Acetylated and Hydroxypropylated Wheat Starch: Paste and Gel Properties Compared with Modified Maize and Tapioca Starches[1]

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ABSTRACT

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Acetylated (0.1 degrees of substitution) or hydroxypropylated (0.1 molar substitution [MS]) distarch phosphate from wheat gave pastes of lower consistency and gels (6-10% starch solids) with a lower elastic modulus but a higher elastic limit than those of starch from normal corn (dent). Depending on cooking conditions, hydroxypropylated wheat starch (MS 0.15) formed a gel or paste at 25°C and 5-7.5% starch solids. Prolonged cooking of the modified starch (6.5%) in 25% sucrose at pH 3.5, or stirring the cooked (water, pH 6.5) paste during cooling gave a paste at 25°C. With 5.0% starch solids in 25% sucrose at pH 3.5, cooking the hydroxypropylated wheat starch 20 min at 95°C gave a paste whose resistance

to deformation after aging 6 hr at 25°C was 90% of a commercial sample of hydroxypropylated (MS 0.13) waxy corn starch. After 48 hr at 25°C, the two pastes showed equal resistance to deformation, which was higher than that of a commercial sample of hydroxypropylated (MS 0.13) tapioca starch. The freeze-thaw stability of a gel of the hydroxypropylated wheat starch (10% solids in water at pH 6.5) was intermediate between that of gels from hydroxypropylated tapioca and waxy maize starches. The soft gel of the hydroxypropylated wheat starch (6.5%) in 25% sucrose at pH 3.5 had a low stickiness value.

Modified maize starches are widely used in foods in the United States but not modified wheat starch. Wootton and Bamunuarachchi (1978) reported the water-binding capacities of 13 modified wheat starches made in Australia. Workers in the

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same laboratory also measured the digestibility of hydroxypropylated wheat starch (Wootton and Chaudhry 1981).

In this investigation, we prepared acetylated distarch phosphate and hydroxypropylated distarch phosphate from normal maize and wheat and compared their paste and gel properties. We also compared the paste and gel properties of commercial samples of acetylated or hydroxypropylated waxy maize, tapioca, and wheat starches.

MATERIALS AND METHODS

Prime wheat starch (0.3% protein) and hydroxypropylated

wheat starch (WH 5.1) were obtained from Midwest Grain Products, Inc., Atchison, KS. Normal maize, two acetylated waxy corn starches (WxA 1.3 and WxA 1.8), two hydroxypropylated waxy corn starches (WxH 4.7 and WxH 7.5), and a hydroxypropylated tapioca starch (TH 4.4) were products of National Starch and Chemical Corp., Bridgewater, NJ. A second sample of hydroxypropylated tapioca starch (TH 4.3) was from another manufacturer. Moisture in starch was determined by loss of weight after heating for 1 hr at 130°C in a forced-draft oven. Lipids in starch were determined gravimetrically by exhaustive extraction with propanol/water (75:25) (Morrison and Coventry 1985).

Modification and Extent of Modification

Prime corn and wheat starches were doubly modified by acetylation and cross-linking with acetic anhydride and phosphorus oxychloride (Wurzburg 1964, Wetzstein and Lyon 1956) or by hydroxypropylation and cross-linking with propylene oxide and phosphorus oxychloride (Tuschhoff et al 1969). A low or high degree of cross-linking was achieved using 0.01 or 0.02% phosphorus oxychloride. The extent of acetylation or hydroxypropylation of a modified starch was determined as described in the Food Chemicals Codex (1981) or by Johnson (1969), respectively. Degrees of substitution (DS) and molar substitution (MS) were calculated in the normal fashion (Rutenberg and Solarek 1984).

Paste and Gel Properties

Amylograms were obtained using a Brabender Viscograph-E (C. W. Brabender Instruments, Inc., Hackensack, NJ) according to the procedure described by Tipples (1980). Starches (5–12%) were pasted either in water or in an aqueous medium containing 25% by weight of sucrose. The aqueous sucrose medium was either pH 3.5 (0.5% malic acid), pH 4.0 (0.25% malic acid), or

TABLE I
Level of Cross-Linking and Acetyl (Ac) or Hydroxypropyl (HP) Content of Doubly Modified Wheat and Corn Starches

Starch Source	Cross-Linking Agent, POCL₃ (%)	Acetylated		Hydroxypropylated	
		Ac (%)	Code Name	HP (%)	Code Name
Wheat	0.01	2.5	W1A	3.6	W1H
Corn	0.01	2.5	C1A	3.5	C1H
Wheat	0.02	2.5	W1A	3.6	W2H
Corn	0.02	2.5	C2A	3.6	C2H

Fig. 1. Amylograms of native and acetylated distarch phosphate derivatives of wheat and normal corn at pH 6.5 and 7.5% starch solids. Starches with high and low levels of cross-linking were reacted, respectively, with 0.01 and 0.02% phosphorous oxychloride. Native wheat (**A**), modified wheat (**A′**), native corn (**B**), modified corn (**B′**). Temperature profile (— —).

pH 6.5 (approximately 1 ml of 2.5% aqueous sodium bicarbonate).

To prepare gels and pastes at 25°C, all starches were cooked in the amylograph at 1.5°C/min from 30 to 95°C and then held at 95°C for 5–90 min. The hot pastes were either stir-cooled in the amylograph at 1.5°C/min from 95 to 30°C prior to pouring into molds, or they were poured directly into molds and statically cooled to 25°C. Commercial starches were generally cooked in 25% sucrose solution at pH 3.5, 4.0, or 6.5 as described above.

Hot pastes were poured into shallow petri dishes (50 × 17 mm) or deep dishes (50 × 30 mm). The depth of each mold was increased approximately 5 mm by taping aluminum foil around its rim. The petri dishes were covered, and the gels were stored for 24 hr at 4 and 25°C. After the aluminum foil was removed, a smooth, freshly cut surface was created by removing the excess gel above the rim with a wire cheese cutter.

