Moisture Adsorption of Damaged Wheat Starch[1]

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ABSTRACT

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The moisture adsorption characteristics of wheat starch damaged by ball milling were studied at 30°C, and the adsorption isotherms were analyzed according to the available models. Damaged starch showed lower and higher sorptive capacities than undamaged starch in the regions of low and high water activity, respectively. The Chung-Pfost equation was the best-fitting equation for the adsorption data of undamaged starch. As the degree of starch damage increased, the adsorption isotherm deviated more from the Chung-Pfost equation. The Oswin equation was the best-fitting equation for the adsorption isotherm of damaged starch.

The water molecule is highly polar because of the asymmetry of electrical charges and has a vapor-state dipole moment. The polarity produces intermolecular attractive forces between water molecules and other polar organic groups of various food components (Multon et al 1980, Fennema 1985).

Stereochemistry plays an essential role in the hydration of starch. Water-bonding sites are exclusively the hydroxyl groups of the starch molecules. Since starch is partially crystallized, the water molecules are essentially adsorbed in amorphous zones; in crystalline zones, interchain bonds are too strong and steric accessibility too difficult for water molecules to be bonded (Multon et al 1980). The types of association between starch and water were described by Leach (1965). The first 8–11% of the water was the most tenaciously bound, and it may therefore represent chemically bound water. Up to 40–50% of the water could be retained in the starch as a result of absorption. Moisture-adsorption isotherms of wheat starch have been studied by many researchers (Bushuk and Winkler 1957, Gur-Arieh et al 1967, Nara et al 1969).

The behavior of starch toward water vapor is altered by physical damage. The principal valence bonds as well as the secondary valence bonds of starch molecules are broken during mechanical modification, resulting in an increased number of free hydroxyl groups. The increase in free hydroxyl groups and the decomposition of the polymer result in the changed characteristics of the damaged starch (Meuser et al 1978).

The objectives of this study were to 1) obtain sorption-equilibrium moisture data for starch of different wheat classes, 2) find the effect of the mechanical modification of starch on its sorption characteristics, and 3) evaluate some selected mathematical models describing the moisture-adsorption isotherms.

MATERIALS AND METHODS

Wheat Samples

The durum wheat varieties Vic and Ward and the hard red spring wheat variety Stoa, grown in 1986 at the North Central Branch of North Dakota State University Experiment Station in Minot, were used. The hard red winter wheat variety Centurk 78 was obtained from the Department of Grain Science and Industry of Kansas State University. Soft red winter and white wheat samples were obtained from International Multifoods Corp., Columbus, OH, and from Fisher Flour Mills Co., Seattle, WA, respectively. The wheat samples were classified according to type as follows: two durum varieties as "durum wheats," hard red spring and hard red winter wheats as "hard wheats," and soft red winter and white wheats as "soft wheats."

Starch Isolation

Starch was isolated from wheat samples by the procedure of Adkins and Greenwood (1966) with slight modifications to minimize starch damage. Each wheat sample was steeped for 24 hr at 10°C in 0.02M acetate buffer into which mercuric chloride had been added to the 0.01M level. The softened wheat was washed and wet milled at low speed for the first 2 min and at high speed for another 5 min in a Waring Blendor. The wet-milled material was screened on a U.S. No. 20 sieve, and the overs containing bran and pericarp were discarded. The material was screened again on a U.S. No. 100 sieve to separate most nonstarch materials. The starch was then recovered from the filtrate by centrifugation at $1,000 \times g$ for 5 min and washed four times by resuspension in distilled water. The recovered prime starch was air dried at room temperature and passed through a U.S. No. 70 sieve.

Ball Milling of Starch

Ball milling of isolated starch samples was performed in a jar mill (model 8712-1, Norton Chemical Process Products Division, Akron, OH), using 4.5 kg of carborundum stones as grinding media. The mill was driven at 42 rpm by an electric motor. Starch (300 g) was ball milled for 2 and 24 hr at ambient laboratory conditions.

Degree of Starch Damage

The degree of damage to each ball-milled wheat starch sample was determined by the colorimetric procedure of Williams and Fegol (1969) with certain modifications, made to analyze the damaged starch samples instead of wheat flour. Starch samples (0.25 g of dry matter) and prewashed sea sand (1 g) were placed into a 50-ml test tube. After addition of 25 ml of extracting solution and brief mixing, the soluble starch was extracted at 50°C in a water bath for 15 min with thorough shaking at 5-min intervals. About 0.2 g of Celite was added to the suspension after extraction, and the tube was allowed to stand for 3 min before the suspension was filtered through Whatman No. 4 filter paper. Duplicate aliquots (0.25 ml) were pipetted into test tubes containing 9.75 ml of diluting solution. Iodine reagent (0.5 ml) was added to each tube, and the tubes were mixed thoroughly. After the solution stood at 30°C for 15 min, the absorbance at 555 nm was determined against a reagent blank using a spectrophotometer.

