it in water, which leads to granule hydration, swelling, and at a high enough temperature, solubilization of starch molecules. These events are referred to collectively as starch gelatinization (Zobel 1984). The most important starch properties, with respect to its utilization, are often related to the properties of the gelatinized pastes. In general, maize and sorghum starches have similar properties (Morrison et al 1984). Although sorghum is one of the major cereal crops produced, it is generally considered to be inferior to maize for food, feed, or industrial uses. Previous work (Subramanian et al 1994) has shown that considerable variation exists in the loss of viscosity under shear for different sorghum starch samples. The purpose of this study was to identify the reasons why starch from certain cultivars of sorghum shear-thinned less than starch from others.

MATERIALS AND METHODS

Starches

Seven sorghum samples were used. Four cultivars were grown in Mexico: UANL-1-V-187, Bajio, Tamaulipas, and Blanco 86 (kindly supplied by Arancia S.A. De CV, Guadalajara, Mexico). Two cultivars were grown in the United States: Dorado and Dekalb 42Y (at the Kansas State University Agronomy farm). The seventh sample was a commercially grown bronze-colored local sorghum. The sample was bright, clean, and appeared to be free of mold or weathering. Starches were isolated from these sorghums by the steeping and wet milling procedure of Watson et al (1955) with minor modifications. Whole grain (300 g) was soaked with occasional stirring in 750 ml of distilled water containing 1.22 g of sodium metabisulphite at 50°C for 24 hr. The steep water was then decanted, and the grain was ground with an equal volume of water (equal to volume of grain) using a blender for 3 min at full speed. The slurry was filtered in succession through sieves of 50, 100, 180, and 325 mesh. The material remaining on the sieves was rinsed and then discarded. The filtrate was allowed to stand for 3 hr and then centrifuged at 1,100 × *g* for 10 min. The grey-colored top layer was removed with a spatula and discarded. Excess water was added, and the sample was resuspended and centrifuged at 1,100 × *g* for 3 min. The washing and centrifugation steps were repeated until the top starch layer was white. The starch was suspended in water and filtered through a Buchner funnel with Whatman No. 4 filter paper by continuous washing with water. Finally, starch was dried for 36 hr at 40°C.

Consistency of Starch Pastes

Amylograms were produced with a Brabender Viscograph-E (C.W. Brabender, South Hackensack, NJ) operated with a bowl speed of 75 rpm and with 7.5% starch (dwb) in 450 ml of distilled water.

Shear Thinning

The starch pastes were allowed to shear thin by stirring in the amylograph at 95°C at 75 rpm for 60 min. The percent of thinning was calculated as the decrease in viscosity from the peak viscosity to the viscosity after 60 min of stirring.

Swelling Power and Solubility

Starch paste samples of ~50 g were drawn from the viscoamylograph bowl at peak viscosity and also after holding the sample at 95°C for 1 hr. The final volume was adjusted to 250 ml with distilled water. From this, 30-ml aliquots were centrifuged at 1,100 × *g* for 10 min. The supernatant and sediment were separated by decanting, and the swollen starch sediment was weighed. Swelling power (g/g) was calculated as the ratio of the weight of the wet sediment to the initial weight of the dry starch. The supernatant was made up to 50 ml. A 20-ml aliquot was evaporated to dryness at 130°C overnight and weighed. The weight was corrected for the volume of supernatant and the initial weight of the dry starch. This was expressed as the percentage of soluble starch dissolved in the continuous phase.

Effect of Temperature on Swelling and Solubility

To study the effect of temperature on swelling power and solubility, one sorghum starch sample was heated in the amylograph to various temperatures (80, 85, 90, and 95°C). Swelling power and percent of solubility were determined at the desired temperature and also after holding the starch pastes for 1 hr at that temperature.

The effect of temperature on paste consistency and shear thinning was studied for one sorghum starch. The hot paste was sheared for 60 min at various temperatures (80, 85, 90, and 95°C).