The texture of a gel (5–12% starch solids) was determined in duplicate or triplicate using a Voland-Stevens texture analyzer (Voland Corp., Hawthorne, NY) fitted with a chart recorder. A thin gel (17 mm) was compressed at a speed of 0.2 mm/sec to a distance of 4 mm using a cylindrical plunger (diam. = 25.4 mm) with the chart recorder speed at 20 cm/min. The peak height at 4 mm compression was termed firmness, and the negative area of the curve during retraction of the probe was termed stickiness. The deep gels were used to obtain load-penetration curves (Marrs et al 1980). A spherical probe (diam. = 12.7 mm) was advanced at a rate of 0.5 mm/sec 15 mm into a gel and then retracted at the same speed. Four parameters were noted on a load-deformation curve of a gel; elastic modulus, force at rupture, deformation at rupture, and loss of force after rupture. One parameter, the maximum force of deformation, was noted for a paste. The standard error of the mean was <3% for the force at rupture of a WH 5.1 gel and for the maximum force of deformation of a WxH 4.7 paste. Those standard error of the mean values were determined on samples (6.5% starch solids) cooked at pH 3.5 or 6.5 in 25% sucrose, respectively, and cooled for 6 or 48 hr at 25°C.

Freeze-Thaw Stability of Gels

To measure freeze-thaw stability, gels at 10% starch solids in water at pH 6.5 were aged for 24 hr at 25°C followed by freezing at −20°C for 24 hr and thawing for 4 hr at 25°C. After 1–15 freeze-thaw cycles, the liquid separated by syneresis from a gel was collected by vacuum filtration on a sintered (medium porosity) glass funnel fitted with Whatman No. 4 filter paper.
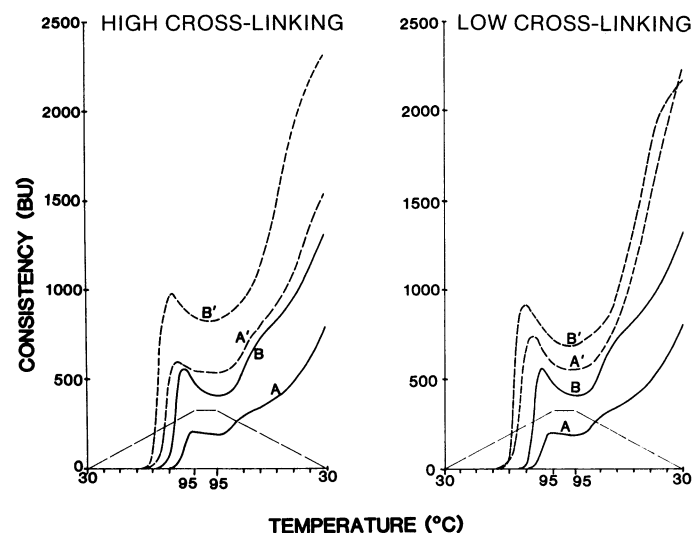
RESULTS AND DISCUSSION

The acetyl and hydroxypropyl contents of the doubly modified wheat starches were almost identical to the levels of substitution in the doubly modified maize starches (Table I). All eight doubly modified starches prepared in the laboratory had DS or MS values of 0.1. The percent lipids in the modified corn and wheat starches were 0.8–1.0%, which is nearly the same level as in the native starches. The moisture content of starches varied from 9.5 to 11.5%.

Pasting of Doubly Modified Wheat and Normal Corn Starches

The pasting curves of the acetylated and hydroxypropylated starches at 7.5% starch solids and pH 6.5 are shown in Figures 1 and 2, respectively. When comparing native corn and wheat starch or their similarly modified forms, corn starches always showed higher consistency than wheat starches in freshly cooked pastes. Acetylation of wheat starch increased its paste consistency somewhat more than that for normal maize, especially at the low level of cross-linking (Fig. 1). The reverse was true for hydroxypropylation (Fig. 2). The pasting curve (A′, Fig. 1) of W1A was approximately 200 Brabender units (BU) below that of C1A (B′, Fig. 1), whereas those of the other modified wheat starches were usually 300–500 BU below the consistencies of the corresponding maize starches.

Gel Properties

Gel strength. With 10% starch solids in water at pH 6.5, native wheat starch gave a gel that was almost twice as firm as that from normal corn (Table II). Acetylation or hydroxypropylation to DS or MS 0.1 reduced the gel strength of both starches, but surprisingly, modified wheat starch gels were less firm than those of similarly modified normal corn at 8–12% solids (Fig. 3). Commercially made, modified waxy maize starches, whose pastes did not gel upon cooling to 25°C for 24 hr, gave the lowest resistance to deformation, as expected (Table II).

Hot pastes of wheat and normal corn starch are composite structures comprised of swollen granules in a continuous phase of dissolved amylose molecules (Miles et al 1985). Those workers showed that the shear modulus of a gel from normal starch (~10% solids) under dynamic loading reached a constant value in 1–2 hr at 25°C, which was attributed to the amylose molecules in the dissolved phase associating through "junction zones" to form a continuous network that enmeshed the swollen granules. Continued aging of the starch gel for periods of days gave further increases in shear modulus, as the amylopectin in the swollen granules began to crystallize.

The higher gel strength (aged 24 hr at 25°C) of unmodified wheat versus corn starch at greater than 6% solids has been attributed (Takahashi and Seib 1988) to a higher proportion of linear molecules in wheat amylose and to its average larger size (Hizukuri 1988). Why are gels from doubly modified corn starch stronger than those from doubly modified wheat starch? We hypothesize that during cross-linking, the larger amylose molecules in wheat are more likely to become bonded to amylopectin than are the smaller amylose molecules in corn. The dissolved phase in a hot paste of the doubly modified corn starches would then contain more amylose than that from doubly modified wheat. In support of that hypothesis, Shi and Seib (1989) found much less amylose was leached from cross-linked potato starch than from similarly cross-linked wheat starch. Amylose molecules in potato starch are approximately four times larger than those in wheat starch (Hizukuri 1988).

