Functional Properties of Oat Starches and Relationships Among Functional and Structural Characteristics[1]

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ABSTRACT

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The pasting, gel strength, and thermal properties of oat (*Avena sativa* L.) starches, isolated from three types of groats containing a range of lipid contents (6.2, 8.0, and 11.2%), were investigated. The relationships between these functional properties and structural characteristics were determined. Two corn (*Zea mays* L.) starches also were evaluated for comparison. The oat starches tended to have a higher pasting temperature and a lower peak viscosity (89.5-93°C and 155-210 BU, respectively) than did corn starches (83.6-86.8°C and 270-310 BU, respectively), as measured by the Brabender Viscoamylograph. The firmness, as measured by the Voland-Stevens texture analyzer, was less for oat than it was for corn starch gels, and firmness was negatively correlated with starch-lipid content during all storage periods. The stickiness was greater for oat than it was for corn starch gels at 5 hr of storage; it was the same for both starches during remaining storage. The stickiness was positively correlated with the starch-lipid content during all storage periods. Differential scanning calorimetry revealed that the oat starches had a lower gelatinization temperature (T_0) and a lower enthalpy (ΔH) value for transition of the starch crystallites than did the corn starches. This suggests less order in the crystalline structure of the former starches. The oat starches also had a higher ΔH value for the transition of the amylose-lipid complex and a lower percentage of retrogradation (%r) than did the corn starches, maybe because of a greater starch-lipid content in the former starches. Furthermore, the T_0 of oat starches was positively correlated with amylose ($r = 0.97$) and starch-lipid ($r = 0.92$) contents ($P < 0.01$), whereas %r was negatively correlated with amylopectin content ($r = -0.84$, $P < 0.01$).

The functional properties of starches, especially pasting properties, gelatinization, and retrogradation, are important for use in food products and industrial applications of starch. Several researchers have demonstrated the unique functional properties of oat starches. Paton (1977) studied the pasting properties of a wide range of oat cultivars, using the Ottawa starch viscometer, and reported gelatinization curves similar to those of other cereal starches. However, cooked starch granules of some oat samples were more sheer-sensitive than those of corn, wheat (*Triticum aestivum* L.), or rice (*Oryza sativa* L.) starch. Paton (1977) also observed that, although oat starch exhibited high setback viscosity values, the cooled gel was clearer, less firm, more elastic, more adhesive, and less susceptible to retrogradation than were those of corn, wheat, and rice starches. MacArthur and D'Appolonia (1979), using a viscoamylograph, found results similar to those reported by Paton (1977).

Gelatinization and retrogradation of oat starch also has been studied with differential scanning calorimetry (DSC) (Paton 1987, Gudmundsson and Eliasson 1989, Hoover and Vasanthan 1992, Sowa and White 1992). Paton (1987) showed that native oat starch (cv. Sentinel) exhibited two endotherms. The enthalpy value of the low-temperature endotherm (M_1, corresponding to melting of starch crystallites) was slightly lower, and the enthalpy value of the high-temperature endotherm (M_2, corresponding to the melting of the amylose-lipid complex) was about two times greater than values reported for wheat and rice starches (Paton 1987). Similar results were reported by Gudmundsson and Eliasson (1989) on several oat cultivars (Chicauhua, Sv, 81563, Svea, and Vital) and by Sowa and White (1992) on oat starch from E77, Dal, and MO42-17 cultivars. Hoover and Vasanthan (1992), however, found a slightly lower enthalpy value of M_2 for AC Hill oat starch than for wheat starch. But the properties of AC Hill oat starch were not typical of oat starch in general because of a small amylose (AM) content and decreased AM binding by native lipids. Furthermore, Paton (1987) and Gudmundsson and Eliasson (1989) showed that native oat starch had less retrogradation than did corn, wheat, or rice starches, but defatted oat starch had increased retrogradation when compared with native oat starch. The starch-lipid content of oat starch may play a role in decreasing retrogradation (Paton 1987, Gudmundsson and Eliasson 1989).