Lipid Reconstitution Studies

Sorghum starch (local, undefatted) and the same starch defatted with methanol or propanol and water were analyzed by the viscograph. In addition, lipids extracted with methanol or with propanol and water from the local sorghum starch were reconstituted with their respective defatted starches. The local sorghum starch was also treated with propanol and water at room temperature.

[1]Contribution 94-123-J. Kansas Agricultural Experiment Station, Manhattan.
[2]Graduate research assistant and professor, respectively, Department of Grain Science and Industry, Kansas State University, Manhattan.
[3]Present address: ConAgra Inc., 2050 Market Street NE, Decatur, AL 35601.

Chemical Analyses

Moisture content was determined as weight loss after heating at 130°C for 1 hr in an air oven (AACC 1983). Starches were defatted by refluxing either with anhydrous methanol or with propanol and water (3:1) at 100°C (Morrison 1988). Nitrogen content was estimated with a LECO nitrogen analyzer by combustion technique. Iodine affinity for these sorghum starches was determined by the procedure of Schoch (1964). Total phosphorus in starch was determined by converting phosphorus from ash of organic material to orthophosphate (Smith 1967). Lipids were extracted from starch by refluxing with anhydrous methanol or a mixture of propanol and water (3:1) at 100°C using the procedure described by Morrison and Coventry (1985).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was conducted using a Perkin Elmer (Norwalk, CT) DSC-2 equipped with FTS Systems Flexi-cooler and temperature controller. The calorimeter was calibrated with indium, and samples were analyzed by DARES (Data Acquisition, Retention and Examination System for Differential Scanning Calorimetry, version 1.4, Industrial Technology, Research Institute, Cambridge, UK). Starch-water samples (1:3) were scanned from 7 to 127°C at 10°C/min.

RESULTS AND DISCUSSION

Swelling and Viscosity Characteristics

Starch samples that were defatted with methanol had a lower initial swelling temperature (mean value of 71.1°C) (Table I) and also a lower peak viscosity temperature (mean value of 87.4°C) than did samples defatted with propanol and water, which had corresponding temperatures of 74.1°C and 95°C (Table II). The values for the methanol defatted samples were very similar to those for undefatted starch samples isolated from the same cultivars (Subramanian et al 1994).

For the methanol defatted samples, there was considerable variation among the cultivars in the decrease in viscosity occurring between peak temperature and 95°C (Table I). The rate of decrease in viscosity for these cultivars was 14.6–35.5 BU/min, with a mean value of 24.4 BU/min. The rate of decrease for the methanol defatted samples is somewhat greater than that reported by Subramanian et al (1994) for undefatted sorghum starches isolated from the same cultivars. On the other hand, all the propanol-water defatted samples gave a maximum peak viscosity at 95°C (Table II). For the methanol defatted samples, paste consistencies were 558–726 BU, with a mean value of 644 BU (Table III). For the propanol-water defatted samples, the paste consistencies were 390–720 BU, with a mean value of 498 BU (Table IV).

Shear Thinning

After 60 min of stirring at 95°C in the amylograph, the reduction in paste consistency for methanol defatted samples was 33.0–50.0%, with a mean of 41.9% (Table III). In general, shear thinning was greater for the methanol defatted samples than for nondefatted samples. For the propanol-water defatted samples, the reduction in paste consistency was 0–21.1%, with a mean value of 6.6% (Table IV). Four cultivars, Tamaulipas, UANL-1-V-187, Blanco 86, and Bajio, showed essentially stable paste consistencies for propanol-water defatting with stirring at 75 rpm for 60 min. However, considerable shear thinning occurred in the Dorado and Dekalb 42Y starches under the same conditions.

Swelling Power and Solubility

Swelling power and solubility of methanol defatted sorghum starches are given in Table V. The methods of determining swelling power and solubility were changed to more accurately reflect the amylograph value. Therefore, swelling power values cannot be directly compared to those reported for nondefatted starch samples isolated from the same cultivars (Subramanian et al 1994). At peak viscosity, swelling power of sorghum starches varied from 13.8 to 14.9, with a mean value of 14.3. The swelling power increased during holding of the hot pastes at 75 rpm at 95°C for 60 min. The values ranged from 19.4 to 27.6, with a mean value of 22.3. The range of values was much larger after the 60 min of holding than it was at the peak.