Load-penetration experiments in deep gels confirmed the higher firmness of modified corn starch compared with modified wheat. The elastic modulus of modified corn (C1A or C1H) was higher than that of modified wheat (W1A or W1H), but the elastic limit (deformation at rupture) was higher for modified wheat (Table III). Thus, gels of modified corn starch were generally firmer but more brittle than those of modified wheat starch.
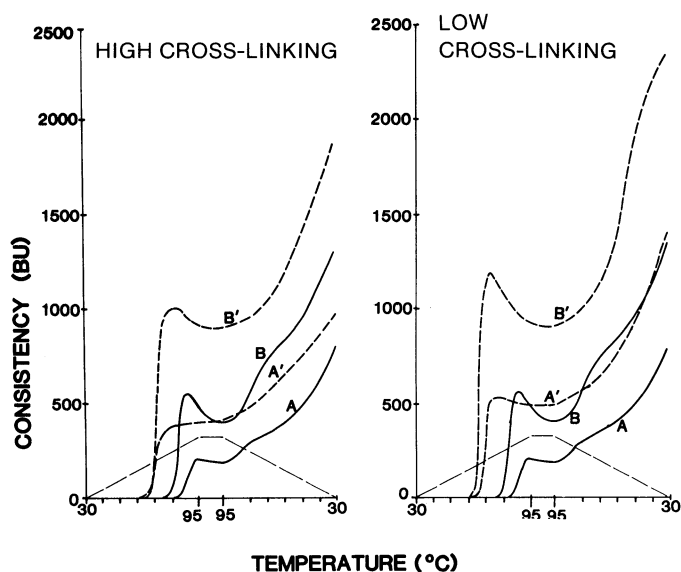

Fig. 2. Amylograms of native and hydroxypropylated distarch phosphate derivatives of wheat and normal corn at pH 6.5 and 7.5% starch solids. Low and high levels of cross-linking as described in caption to Fig. 1. Native wheat (**A**), modified wheat (**A′**), native corn (**B**), modified corn (**B′**). Temperature profile (— —).

Freeze-thaw stability. Gels of unmodified wheat and normal corn starch in water at pH 6.5 showed poor freeze-thaw stability. Modified wheat starch, especially acetylated distarch phosphate, showed somewhat better freeze-thaw stability than acetylated

TABLE II
Firmness of Starch Gels from Native and Doubly Modified Corn and Wheat Starch

Sample	Gel Firmness[a] (kPa)	
	4°C	25°C
Unmodified		
Corn	6.25	4.62
Wheat	10.79	8.19
Cross-linked/acetylated		
Corn, highly cross-linked (C1A)	2.41	2.52
Wheat, highly cross-linked (W1A)	1.80	1.88
Corn, low cross-linking (C2A)	3.30	3.41
Wheat, low cross-linking (W2A)	2.79	2.58
Cross-linked/hydroxypropylated		
Corn, highly cross-linked (C1H)	3.45	3.53
Wheat, highly cross-linked (W1H)	2.95	2.85
Corn, low cross-linking (C2H)	5.22	4.52
Wheat, low cross-linking (W2H)	4.33	3.55
Commercial starches[b]		
Acetylated waxy corn (WxA 1.3)	1.78	1.73
Acetylated waxy corn (WxA 1.8)	2.15	2.08
Hydroxypropylated waxy corn (WxH 4.7)	1.55	1.38
Hydroxypropylated waxy corn (WxH 7.5)	1.16	1.05

[a] Average of duplicate determinations. Starch-water slurry at pH 6.5 with 10% solids cooked at 1.5°C/min from 30 to 95°C, held at 95°C for 5 min, then poured into molds and aged 24 hr at 4 or 25°C. Firmness was determined using the cylindrical probe (A = $5.06 \times 10^{-4} m^2$). Firmness in units of force (N) can be calculated by multiplying the pressure values (kPa) by 0.5.

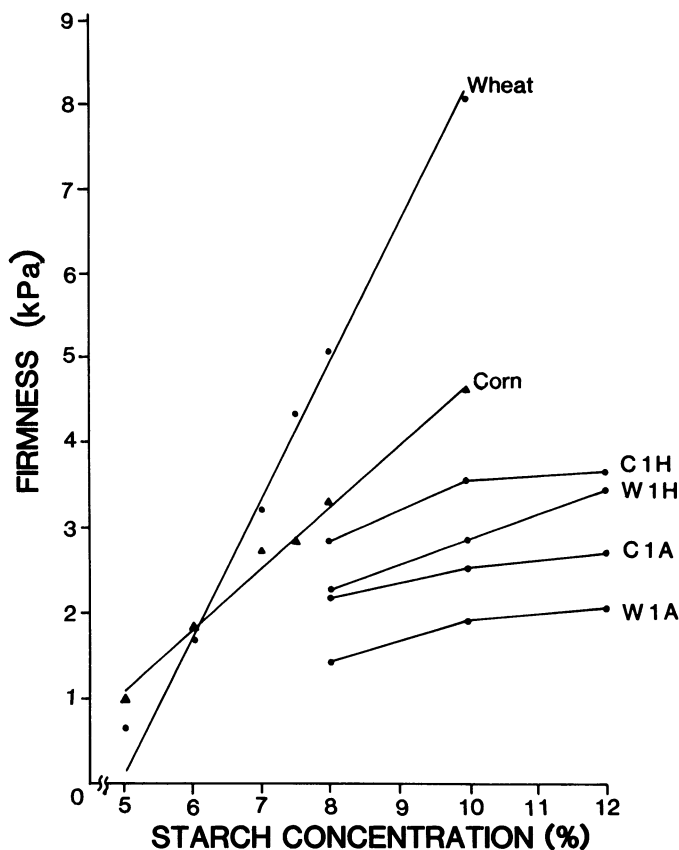[b] Commercially modified starches gave pastes instead of gels.