Previous studies evaluated the structure and physicochemical properties of starch granules (Wang and White 1994a) and of starch fractions (Wang and White 1994b) from oat starch extracted from groats containing three widely different amounts of lipids. From previous data, the starch-lipid contents of the three types of starches (E77, Dal, and L996) were 1.08, 1.16, and 1.18%. The AM contents were 22.1, 25.6, and 26.6%, respectively. The lipid contents of the original groats ranged from 6.2 to 11.2%. The objectives of the present study were: 1) to evaluate these same oat-starch types for their functional properties as measured on the viscoamylograph, the texture analyzer, and the differential scanning calorimeter; and 2) to relate these properties to the previously measured structural and physicochemical properties of their starch granules and fractions.

MATERIALS AND METHODS

Starch Types

Three types of oats (E77, Dal, and L996) with different oil contents in the whole grains (6.2, 8.0, and 11.2%, respectively) and one corn genotype (B73×MO17) were grown in Ames, IA, in 1991. After harvest, the corn kernels and the dehulled oat groats were stored at 4°C and 45% rh until analyzed.

Corn starch (PFP) was obtained from Sigma Chemical Company (St Louis, MO). The starch had a purity of about 99% calculated on a dry-weight basis. The moisture content of the starch was 11%.

Starch Isolation

Starches were extracted and purified as described previously (Sowa and White 1992), with modifications by Wang and White (1994a). All starch types were isolated in two replicate extractions. All data on starches are the average of two determinations per replicate unless otherwise stated.

Pasting

Pasting characteristics of starch suspensions (6% w/w, dwb) adjusted to pH 5.5 were measured by using the Brabender

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TABLE I
Pasting Properties of Starches[a]

Starch	Pasting Temperature (°C)	Brabender Viscosity Units, BU					
		Peak	95°C	95°C Hold	50°C	Setback[b]	50°C Hold
E77	89.5	190	80	170	410	240	355
Dal	93.0	210	10	210	315	105	285
L996	92.0	155	30	145	350	205	340
B×MO	83.6	310	305	295	482	187	470
PFP	86.8	270	250	240	420	180	395

[a] Starch concentration 6% (w/w, db). Values are from one determination.
[b] Setback denotes the viscosity difference between the starch at 95°C after 30 min and at 50°C before holding (Hoover and Sosulski 1985).

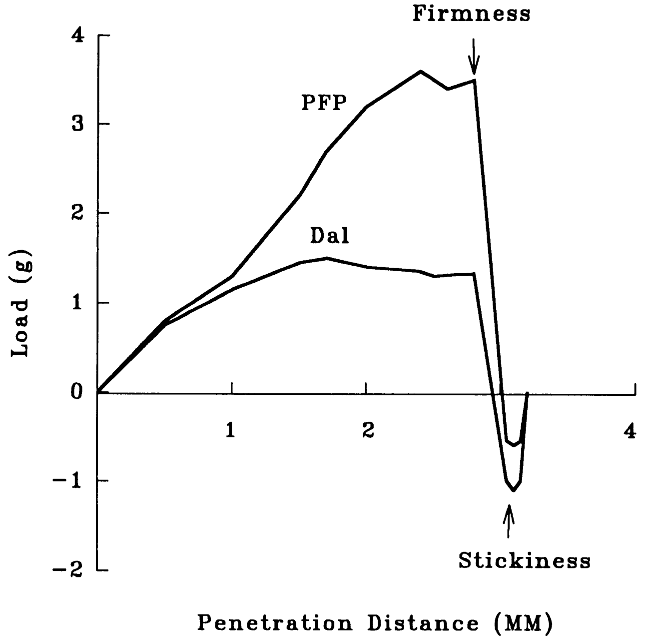

Fig. 1. Load penetration curve of 6% (w/w) oat starch (Dal) and corn starch (PFP) gels measured by the Voland-Stevens texture analyzer. The gels were aged for 5 hr at 25°C before measurement.