Adsorption Isotherm

Starch samples were dried at 37°C for 48 hr under vacuum (660 mm of Hg) before the adsorption experiment.

A static method using a sulfuric acid solution to maintain a constant relative humidity was used to obtain a moisture-adsorption isotherm at 30°C. One-pint mason jars were filled one-third full with various concentrations of sulfuric acid solutions. A support made of copper tubing (1/8-in. i.d.) was welded through the cover of the mason jar, and a stopcock was attached to the outside end of the support. Duplicate predried samples (about 1 g) were put into small hexagonal polystyrene weighing dishes (2 in. × 2 in., Fisher Scientific Co.) and placed over the sulfuric acid solutions in jars. One magnetic stirring bar was put into each jar.

The jars were evacuated so that measurements were made in an atmosphere of water vapor alone and so that equilibria were reached in a short time. Finally, the jars were placed in a constant-temperature cabinet held at $30 \pm 0.1°C$. The sulfuric acid solutions in the jars were stirred daily with a magnetic stirrer. Under the above conditions, an equilibration period of 72 hr was sufficient to establish moisture equilibrium.

The vapor pressures of various concentrations of sulfuric acid solutions and the saturation vapor pressure of water were obtained from a reference table (Perry 1973). Relative humidity in all experiments ranged from 9.7 to 94.3%.

Moisture content of the equilibrated samples was determined by the method of Chung and Pfost (1967a). Samples were predried in a convection oven at 50°C for 24 hr, then finally dried at 130°C for 2 hr.

Analysis of Data

The sorption isotherm equations (Table I) were selected from a preliminary study. The equations were rearranged to express the moisture content (m) as a function of the water activity (a_w).

Each set of the sorption data was fitted to the seven isotherm equations using the NLIN procedure, a nonlinear regression analysis procedure, of the Statistical Analysis System (SAS Institute 1985). The sum of squares for error (SSE) was used to estimate the goodness-of-fit (Ott 1988).

RESULTS AND DISCUSSION

The degrees of starch damage of the ball-milled starch samples are listed in Table II.

The moisture-adsorption isotherm of damaged starch from Vic durum wheat is illustrated in Figure 1 as an example. The isotherms of damaged starch were steeper than that of undamaged starch. In the region of low water activity, the equilibrium moisture content of damaged starch was lower than that of undamaged starches. In the region of high water activity, on the other hand, the trend was just the opposite; the equilibrium moisture content of damaged starch was higher than that of undamaged starches.

The results of the analysis of variance (Table III) showed that the sorptive capacity of wheat starch was significantly affected by the water activity and the ball-milling time. However, there were no significant effects of wheat types and samples.

When the data were analyzed separately according to a_w ranges (low = 0.097–0.462, high = 0.666–0.943), significant differences were found in sorptive capacity of damaged starches with ball-

TABLE I
Moisture Adsorption Isotherm Equations for Ball-Milled Wheat Starch

Equation[a]	Reference
$m = A + B\,a_w + C\,a_w^2 + D\,a^3$	Alam and Shove (1973)
$m = \dfrac{1}{B}\,[\ln A - \ln(-\ln a_w)]$	Chung and Pfost (1967b)
$m = \dfrac{a_w}{A\,a_w^2 + B\,a^w + C}$	Bizot (1983)[b]
$m = \left(\dfrac{A}{B - \ln a_w}\right) 0.5$	Harkins and Jura (1944)
$m = \left(\dfrac{-\ln(1 - a_w)}{A}\right) 1/B$	Henderson (1952)
$m = A\left(\dfrac{a_w}{1 - a_w}\right) B$	Oswin (1946)
$m = A - B\ln(1 - a_w)$	Smith (1947)

[a] m = equilibrium moisture content (g of water per g of solid), a_w = water activity, A, B, C, D = constants.
[b] G.A.B. method.

milling times (Tables IV and V). In the low a_w range, the moisture-sorptive capacity decreased with ball-milling time. In the high a_w range, on the other hand, it increased with ball-milling time.

Between 0 and 0.1 a_w, water is strongly and directly bonded on polar sites of starch. Between 0.1 and 0.65 a_w, water molecules are bonded either on those previously bound or on polar sites previously hidden inside the structure and now accessible due to swelling. Above 0.65 a_w, water molecules accumulate in small capillaries and intergranular spaces of starch (Multon et al 1980). In our study, the damaged starch showed lower moisture-sorptive capacity than the undamaged starch below 0.65 a_w (Fig. 1), where water molecules existed in a bound manner.