The propanol-water defatted starches had swelling power values of 12.5–13.9, with a mean value of 13.1 at peak viscosity (Table VI). The corresponding values after holding for 60 min at 95°C were 13.8–15.4, with a mean value of 14.8. Thus, the propanol-

TABLE I
Swelling and Viscosity Characteristics of Methanol Defatted Sorghum Starches

Cultivar	Temperature (°C)		Time from Initial to Peak Viscosity (min)	Decrease in Viscosity from Peak to 95°C (BU/min)
	At Initial Swelling	At Peak Viscosity		
Dorado	70.0	87.5	11.7	25.2
Tamaulipas	72.5	84.0	7.7	14.6
UANL-1-V-187	72.0	87.5	10.3	22.0
Blanco 86	71.0	91.0	13.3	27.8
Bajio	69.0	89.5	13.7	35.5
Dekalb 42Y	72.0	85.0	8.7	21.2
Standard error	± 1.2	± 0.3	± 0.8	± 0.9

TABLE II
Swelling and Viscosity Characteristics of Propanol-Water Defatted Sorghum Starches

Cultivar	Temperature (°C)		Time from Initial to Peak Viscosity (min)
	At Initial Swelling	At Peak Viscosity	
Dorado	71.0	95.0	16.0
Tamaulipas	76.0	95.0	12.7
UANL-1-V-187	76.0	95.0	12.7
Blanco 86	76.0	95.0	12.7
Bajio	72.0	95.0	15.3
Dekalb 42Y	73.5	95.0	14.3

TABLE III
Viscosity and Shear Thinning (%) of Methanol Defatted Sorghum Starches

Cultivar	Viscosity (BU)			Shear Thinning[a] (%)	Shear Thinning Nondefatted Starch[b] (%)
	At Peak Viscosity	At 95°C	After Holding 1 hr at 95°C		
Dorado	696	570	405	41.8 bc	34
Tamaulipas	650	543	405	37.7 cd	34
UANL-1-V-187	603	493	348	42.3 bc	25
Blanco 86	558	484	374	33.0 d	20
Bajio	633	503	337	46.8 ab	34
Dekalb 42Y	726	585	363	50.0 a	51

[a]Different letters indicate statistically significant differences at 0.05 level (Duncan's multiple range test).
[b]Calculated from data of Subramanian et al (1994).

TABLE IV
Viscosity and Thinning (%) of Propanol-Water Defatted Sorghum Starches

Cultivar	Viscosity (BU)		Shear Thinning (%)
	At Peak Viscosity	After Holding for 1 hr at 95°C	
Dorado	720	568	21.1
Tamaulipas	470	460	2.1
UANL-1-V-187	415	400	3.6
Blanco 86	390	390	0
Bajio	415	415	0
Dekalb 42Y	575	500	13.0

TABLE V
Swelling Power and Solubility of Methanol Defatted Sorghum Starches[a]

Cultivar	Swelling Power (g/g)			Solubility (%)		
	Peak	1 hr 95°C	Difference	Peak	1 hr 95°C	Difference
Dorado	14.7	21.0	6.3	12.0	24.9	12.9
Tamaulipas	14.1	19.4	5.3	15.6	24.5	8.9
UANL-1-V-187	14.7	21.3	6.6	14.2	24.7	10.5
Blanco 86	14.9	19.7	4.8	15.4	23.2	7.8
Bajio	13.8	24.7	10.9	14.0	26.5	12.5
Dekalb 42Y	13.8	27.6	13.8	12.4	27.9	15.5
Standard error	± 0.94	± 1.44		± 1.25	± 1.88	

[a]All values represent average of four determinations (dmb).