Viscoamylograph (C. W. Brabender Instruments, South Hackensack, NJ) equipped with a 700·cmg sensitivity cartridge operated at a bowl speed of 75 rpm. The temperature was raised from 30 to 95°C at a rate of 1.5°C/min, maintained at 95°C for 30 min, and lowered to 50°C at the same rate and held for 30 min. Parameters are noted in Table I. Because of a limited sample size, starch from the two replicate extractions was pooled, and only one measurement was made.

Gel Strength

The starch paste prepared with the viscoamylograph was used to measure the gel strength after storage. The paste from each starch type was poured into eight aluminum dishes (27 mm, i.d. × 27 mm). Aluminum foil was taped around the rims of the dishes to increase the depth of the gel to 1 cm above the rims (Takahashi et al 1989). Immediately before each measurement, the aluminum foil was removed, and the surface gel was sliced off carefully with a cheese cutter to prepare a fresh and smooth surface for texture analysis. The gel strength of the starch paste was measured at five different locations on each gel sample. Two gel samples per starch type were determined after 5 hr at 25°C and after 24, 72, and 168 hr of storage at 4°C by using a Voland-Stevens texture analyzer (Texture Technologies, Scarsdale, NY) fitted with an L6512 series flatbed recorder. The gel was compressed at a speed of 0.2 mm/sec to a distance of 2.9 mm by using a punch probe (TA 53, 3-mm diameter), with the chart recorder speed at 10 cm/min. The peak height at 3-mm compression was termed firmness; the negative peak height during retraction of the probe was termed stickiness (Fig. 1) according to Takahashi and Seib (1988).

Thermal Analysis of Starches

The thermal properties of the starches were studied using a Perkin-Elmer DSC-7 analyzer equipped with a thermal-analysis data station (Perkin-Elmer Corp., Norwalk, CT). The gelatinization of starch was accomplished as previously described by White et al (1990). Approximately 4.0 mg (dwb) of starch was weighed accurately into an aluminum sample pan. Up to 8.0 mg of distilled water was added, by weight, to give a starch-to-water ratio of 2:1. The pan was hermetically sealed with a volatile sample sealer and allowed to equilibrate for 1 hr before analysis. An aluminum sample pan containing 8 ml of distilled water was used as the reference. Samples were heated at a rate of 10°C/min from 30 to 120°C. Onset temperature (T_o), peak maximum temperature (T_p), and enthalpy of transition (ΔH) were computed automatically. At the water level used, the endotherms were essentially symmetrical, which allowed the gelatinization range (R) to be calculated as $2(T_p - T_o)$, as previously described by Krueger et al (1987). In addition, the peak height index (PHI), which is the ratio $\Delta H/(T_p - T_o)$, was calculated to allow a quantitative evaluation of variations in peak shape (Krueger et al 1987). Enthalpies (Table II) were calculated on the dry weight of starch. The results are the average of three scans for each of two extractions for one starch type.

After the DSC run, gelatinized starch samples (in the original sealed pan) were stored at 4°C for seven days for retrogradation determinations as described by White et al (1989). The previously gelatinized starch sample was removed from 4°C storage and allowed to equilibrate at room temperature for 1 hr before being rescanned using DSC as described. In addition to the DSC parameters previously listed, the percentage of retrogradation (%r) was calculated as $\Delta H_{\text{retrogradation}}/\Delta H_{\text{gelatinization}}$, as previously described (White et al 1989).

Statistical Analyses

Statistical analyses were performed on all replicated data for each experiment using the SAS program (SAS 1990). Individual analyses on each replicate were used to calculate least significant differences, which were computed at a significance level of $P < 0.05$. Correlations were computed among functional properties and previously measured structural and physicochemical properties of starch granules (Wang and White 1994a) and fractions (Wang and White 1994b).