Fig. 3. Firmness of gels aged 24 hr at 25°C after cooking in water at pH 6.5 in the amylograph (30 to 95°C at 1.5°C/min, hold at 95°C for 5 min). Grams-force recorded by the Voland-Stevens instrument was converted to pressure (kPa) using $F = ma$ and the area of the cylindrical probe. The pressure values for firmness in kPa can be converted to force (N) by multiplying by 0.5.

starch of normal corn (Table IV). Acetyl or hydroxypropyl groups retarded syneresis almost equally as well in gels of modified wheat starch, whereas hydroxypropyl groups were somewhat more effective in gels of modified normal corn starch.

Paste and Gel Properties of Commercial Hydroxypropylated Wheat, Tapioca, and Waxy Maize Starches

Table V lists four commercial samples of hydroxypropylated starches with their levels of molar substitution. The four modified starches appeared to be cross-linked, as evidenced by their hot paste stability at pH 6.5 when the amylograph temperature was held at 95°C for 10 min (Fig. 4). The paste consistency of doubly modified wheat starch (WH 5.1) was the lowest among the samples. Matching the consistency of 7.5% TH 4.4 and 7.5% WxH 7.5 in the amylograph required approximately 8.5 and 9.5%, respectively, of WH 5.1 (curves not shown). But, because the modified wheat starch formed gels, the relatively thin hot paste of hydroxypropylated wheat starch, WH 5.1, increased more in "consistency" upon cooling and aging at 25°C than did the pastes from the hydroxypropylated modified waxy corn and tapioca

TABLE III
Gel Textures of Native and Doubly Modified Corn and Wheat Starches (8% solids) Determined from Load/Penetration Curves[a]

Sample	Elastic Modulus (N/mm)	Force at Rupture (N)	Deformation at Rupture (mm)	Loss of Force after Rupture (N)
Unmodified				
Corn	0.122	1.09	9.0	0.63
Wheat	0.138	0.99	7.1	0.47
Cross-linked/acetylated				
Corn, low				
cross-linking (C1A)	0.052	0.47	8.0	0.21
Wheat, low				
cross-linking (W1A)	0.042	0.43	10.4	0.18
Cross-linked/hydroxy-propylated				
Corn, low				
cross-linking (C1H)	0.054	0.37	6.9	0.10
Wheat, low				
cross-linking (W1H)	0.050	0.43	11.6	0.17

[a] Starches were cooked and cooled (25°C) as described in Table II. Load-penetration curves were obtained using the spherical probe.

TABLE IV
Syneresis (%) from Starch Gels after Freezing and Thawing

	Number of Cycles		
Sample	1	2	3
Unmodified			
Corn	65	64	67
Wheat	55	61	65
Acetylated/cross-linked			
C1A	1	24	27
C2A	0	14	27
W1A	0	0	3
W2A	0	2	4
Hydroxypropylated/cross-linked			
C1H	0	8	16
C2H	0	10	22
W1H	0	0	11
W2H	0	1	7
Commercial Starches			
Acetylated waxy corn (WxA1.3)	0	33	33
Acetylated waxy corn (WxA1.8)	0	10	26
Hydroxypropylated waxy corn (WxH4.7)	0	1	5
Hydroxypropylated waxy corn (WxH7.5)	0	0	0

[a] Starch-water slurries (pH 6.5) with 10% starch solids were cooked and poured into molds as described in Table II. The gels were covered, aged 24 hr at 25°C, then subjected to freeze-thaw testing.

(see details below).

We used a model system at pH 3.5, 4.0, or 6.5 to simulate pasting of starch, for example, in a cherry, peach, or a pecan pie filling. The model system contained 5–7.5% starch solids, 25% sucrose, and 0.25% (pH 4) or 0.5% (pH 3.5) malic acid or a trace of sodium bicarbonate (pH 6.5). The amylograms at 6.5% starch solids in Figure 5 showed acid-thinning of the pastes at pH 3.5 during prolonged stirring at 95°C. Because of acid-thinning, prolonged cooking of the hydroxypropylated wheat starch affected its final texture upon cooling and holding at 25°C.

Gels from commercial hydroxypropylated starches cooked at pH 3.5. The load-penetration curves are shown in Figure 6 for WH 5.1 cooked 5 min at 95°C, pH 3.5, in 25% sucrose followed by cooling and aging of the paste for 4 or 48 hr at 25°C. At 5% starch solids, the modified wheat starch (WH 5.1) gave a paste, but at 5.5–6.0% starch solids, it gave a soft gel whose rupture point was barely perceptible on the curve. The force needed to deform the paste or gel of 5–6% WH 5.1 increased slightly upon storage for 48 hr at 25°C (Fig 6). It should be noted that the designation of a gel phase after cooling a cooked starch was based on whether a rupture point was observed in the load-deformation curve. In the absence of a rupture point, the load at maximum deformation (15 mm) was the highest load observed on the load-penetration curve.