TABLE VI
Swelling Power and Solubility of Propanol-Water Defatted Sorghum Starches[a]

Cultivar	Swelling Power (g/g)		Solubility (%)	
	Peak	1 hr 95°C	Peak	1 hr 95°C
Dorado	13.2	15.1	13.5	17.4
Tamaulipas	12.9	14.9	19.5	21.7
UANL-1-V-187	13.9	15.2	19.7	22.5
Blanco 86	12.8	14.1	19.4	21.9
Bajio	12.5	13.8	17.2	19.7
Dekalb 42Y	13.4	15.4	17.3	20.4

[a]All values represent average of four determinations (dmb).

TABLE VII
Reconstitution of Lipid with Local Sorghum Starch

Treatment	Temperature (°C)		Time from Initial to Peak Viscosity (min)	Viscosity (BU)		Shear Thinning (%)
	IS[a]	PV[b]		At Peak	After 1 hr	
Undefatted	68.0	91.0	15.3	700	280	60.0
Methanol defatted	68.0	84.0	10.7	665	320	51.9
Methanol defatted and lipids added back	64.0	90.0	17.3	685	295	56.9
Propanol-water defatted	72.0	95.0	15.3	630	460	27.0
Propanol-water defatted and lipids added back	72.5	94.0	14.3	750	590	21.3
Propanol-water defatted at room temperature	67.5	89.5	14.7	625	305	51.2
Standard error				± 50	± 40	

[a]IS = at initial swelling.
[b]PV = at peak viscosity.

water defatted starches had much lower swelling power than the methanol defatted samples.

Solubility values for the methanol defatted sorghum starches are given in Table V. The solubility values at peak viscosity were 12.0–15.6%, with a mean value of 13.9%, and the corresponding solubility values after holding the hot pastes at 95°C for 60 min were 23.2–27.9%, with a mean value of 25.3%. For the propanol-water defatted samples, the solubility values at peak viscosity (95°C) were 13.5–19.7%, with a mean value of 17.8%, and the corresponding solubility values after holding for 1 hr at 95°C were 17.4–22.5%, with a mean of 20.6% (Table VI). Thus, propanol-water defatting of sorghum starch gave lower levels of solubility after holding for 1 hr at 95°C.

Lipid Reconstitution Studies

Starch granules started to swell at an initial temperature of 68°C, independent of whether they had been defatted with methanol or not (Table VII). For the methanol defatted starch, the temperature at the peak viscosity of the paste (84°C) was lower than that for the undefatted starch sample (91°C). On the other hand, propanol-water defatting caused an increase in both the initial swelling temperature (72°C) and the temperature at peak viscosity (95°C).

Reconstituted methanol-extracted lipids gave initial swelling of the granules in the amylograph at 64°C, which was lower than the temperature for the methanol defatted starch or the native nondefatted starch. Reconstitution of lipids extracted with propanol-water gave no variations in initial swelling temperature (72.5°C) or temperature at maximum peak viscosity (94°C) compared to the starch that was just defatted with propanol-water. However, these values were significantly different from those for the native undefatted starch.

When the local sorghum starch was treated with propanol and water but at room temperature, little variation was observed in comparison to the undefatted starch. This suggests that the heat treatment at 100°C was responsible for the changes in properties of the propanol-water defatted starch.

No significant differences were found between the 100% methanol defatted starch and the undefatted starch sample. Paste consistencies after 1 hr of holding at 95°C were also not significantly different. The undefatted and methanol defatted starches showed 60 and 51.9% thinning of the paste, respectively, under elevated and prolonged heating conditions. On the other hand, propanol-water defatting produced a relatively stable paste consistency. During 1 hr of holding at 95°C, the consistency of the paste was decreased by 27%.

When starch was extracted with methanol and the lipids added back to the defatted starch, the results were essentially equal to those for the undefatted starch. This was not true when the defatted starch was reconstituted with the propanol-water extractable lipids. These conditions produced 21.3% thinning, as compared to 60% thinning for the undefatted starch.