RESULTS AND DISCUSSION

Pasting

Figure 2 and Table I illustrate the pasting properties of the oat and corn starches obtained with the viscoamylograph. The viscosity patterns of the oat and corn starch pastes showed a B-type curve, which, according to Schoch and Maywald (1968), is formed from normal cereal starches. The B-type starch pastes have a lower pasting peak and much less thinning during cooking than do the A-type starch pastes (including high-swelling starches, such as potato [*Solanum tuberosum* L.], tapioca [*Manihot utilissima* L.], waxy cereal starches, and ionic starch derivatives),

TABLE II
Differential Scanning Calorimetry Properties of Starches[a,b]

		Endotherm (M_1)					Endotherm (M_2)		
Days of Storage	**Starch**	**T_0 (°C)**	**ΔH (cal/g)**	**R (°C)**	**PHI**	**%r**	**T_0 (°C)**	**ΔH (cal/g)**	**R (°C)**
0	E77	56.1	2.41	9.8	0.49	...	92.4	0.42	16.6
	Dal	59.3	2.78	12.1	0.45	...	91.9	0.72	20.5
	L996	60.0	2.40	10.8	0.44	...	91.0	0.53	15.9
	B×MO	69.5	3.07	7.1	0.87	...	92.4	0.27	15.7
	PFP	67.6	3.06	6.9	0.88	...	92.1	0.28	15.9
	LSD[c]	0.7	0.32	1.4	0.08		2.0	0.10	5.2
7	E77	40.2	0.68	17.7	0.10	28.2			
	Dal	42.6	0.95	19.3	0.10	34.6			
	L996	40.7	0.99	20.1	0.10	41.2			
	B×MO	38.2	1.89	26.0	0.14	61.5			
	PFP	39.1	1.78	25.6	0.13	60.9			
	LSD	3.5	0.20	2.5	0.05	4.5			

[a] Values are the mean of three separate determinations.

[b] M_1 = Low temperature endotherm, M_2 = high temperature endotherm, respectively. T_0 = onset temperature. ΔH = enthalpy of the phase transition. R = range of the phase transition calculated as $2(T_p - T_0)$. PHI = peak height index = $\Delta H/(T_p - T_0)$. %r = retrogradation percentage = $\Delta H_{\text{retrogradation}}/\Delta H_{\text{gelatinization}} \times 100$.

[c] Least significant difference at a significance level of $P < 0.05$.

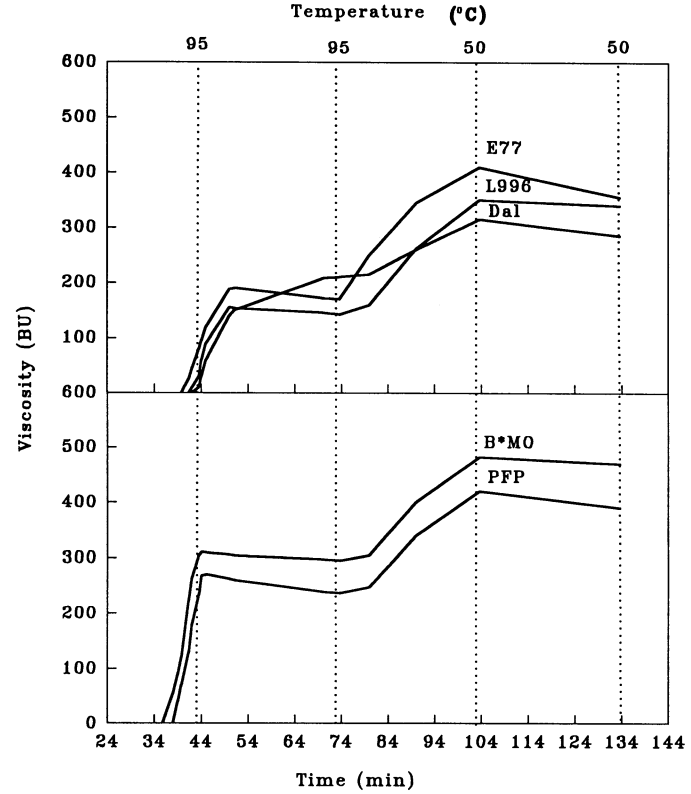

Fig. 2. Brabender Viscoamylograph curves of oat starches (E77, L996, and Dal) and corn starches (B×MO, PFP) (6%, dwb).

because the granules do not swell excessively, which also prevents them from becoming fragile.