The doubly modified wheat starch, WH 5.1, was cooked at 5–7.5% starch solids and pH 3.5, and the pastes were cooled to 25°C and held up to 72 hr. The force to rupture a gel or the force at maximum deformation for a paste was plotted against

TABLE V
Hydroxypropyl Content of Selected Commercial Starches

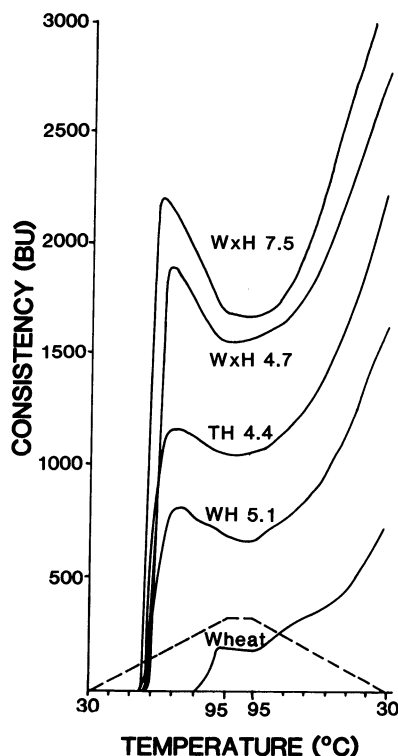| Starch Source	Hydroxypropyl	
	Wt %	MS
Waxy corn (WxH 4.7)	4.7	0.13
Waxy corn (WxH 7.5)	7.5	0.22
Tapioca (TH 4.4)	4.4	0.13
Wheat (WH 5.1)	5.1	0.15

[a] Molar substitution.

Fig. 4. Amylograms of commercial samples of native wheat starch and hydroxypropylated starches from wheat (WH 5.1), tapioca (TH 4.4), waxy corn (WxH 4.7), and waxy corn (WxH 7.5) cooked in water at pH 6.5 and at starch solids of 7.5%.

the aging period (Fig. 7). As previously shown in Figure 6, cooking and cooling 5% WH 5.1 gave a paste whose maximum force of deformation increased slightly after 48 hr (Fig. 7). The "zero" age in Figure 7 was assigned to a sample when its core temperature reached 25° (approximately 2 hr).

At the critical concentration of 5.5%, WH 5.1 gave a very slight gel upon cooling (Fig. 6), which slowly increased in firmness after
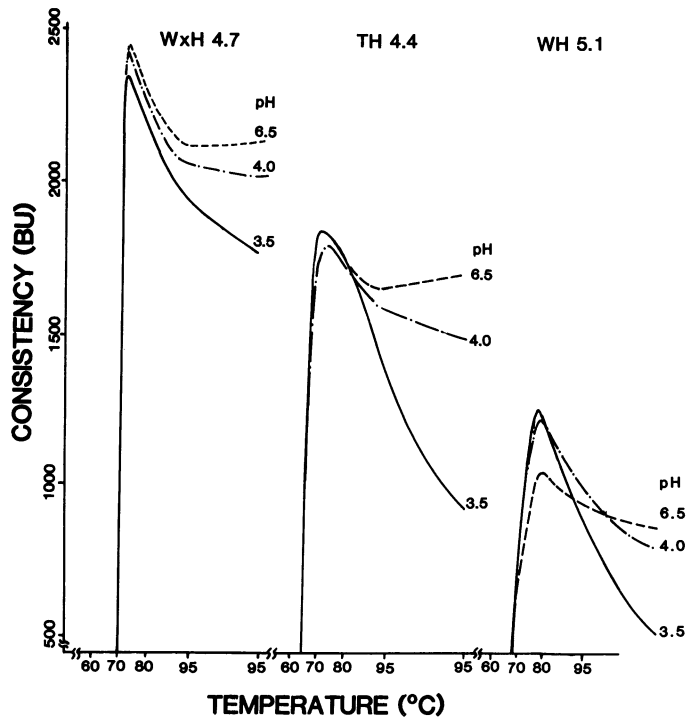
aging more than 4 hr (Fig. 7). The increase in firmness was likely due to a gradual increase in the junction zones formed between amylose molecules in the continuous phase.

The aging behavior of the WH 5.1 gel in 25% sucrose at pH 3.5 changed again above 6.5% starch solids, where the curve in Figure 7 shows a double inflection. Upon cooling the 6.5% paste, a gel immediately formed, and its strength reached a maximum in approximately 2 hr, where it remained constant for approximately 24 hr and then began another rise that appeared to be sustained beyond 72 hr (Fig. 7). This double-inflection curve might have been anticipated from the results of Miles et al (1985). The first inflection in the curve at >6.5% starch solids in Figure 7 could be due to completion of junction zones between amylose, whereas the second inflection could be due to amylopectin crystallization.

The gelling tendency of WH 5.1 cooked at concentrations >5.5% in 25% sucrose at pH 3.5 was eliminated or delayed by overcooking (Fig. 8). Cooking the paste having 6.5% WH 5.1 at pH 3.5 for 5 or 20 min gave a gel at 25°C as evidenced by a rupture point in the force-deformation curves. Cooking for 90 min, however, gave a paste at 25°C whose consistency was low and did not change upon aging for 72 hr. Cooking hydroxypropylated waxy corn and tapioca (6.5%) for 5 min at pH 3.5 in 25% sucrose gave pastes whose consistencies were decreased by cooking for 20 min (Fig. 8). Ring and co-workers (1987) showed that more than 10% waxy maize in water is needed to obtain amylopectin gels compared with approximately 1% for amylose. The modified tapioca (TH 4.4) did not gel, even though its paste could contain 1.1% amylose, apparently because the cross-linking of the starch
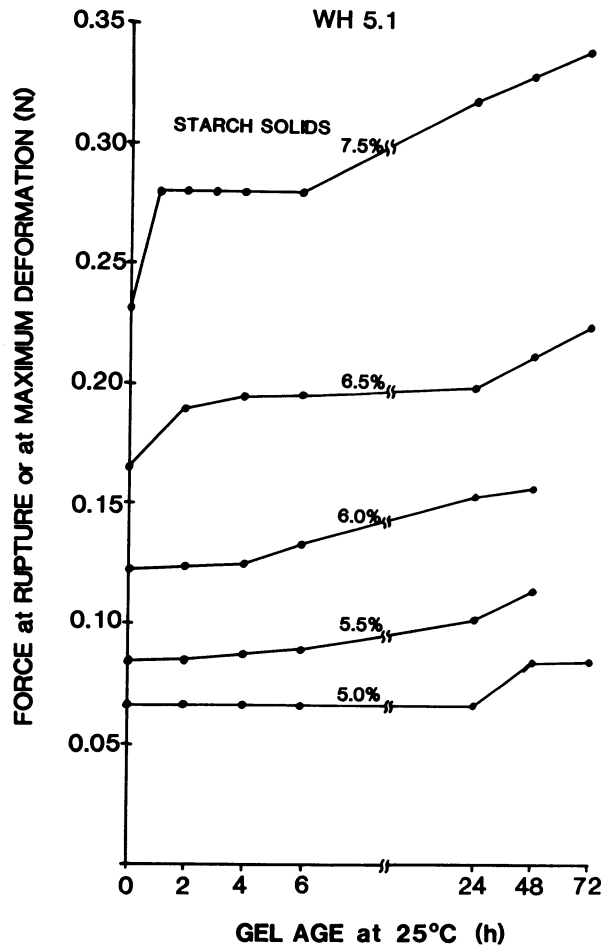