The mechanical damage of starch in the dry state involves cleavage of covalent bonds in amylose and amylopectin (Meuser et al 1978, Evers and Stevens 1985). The free hydroxyl groups resulting from the breaking of covalent bonds of amylose and amylopectin molecules during ball milling seemed to have a great potential to form hydrogen bonding between themselves or with other hydroxyl groups in the molecules. The formation of hydro-

gen bonding might result in decreased numbers of accessible polar sites on which water molecules could bond. In addition, as indicated by Multon et al (1980), the catalytic action of water to crystallize the broken amylose and detached linear branches of amylopectin resulting from ball milling might also explain the decreased sorptive capacity of damaged starch in the low water activity region.

According to Williams (1969), ball-milled starch granules are squashed flat and split longitudinally at the equator; consequently, water may pass freely into the interior of the granule. The less densely packed material inside the starch granule diffuses out, making the granule hollow. The smaller number of polar sites

TABLE II
Degree of Damage of Ball-Milled Wheat Starch

Wheat Sample	Ball-Milling Time	Absorbance at 555 nm
Vic durum	0	0.0011 ± 0.0080
	2	0.0610 ± 0.0028
	24	1.2818 ± 0.0153
Ward durum	0	0.0004 ± 0.0011
	2	0.0579 ± 0.0012
	24	1.2722 ± 0.0305
Hard red spring	0	0.0041 ± 0.0015
	2	0.0541 ± 0.0001
	24	1.1949 ± 0.0138
Hard red winter	0	0.0032 ± 0.0021
	2	0.0589 ± 0.0011
	24	1.1668 ± 0.0214
Soft red winter	0	0.0001 ± 0.0009
	2	0.0559 ± 0.0017
	24	1.0514 ± 0.0112
White	0	0.0044 ± 0.0007
	2	0.0300 ± 0.0001
	24	1.0364 ± 0.0052
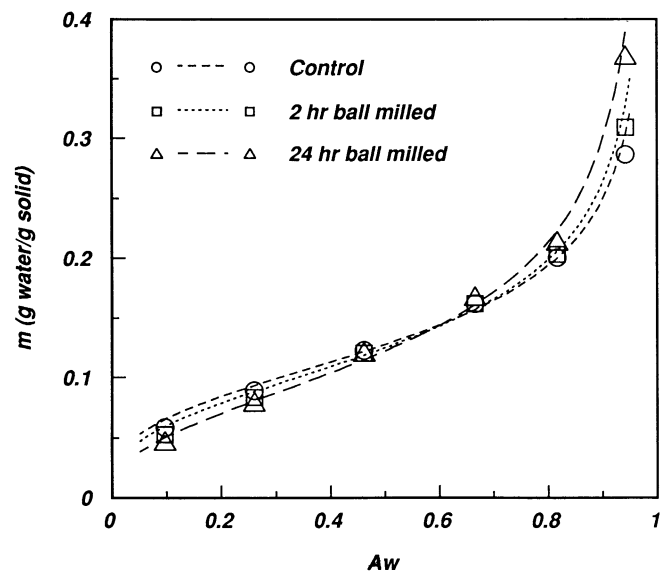
Fig. 1. Moisture-adsorption isotherm of ball-milled Vic durum wheat starch at 30°C.

TABLE III
Analysis of Variance for Moisture Sorptive Capacity of Ball-Milled Wheat Starch

Source	Degrees of Difference	Sum of Squares	F Value	P > F
Wheat type	2	0.000023	0.07	0.9355
Sample	3	0.000063	0.12	0.9468
Water activity	5	1.652018	1,914.97	0.0001
Ball-milling time	2	0.002706	7.84	0.0005
Error	203	0.035025		
Corrected total	215	1.689835		

TABLE IV
Duncan's Multiple Range Test for Sorptive Capacity of Ball-Milled Wheat Starch in Low a_w Range

Factor	Mean Sorptive Capacity[a] (g of water/g of solid)
Wheat type[b]	
Soft	0.0854 a
Hard	0.0850 a
Durum	0.0845 a
Water activity level[b]	
0.462	0.1216 a
0.261	0.0831 b
0.097	0.0503 c
Ball-milling time[b] (hr)	
0	0.0907 a
2	0.0854 b
24	0.0790 c

[a] Means of each effect with same letter are not significantly different ($P = 0.05$).
[b] n = 36.

TABLE V
Duncan's Multiple Range Test for Sorptive Capacity of Ball-Milled Wheat Starch in High a_w Range

Factor	Mean Sorptive Capacity[a] (g of water/g of solid)
Wheat type[b]	
Durum	0.2291 a
Hard	0.2272 a
Soft	0.2270 a
Water activity[b]	
0.943	0.3166 a
0.817	0.2049 b
0.666	0.1618 c
Ball-milling time[b] (hr)	
0	0.2172 b
2	0.2223 b
24	0.2438 a

[a] Means of each effect with same letter are not significantly different ($P = 0.05$).
[b] n = 36.