The oat starches tended to have higher pasting temperatures (89.5–93°C) than did corn starches (83.6–86.8°C) (Table I). Among the oat starches, the E77 starch tended to have the lowest pasting temperature (89.5°C), followed by L996 and Dal starches with pasting temperatures of 92 and 93°C, respectively. The peak viscosities for the oat starches were lower and occurred later than did those of the corn starches, with Dal starch having the greatest (210 BU) and latest (70.5 min) peak viscosity among the oat starches (Fig. 2). The differences in both pasting temperature and peak viscosity between oat and corn starches may be attributed to larger quantities of starch lipid in the oat starches, as described elsewhere (Wang and White 1994a). Hoover and Vasanthan (1992) studied native and defatted oat and wheat starches, and they found that lipid removal decreased pasting temperature. They suggested that defatting increased granular strength. The results in the present study are consistent with this view, because the starch-lipid in the oat may have increased the pasting temperature.

The corn starches had a fairly stable paste viscosity during the 30-min shearing at 95°C, whereas the viscosity of the E77 and L996 oat starches first increased until peak viscosity was reached (Fig. 2), and then remained relatively stable. The Dal starch continued to gelatinize during the 30-min shearing. Using an Ottawa starch viscometer in a study of 16 oat starch types at 9% concentration (dwb), Paton (1977) reported that, during the short period of shearing at 95°C, 10 of the cooked starch samples were less stable than were corn, wheat, and rice starches. However, the other six oat starch samples were equally stable. MacArthur and D'Appolonia (1979) also found a greater shear sensitivity for oat starches than for wheat starches using the viscoamylograph with 9% concentration (dwb). Discrepancies between our studies and those of others may be the result of differences in the oat starch types, concentrations of starches, or experimental methods and equipment used. A direct comparison between the present data and those of other authors was difficult.

During cooling of the hot pastes from 95 to 50°C, the oat starches tended to exhibit a slightly higher setback viscosity than did the corn starches, except for Dal starch. These results (except for Dal starch) agree with those Paton (1977) and MacArthur and D'Appolonia (1979). Generally, high setback values are associated with greater starch paste retrogradation. Paton (1977) reported, however, that oat starch pastes had high setback characteristics but showed little evidence of high turbidity, surface skin formation, or shrinkage normally associated with retrogradation upon storage. Hoover and Vasanthan (1992) explained that setback values reflect the extent of water immobilization around the charged centers of starch components and those of free and helically complexed lipid molecules, rather than starch paste retrogradation. The association of water molecules with these charged centers would decrease the effective water concentration in the continuous phase, resulting in a rise in viscosity during the cooling cycle. Among native starches, the extent of water immobilization (setback) may be greater in oat starches because of the presence of more charged centers (from the lipid) in the continuous phase.

In the present study, the Dal starch showed unique characteristics among the three oat starches: it had the highest pasting temperature and peak viscosity and the least setback viscosity. Earlier, we reported that granular and molecular structure of these starches showed Dal amylopectin (AP) had the lowest limiting viscosity number [η] among these oat starches (Wang and White 1994b). MacArthur and D'Appolonia (1979) studied three oat starch types (Dal, Froker, and Cayuse) and found Dal starch had the highest granule density and the lowest (slightly) water-binding capacity of the other starches. These results may indicate that Dal starch has a more compact structure than do the other oat cultivars used in both studies.