Fig. 5. Amylograms of waxy corn (WxH 4.7), tapioca (TH 4.4), and hydroxypropylated wheat (WH 5.1) at 6.5% starch solids cooked in 25 wt % sucrose at pH values of 3.5, 4.0, and 6.5.

Fig. 6. Load-penetration curves for gels of 5–6% hydroxypropylated wheat (WH 5.1) after cooking in 25 wt % sucrose at pH 3.5. Pastes were cooked in the amylograph (30 to 95°C at 1.5°C/min and 95° for 5 min) and then cooled and held at 25°C for 4 (- - -) or 48 hr (—).

Fig. 7. Effect of aging gels (≥ 5.5% starch solids) or pastes (5% starch solids) of WH 5.1 on the force at rupture or the force at maximum deformation. Cooking was done in 25% sucrose at pH 3.5 in the amylograph (30 to 95°C at 1.5°C/min and 95° for 5 min). The gels and pastes were aged at 25°C.

resulted in most of its amylose (17% in tapioca) being covalently linked to amylopectin in the granules.

Despite the low hot-paste viscosity of hydroxypropylated wheat starch compared with hydroxypropylated tapioca and waxy maize (Fig. 5), the resistance to deformation of its cooled paste after 48 hr at room temperature was not so different from the other two (Fig. 9). With 5.0% starch cooked for 5 min at 95°C in 25% sucrose at pH 3.5, the consistency of the WH 5.1 cold paste after 48 hr at 25°C was the same as that from WxH 4.7 and somewhat greater than that from TH 4.4. It is likely that 5% WH 5.1 gave a slight gel phase that was not detected by the static load instrument used in this work.

The stickiness of the pastes and gels of the commercial hydroxypropylated starches was compared by the negative areas in the force-deformation curves using the cylindrical probe (Fig. 10). Hydroxypropylated wheat (6.5%) cooked for 5 or 20 min at pH 3.5 in sucrose and cooled for 24 hr at 25°C gave narrow negative spikes, indicating a clean, quick break of the WH 5.1 gel. But extensive cooking for 90 min gave a paste whose negative curve broadened and almost matched that observed for hydroxypropylated tapioca cooked for 20 min. Hydroxypropylated waxy maize (WxH 4.7) showed a broad negative peak with 50% larger area than that for WH 5.1 and TH 4.4, indicating that WxH 4.7 was stickier.

Gels of commercial hydroxypropylated starches at pH 6.5 and 4.0. Typical load-penetration curves are shown in Figure 11 for WH 5.1, WxH 4.7, and TH 4.4 at 6.5% starch solids after cooking for 20 min at 95°C in sucrose solution at pH 3.5, 4.0, or 6.5, and then cooling the pastes and aging them at 25°C for 6 hr. The load curves for modified waxy corn and tapioca starches
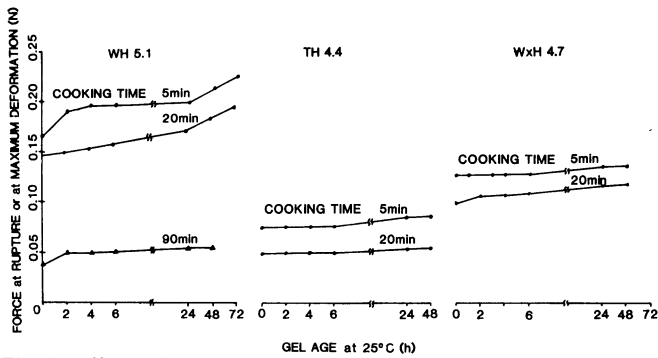
showed no gel phase, and the consistencies of the pastes were lowest at pH 3.5.

The load curves for modified wheat starch (6.5% in 25% sucrose) in Figure 11 indicate the presence of a gel at all three pH values, although the gel at pH 3.5 was very weak. As stated earlier, the critical concentration of WH 5.1 to form a gel in 25% sucrose at pH 3.5 was more than 5.5%. However, in water at pH 6.5 without sucrose, the critical concentration of WH 5.1 to form a gel after aging 24 hr at 25°C increased to approximately 7.5% starch solids (data not shown). The negative areas of the load penetration curves in Figure 11 again indicate that WH 5.1 gave a somewhat cleaner break than TH 4.4 and WxH 4.7.

Figure 12 shows that the resistance to deformation of the cold pastes from WxH 4.7 and TH 4.4 at 6.5% starch solids in 25% sucrose changed little at pH 3.5–6.5 during aging at 25°C up to 24–48 hr. In contrast, the force to rupture the gels formed by WH 5.1 increased with age. The curves for WH 5.1 gels at pH 4 and 6.5 in Figure 12 again showed a double inflection when the force to rupture was plotted against gel age (0–72 hr); however, the curve at pH 3.5 showed a single inflection. In addition, WH 5.1 gels cooked at pH 6.5 (20 min, 95°C) appeared more clear than those cooked (5 min, 95°C) at pH 4 or pH 3.5.