TABLE VIII
Differential Scanning Calorimetry of Sorghum Starches[a]

Cultivar	Undefatted		Methanol Defatted		Propanol and Water Defatted	
	T_o[b]	ΔH[c]	T_o	ΔH	T_o	ΔH
Dorado	60.4	2.96	58.4	2.97	68.1	1.73
Tamaulipas	69.5	3.31	67.8	3.17	73.4	2.00
UANLV	69.7	3.39	68.7	3.38	75.9	2.33
Blanco	69.7	3.30	68.5	3.34	73.1	3.11
Bajio	64.0	2.84	62.5	3.15	68.5	2.70
DK42Y	64.9	3.29	63.3	3.25	68.8	2.97

[a]Values are the mean of two independent determinations (dmb). Standard error of $T_o = \pm 0.9$, $\Delta H = \pm 0.10$.
[b]Onset temperature. Standard error ± 0.9.
[c]Enthalpy. Standard error ± 0.10.

Differential Scanning Calorimetry

Hot anhydrous methanol was a reasonably efficient solvent for extraction of starch lipids, and it had a negligible effect on the onset temperature and ΔH of native starches (Table VIII). This is in agreement with earlier reports (Tester and Morrison 1990). The DSC endotherms showed significantly higher onset temperatures for the amylopectin peaks in propanol-water defatted samples than in corresponding undefatted samples. Also, the enthalpy of gelatinization of samples defatted with the propanol and water mixture was less than that of undefatted samples.

TABLE IX
Effect of Temperature on Swelling and Solubility of Methanol Defatted Sorghum Starch[a]

Temperature (°C)	Swelling Power (g/g)		Solubility (%)		Shear Thinning (BU)		
	Initial	After Holding 1 hr	Initial	After Holding 1 hr	Initial	After Holding 1 hr	Shear Thinning (%)
80	14.6	18.4	9.1	11.8	655	552	15.7
85	17.0	22.7	11.0	15.0	685	495	27.7
90	18.4	26.6	13.9	19.0	660	322	51.2
95	22.5	25.4	14.6	25.2	665	230	51.9

[a]All values dmb.

TABLE X
Constituents of Sorghum Starch[a]

Cultivar	Nitrogen (%)	Phosphorus (mg/100 g of starch)	Iodine Affinity (%)	Lipids (%)
Dorado	0.058	100.6	5.95	1.05
Tamaulipas	0.054	9.2	5.74	1.03
UANL-1-V-187	0.127	16.1	5.65	1.27
Blanco 86	0.087	8.3	5.70	1.58
Bajio	0.048	47.1	5.48	1.30
Dekalb 42Y	0.056	10.8	5.54	1.30
Standard error		± 2.19	± 0.048	

[a]Values are dmb.

TABLE XI
Correlation Coefficients (*r*) Among Sorghum Starch Characteristics

Shear Thinning vs.	*r*
Swelling at peak viscosity	−0.72
Swelling after 1-hr hold period	0.91
Solubility at peak viscosity	−0.70
Solubility after 1-hr hold period	0.96
Iodine affinity	−0.50
Phosphorus content	0.18
Lipid content	−0.27

Therefore, we presumed that defatting with propanol and water caused changes in the native granule structure of starch. Amylose-lipid complex peaks were not detected by DSC for samples defatted with either methanol or propanol and water, indicating that most of the internal lipids were extracted by those solvents.

Effect of Temperature on Swelling and Solubility

Steady increases in swelling power and solubility were observed for the starch that was gradually heated from 80 to 95°C (Table IX). Similarly, gradual increases in swelling and solubility were observed for sorghum starch that was held for 1 hr at temperatures of 80–90°C, and a drop in swelling power was observed for those held at 95°C. The solubility increased during the holding period. The increase was more dramatic at the higher temperature. As more granule swelling occurred, more solubles were leached into the solution.

Maximum paste consistency was obtained at 85°C (685 BU); higher temperatures gave no higher values (Table IX). However, drastic changes in shear thinning were observed between 80°C (15.7%) and 90°C (51.2%). Negligible increases were observed at 95°C (51.9%). The lower rate of shear thinning at lower temperature might be because the sorghum starch was not fully swollen.