Correlations were determined between the pasting properties and structural and physicochemical properties of oat starches and fractions. No meaningful correlations were found, except that the pasting temperature was negatively correlated with swelling power at 85°C ($r = -0.99$, $P < 0.05$). In our previous study, the swelling power at 85° C was negatively correlated with starch-lipid content ($r = -0.72$, $P < 0\ 0.02$) (Wang and White 1994a). By indirect comparison, the greater the starch-lipid content, the less the swelling power, and the higher the pasting temperature. In studying lipids and rheological properties of wheat starches, Nierle et al (1990) suggested that extraction with ethanol-water (which removed the lipid) resulted in a decrease of the pasting temperature when compared with the native starch control. Collison (1968) found the removal of the natural lipid increased the extent of starch swelling. Overall, the presence of lipids in starch decreases starch-granule swelling, therefore increasing the pasting temperature.

Gel Strength

A typical load-deformation curve for gels on the texture analyzer is shown in Fig. 1, as previously noted. The firmness of a gel was measured by the load at a depression distance of 2.9 mm. The stickiness was indicated by the negative load portion of the curve. Figure 3 shows the gel firmness of the starch pastes after storage (25°C for 5 hr and 4°C for 24, 72, and 168 hr). At all storage times between 5 and 168 hr, the oat starch gels were significantly less firm ($P < 0.05$) than the corn starch gels, except for E77 starch at 72 hr, which was not significantly different from B×MO corn starch (Fig. 3). Furthermore, among the oat starches, the gel firmness tended to decrease with increased starch-lipid content, except for the Dal starch at 5 and 24 hr. Perhaps the Dal starch gel was least firm at the beginning because, as previously mentioned, its more compact granular structure allowed slower migration of AM from the granule to solution. The high starch-lipid content in oat starches is considered responsible for the soft gel (Gudmundsson and Eliasson 1989). Takahashi and Seib (1988) studied corn and wheat starches with and without native lipids and found that the naturally occurring lipids in prime corn and wheat starches reduced gel strength by ~50% in 7.5% gels. Seemingly, the starch lipid may keep the AM inside the starch granules, thus reducing gel firmness by lowering the concentration of AM in the continuous phase. Furthermore, Doublier et al (1987) reported a rheological investigation of oat starch pastes and found that, for normal cereal starch, AM is preferentially leached and that AP can only begin to solubilize once the AM has leached. For oat starch, both AM and AP are coleached throughout the pasting process. Autio (1990) investigated rheological and microstructural changes of oat and barley starches during heating and cooling and showed that, in oat starch pastes, AM and AP are solubilized at the same time. In present study, the softness of the oat starch may also be related to the fact that the continuous phase of oat starch paste is composed of both AM and AP, whereas that of most other cereal starches is composed of only AM.

Figure 4 shows the stickiness of the oat and corn starch gels after storage. At 5 hr of storage at 25°C, the oat starch gels were stickier than the corn starch gels. During storage at 4°C for 24, 72, and 168 hr, the oat starch gels showed little change in stickiness, whereas the corn starch gels became stickier, especially by 168 hr of storage, when the B×MO corn starch gel was the stickiest among all gels.

Correlations were determined previously among gel strength and physicochemical properties (Wang and White 1994a). The starch-lipid content was negatively correlated with gel firmness ($r = -0.79, -0.89, -0.93$, and -0.91 for 5, 24, 72, and 168 hr of storage, respectively) and positively correlated with gel stickiness ($r = 0.71, 0.94, 0.94$, and 0.94 for 5, 24, 72, and 168 hr of storage, respectively) ($P < 0.05$), suggesting the importance of starch-lipid content on oat starch function.