Fig. 8. Effects of overcooking pastes in the amylograph at 95°C and the time of aging (25°C) on the force to rupture gels or the force at maximum deformation for pastes of WH 5.1, TH 4.4, and WxH 4.7 (6.5% starch) in 25% sucrose at pH 3.5. All curves were for pastes except those for WH 5.1 at 5 and 20 min of cooking, which were gels.
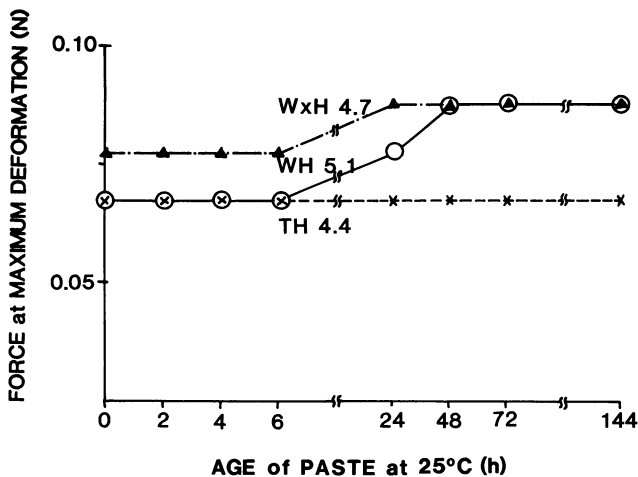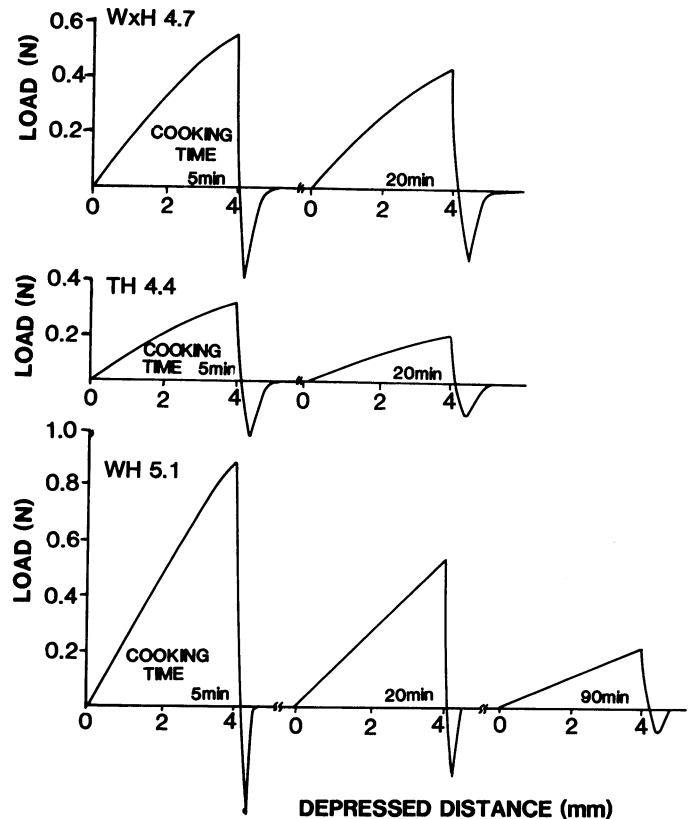

Fig. 9. Force at maximum deformation for pastes with increasing age at 25°C. Starches were cooked in 25% sucrose, pH 3.5, and 5% starch solids in the amylograph from 30 to 95°C at 1.5°C/min and held at 95°C for 5 min.

Fig. 10. Load-deformation curves using the cylindrical probe on gels or pastes of WxH 4.7, TH 4.4, and WH 5.1 after aging 24 hr at 25°C. The starches (6.5%) were cooked in 25% sucrose at pH 3.5 in the amylograph by heating from 30 to 95°C and holding at 95°C for 5, 20, or 90 min.
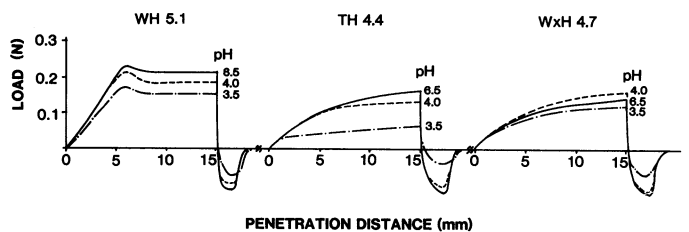

Fig. 11. Load-penetration curves of gels (WH 5.1) and pastes (TH 4.4 and WxH 4.7) after aging 6 hr at 25°C. The starches (6.5%) were cooked at pH 3.5, 4.0, or 6.5 in 25% sucrose in the amylograph by heating from 30 to 95°C at 1.5°C/min and holding at 95°C for 20 min.