Constituents of Sorghum Starches

Nitrogen content of isolated native starches ranged from 0.05 to 0.13%, with a mean of 0.07% (Table X). Iodine affinity values ranged from 5.48 to 5.95%, with a mean value of 5.68%. A wide variation was observed in phosphorus content for starches defatted with propanol and water. Tamaulipas, UANL-1-V-187, Blanco, and Dekalb 42Y had lower phosphorus contents (8.3–16.1 mg/100 g of starch); Bajio had intermediate values; and Dorado had the highest value (100.6 mg/100 g of starch). Dorado and Tamaulipas starches contained lower amounts of lipids (1.05 and 1.03%, respectively). UANL-1-V-187, Bajio, and Dekalb 42Y had intermediate levels with lipid contents around 1.30%, and Blanco 86 had the highest value (1.58%). The iodine affinity, phosphorous content, and amount of lipid all correlated poorly ($r = -0.50$, 0.18, and −0.27, respectively) with shear thinning characteristics (Table XI).

Correlations Among Shear Thinning and Sorghum Starch Characteristics

Shear thinning was negatively correlated with swelling power ($r = -0.72$) and solubility ($r = -0.70$) at peak viscosity. A positive significant correlation was obtained between shear thinning and either swelling or solubility after a 1-hr holding period ($r = 0.91$ and 0.96, respectively).

CONCLUSIONS

Propanol-water defatted starches swelled at higher temperatures than methanol defatted starches. They also differed in the rate and extent of granule swelling. Swelling power and solubility were lower in starches defatted with propanol and water than they were in those defatted with methanol. Shear thinning values dropped considerably as a result of the propanol and water treatment. Native properties of these starches were altered when they were treated with propanol and water at 100°C.

The greater swelling and solubility of starches appears to be responsible for the high shear thinning of starch from some sorghum cultivars. The association of molecules within the starch granule may be weak, allowing the granule to disaggregate, resulting in high shear thinning. The cultivars containing starch with low shear thinning may have a strong structural network within the granules.

LITERATURE CITED

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1983. Method 44-15A, approved October 1975, revised October 1981. The Association: St. Paul, MN.

MORRISON, W. R. 1988. Lipids in cereal starches: A review. J. Cereal Sci. 8:1-15.

MORRISON, W. R., and COVENTRY, A. M. 1985. Extraction of lipids from cereal starches with hot aqueous alcohols. Starch/Staerke 37:83-87.

MORRISON, W. R., MILLIGAN, T. P., and AZUDIN, M. N. 1984. A relationship between the amylose and lipid contents of starches from diploid cereals. J. Cereal Sci. 2:257-271.

SCHOCH, T. J. 1964. Iodometric determination of amylose: Potentiometric titration. Standard method. Meth. Carbohydr. Chem. 4:157-160.

SMITH, R. J. 1967. Characterization and analysis of starches. In: Starch Chemistry and Technology, Vol. 2. R. L. Whistler and E. F. Paschall, eds. Academic Press: New York.

SUBRAMANIAN, V., HOSENEY, R. C., and BRAMEL-COX, P. 1994. Shear thinning properties of sorghum and corn starches. Cereal Chem. 71:272-275.

TESTER, R. F., and MORRISON, W. R. 1990. Swelling and gelatinization of cereal starches. II. Waxy rice starches. Cereal Chem. 67:558-563.

WATSON, S. A., SANDERS, E. H., WAKELY, R. D., and WILLIAMS C. B. 1955. Peripheral cells of the endosperms of grain sorghum and corn and their influence on starch purification. Cereal Chem. 32:165-182.

ZOBEL, H. F. 1984. Gelatinization of starch and mechanical properties of starch pastes. Pages 285-309 in: Starch: Chemistry and Technology, 2nd ed. R. L. Whistler, J. N. BeMiller, and E. F. Paschall, eds. Academic Press: Orlando, FL.

[Received February 24, 1994. Accepted September 4, 1994.]