Correlations determined previously among gel strength and structural properties (Wang and White 1994b) are shown in Tables III–V. Selected correlations from the data are presented in Table VI. The firmness was positively correlated with several structural properties of AP including increased percentage of the low molecular weight (MW) fraction (WF_3), and with the mole percent ratio of F_3/F_2 (M%R) or degree of multiple branching of the AP. The structural properties for the intermediate materials (IM) of WF_3 and M%R also were highly correlated with firmness. These results suggest that greater percentages of low MW components and a higher M%R in the AP and IM fractions, especially in the E77 starch, contributed to increased firmness of the gel. It follows that the percentage of F_2 in AP was negatively correlated with firmness. Increased firmness generally is associated with increased recrystallization and retrogradation of starch, but this was not the case. In fact, the values just mentioned were positively correlated with reduced retrogradation. It could be that the pres-

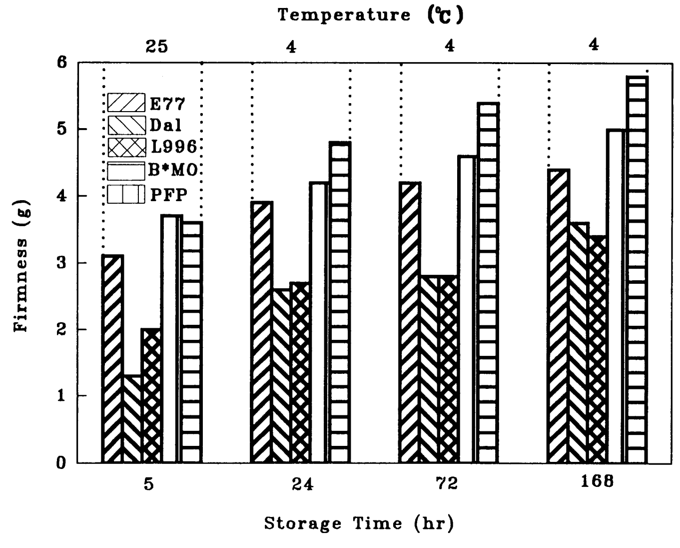

Fig. 3. Firmness of starch gels 6% (w/w) as measured by the Voland-Stevens texture analyzer. Values are the mean of 10 determinations from two separate samples. Least significant difference ($P < 0.05$) is 0.13, 0.29, 0.32, and 0.25 at 5, 24, 72, and 168 hr of storage, respectively.

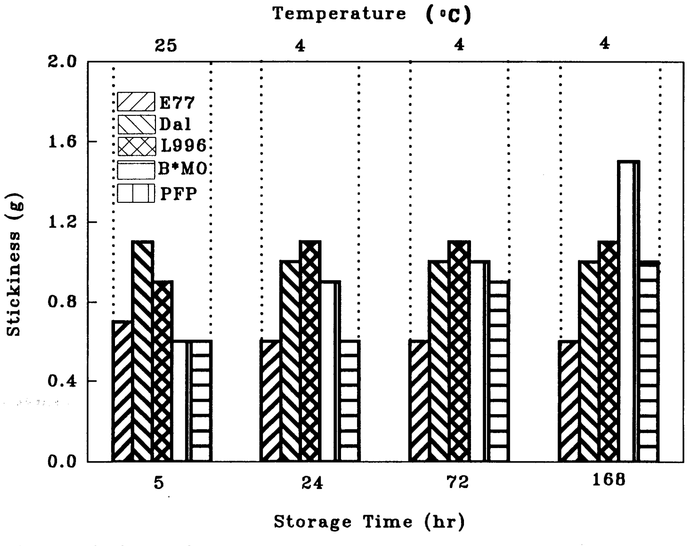

Fig. 4. Stickiness of starch gels 6% (w/w) as measured by the Voland-Stevens texture analyzer. Values are the mean of 10 determinations from two separate samples. Least significant difference ($P < 0.05$) is 0.05, 0.05, 0.08, and 0.09 at 5, 24, 72, and 168 hr of storage, respectively.

ence of smaller, more numerous branches in the AP created greater thickness than did the presence of fewer, longer branches because of the increased ability of the smaller branches to interact with the surrounding water, which was unrelated to retrogradation.