TABLE VI
Best-Fitting Isotherm Equation and Estimated Parameters for Ball-Milled Wheat Starch

Wheat Sample	Ball Milling Time (hr)	Equation	Parameter	Sum of Squares for Error
Vic durum	0	Chung-Pfost	a = 5.74008 b = 16.25314	0.000137
	2	Oswin	a = 0.12376 b = 0.32943	0.000227
	24	Oswin	a = 0.12102 b = 0.39544	0.000289
Ward durum	0	Chung-Pfost	a = 5.39337 b = 15.81009	0.000251
	2	Oswin	a = 0.12119 b = 0.33878	0.000319
	24	Oswin	a = 0.11782 b = 0.40248	0.000441
Hard red spring	0	Chung-Pfost	a = 5.75968 b = 16.15142	0.000044
	2	Chung-Pfost	a = 4.60482 b = 14.79001	0.000250
	24	Oswin	a = 0.11898 b = 0.39358	0.000292
Hard red winter	0	Chung-Pfost	a = 5.95063 b = 16.33497	0.000066
	2	Chung-Pfost	a = 4.65102 b = 14.78123	0.000284
	24	Oswin	a = 0.12065 b = 0.37579	0.000486
Soft red winter	0	Chung-Pfost	a = 5.48696 b = 15.90563	0.000218
	2	Oswin	a = 0.12175 b = 0.32747	0.000251
	24	Oswin	a = 0.11764 b = 0.40053	0.000499
White	0	Chung-Pfost	a = 5.68930 b = 16.01854	0.000070
	2	Chung-Pfost	a = 5.05143 b = 15.28427	0.000195
	24	Oswin	a = 0.11998 b = 0.38841	0.000398

TABLE VII
Duncan's Multiple Range Test for Sum of Squares for Error (SSE) of Isotherm Equations for Ball-Milled Wheat Starch

Ball-Milling Time (hr)	Equation	Mean Sorptive Capacity[a,b] (g of water/g of solid)
0	Smith	0.001030 a
	Henderson	0.000658 b
	Harkins-Jura	0.000571 b
	Oswin	0.000352 c
	G.A.B.	0.000341 c
	Alam	0.000299 c
	Chung-Pfost	0.000131 d
2	Henderson	0.000929 a
	Smith	0.000808 a
	Harkins-Jura	0.000793 a
	Alam	0.000555 b
	G.A.B.	0.000448 bc
	Chung-Pfost	0.000430 bc
	Oswin	0.000339 c
24	Chung-Pfost	0.002873 a
	Henderson	0.002431 b
	Alam	0.001776 c
	Harkins-Jura	0.001499 c
	Smith	0.001054 d
	G.A.B.	0.001035 d
	Oswin	0.000396 e

[a] Means of each effect with same letter are not significantly different ($P = 0.05$).
[b] n = 36.

equation showed the smallest SSE in all wheat classes. The Chung-Pfost equation showed the worst goodness-of-fit among the seven equations studied. This fact indicated that the moisture adsorption isotherms of starch samples deviated from the Chung-Pfost equation as the degree of starch damage increased.

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in the exposed, less densely packed material may also be responsible for the low sorptive capacity of the damaged starch in the low water activity region.

On the other hand, the moisture-sorptive capacity of the damaged starch is higher than that of the undamaged starch at above 0.65 a_w (Fig. 1), where water exists in liquid form in capillaries. The cracked and hollow structure of starch granules and the increased amorphous region of the molecules caused by ball milling seems to contribute to the high moisture-sorptive capacity of the damaged starch.

The best-fitting equations for the adsorption data of the native and damaged starch samples and their estimated parameters are given in Table VI. For all native starch samples, the Chung-Pfost equation was the best-fitting equation. However, as the ball-milling time increased, the Chung-Pfost equation deviated more from the observed equilibrium moisture contents (Tables VI and VII). For 2-hr ball-milled starch samples, the Chung-Pfost equation showed best goodness-of-fit in hard red spring wheat, hard red winter wheat, and white wheat, by showing the smallest SSE. For the two durum wheat starch samples and the soft red winter wheat starch sample, the Oswin equation showed the smallest SSE.

Table VII indicates that the Chung-Pfost equation fits significantly better than the other equations for undamaged starch samples. For 2-hr ball-milled starch samples, however, there were no significant differences among the Oswin, Chung-Pfost, and G.A.B. equations. For 24-hr ball-milled starch samples, the Oswin

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