TABLE VI
Syneresis[a] (%) of Gels of Commercial Hydroxypropylated Starches

Modified Starch	Freeze-Thaw Cycles					
	1	2	3	5	10	15
Waxy corn (WxH 4.7)	0	0	0	4	10	14
Waxy corn (WxH 7.5)	0	0	0	0	7	21
Tapioca (TH 4.4)	0	0	0	0	0	0
Tapioca (TH 4.3)	0	0	0	0	8	22
Wheat (WH 5.1)	0	0	0	0	2	9
Wheat (WH 5.1) + 3% lysolecithin	0	0	0	1	2	10

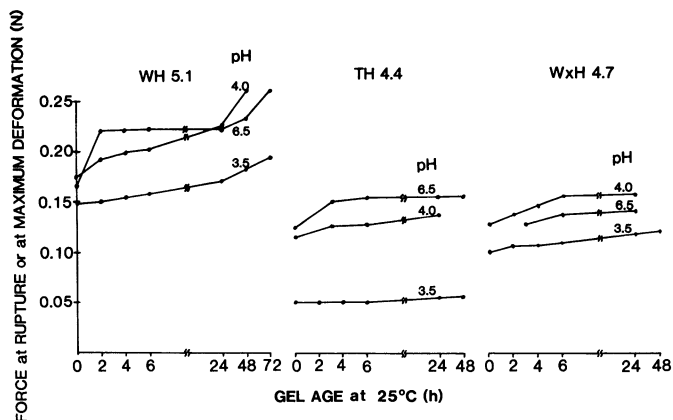[a] Means of duplicate or triplicate determinations on 10% starch solids in water at pH 6.5.

Fig. 12. Effect of aging a gel or paste at 25°C on the force at rupture or the force at maximum deformation for starches cooked at pH 3.5, 4.0, and 6.5. The starches (6.5%) were cooked as described in the caption to Fig. 11.
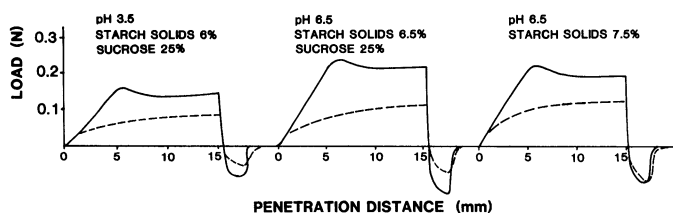
Fig. 13. Load-penetration curves for WH 5.1 in which the hot paste was poured directly (—) into molds or was stir-cooled (- - -) in the amylograph from 95 to 30°C prior to pouring. In both cases, pastes were aged 6 hr at 25°C. The starch (6.5%) was cooked as described under Fig. 11, except 5 min at 95°C was used instead of 20 min.
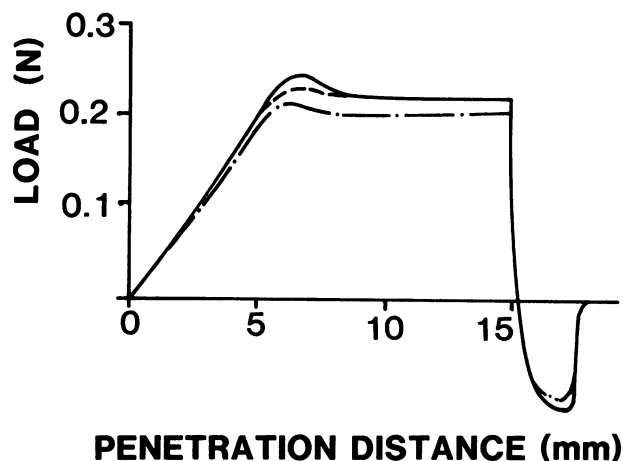
Fig. 14. Load-penetration curves for WH 5.1 (6.5%) cooked in 25% sucrose at pH 6.5 in the amylograph by heating from 30 to 95°C and holding at 95°C for 5 (—), 20 (- - -) and 40 min (- · -). The hot pastes were poured into molds and aged 6 hr at 25°C prior to measurement.

Stirring a hot paste of freshly cooked WH 5.1 while it cooled from 95 to 30°C was an effective way of generating a paste at 25°C rather than a gel. The effect of stir-cooling is shown in Figure 13. Cooking WH 5.1 in sucrose solution for 5 min at pH 3.5 or pH 6.5 followed by stir-cooling from 95 to 30°C gave pastes, whereas static cooling gave gels. The same phenomenon was observed for a paste cooked in water at pH 6.5 and 7.5% starch solids (Fig. 13). Apparently, stirring during cooling prevented formation of an amylose network joined by junction zones (Miles et al 1985). When the stir-cooled paste reached 25°C, the mobility at the amylose molecules was limited due to the high viscosity of the continuous phase. Under those conditions, alignment between molecules to form junction zones was slow, and a metastable paste was produced at 25°C. Another possible explanation, namely, dilution of amylose in the dissolved phase by amylopectin released from fragmented granules, was discounted. Stirring the hot paste of WH 5.1 (6.5%) in 25% sucrose for 40 min at 95°C and pH 6.5 followed by static-cooling still gave a gel (Fig. 14).

Freeze-Thaw Stability of Commercial Hydroxypropylated Starches

Table VI compares the freeze-thaw stability of several commercially available hydroxypropylated starches. WH 5.1 showed approximately equal stability to WxH 4.7, WxH 7.5, and TH 4.3, but less than TH 4.4. The two tapioca samples, TH 4.3 and TH 4.4, differed markedly in freeze-thaw stability for some unknown reason.

The modified wheat starch (WH 5.1) contained 0.8% lipids, which was probably mostly lysolecithin (Morrison and Milligan 1982). When up to 3% lysolecithin was added to WH 5.1 and its gel was prepared (10% starch solids in water), freeze-thaw stability was not improved (Table VI). Apparently, the lysolecithin complexed strongly with amylose and had no effect on the reassociation of chains in the amylopectin fraction. Gray and Schoch (1962) provided evidence that ionic surfactants do modify the paste behavior of amylopectin starches (waxy corn).

It should be pointed out, although the data curves are not shown, that increasing the lysolecithin in hydroxypropylated wheat starch WH 5.1 by 1–3% increased firmness of its gel (10% starch solids in water at pH 6.5). The opposite was true for native wheat starch. A gel of wheat starch containing 2% added lysolecithin showed gel firmness approximately one-fifth that of native wheat starch (Takahashi and Seib 1988).

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