Although the average chain length of the high MW fraction (CLF$_1$) of AP also was highly positively correlated with increased firmness, the fact that only 7.3% of the AP was contained in F$_1$ (Table IV) suggests that this correlation is meaningless and was merely circumstantial.

Values for stickiness generally had correlations that were opposite of those for firmness. Where stickiness values were correlated with a parameter, firmness values were positively correlated. Generally, softer gels tend to have stickier properties.

It is possible that the correlations listed above are only circumstantial and that other factors, such as lipid content, were actually more important to function of the starches. Correlations should be viewed as a suggestion of possible relations between parameters, and further studies should be designed to more closely examine these links.

Thermal Properties

The DSC properties of oat and corn starches are presented in Table II. Representative thermograms are shown in Figure 5. All starches gave two endothermic transitions: the low-temperature endotherm (M$_1$) corresponding to the melting of starch crystallites, and the high-temperature endotherm (M$_2$) corresponding to the melting of an amylose-lipid complex (Paton 1987).

Low-temperature endotherm (M$_1$). As expected (Lineback 1984, Gudmundsson and Eliasson 1989), the gelatinization temperature

TABLE III
Weight Average Degree of Polymerization (DP$_w$) and Apparent Distribution of DP$_w$ for Oat Amylose[a,b]

Sample	Peak DP$_w$[c]	Apparent DP$_w$ Distribution[d] DP$_w$ Lowest	DP$_w$ Highest (estimated)[e]
E77	1,208	392	2,545
Dal	1,185	568	2,149
L996	939	421	2,920
LSD[f]	106	80	163

[a] Data taken from Wang and White 1994b.
[b] Values are the mean of two determinations.
[c] DP$_w$ expressed as weight of glucose units.
[d] Values at 10% (lowest) and 90% (highest) of the molecular weight range.
[e] These values are a little larger than the molecular weight of the standards fitting on the straight line portion of the standard curve, so values are estimated.
[f] Least significant difference at a significance level of $P < 0.05$.

TABLE IV
Percentage Compositions and Chain Length Distribution (CL$_w$) of Isoamylase-Debranched Amylopectin from Oat Starches[a,b]

		Fraction[c]			
	Starch	F$_1$	F$_2$	F$_3$	F$_3$/F$_2$
Peak CL$_w$[d]	E77	204.2	31.8	16.6	
	Dal	190.4	31.3	17.1	
	L996	181.7	30.7	20.1	
	LSD[e]	7.5	3.5	2.9	
Weight%[f]	E77	7.3	31.8	60.9	
	Dal	8.7	46.4	44.9	
	L996	5.6	49.2	45.9	
	LSD	1.0	7.3	7.0	
Mole%[g]	E77	0.8	21.2	78.0	3.7
	Dal	1.2	39.4	59.4	1.5
	L996	0.8	40.9	58.3	1.4
	LSD	1.0	8.1	9.9	0.3

[a] Data taken from Wang and White 1994b.
[b] Values are the mean of two determinations.
[c] F$_1$, F$_2$, and F$_3$ = high, intermediate, and low molecular weight fractions, respectively.
[d] Weight average chain length, expressed as weight of glucose units.
[e] Least significant difference at a significance level of $P < 0.05$.
[f] Percentages of the F$_1$, F$_2$, and F$_3$ fractions within the amylopectin portion as measured by peak area.
[g] Percentages of the F$_1$, F$_2$, and F$_3$ fractions within the amylopectin portion as calculated from weight% and CL$_w$.

TABLE V
Percentage Compositions and Chain Length Distribution (CL$_w$) of Isoamylase-Debranched Intermediate Materials from Oat Starches[a,b]

		Fraction[c]			
	Starch	F$_1$	F$_2$	F$_3$	F$_3$/F$_2$
Peak CL$_w$[d]	E77	280.0	34.5	22.6	
	Dal	341.7	79.9	NA[e]	
	L996	310.9	42.2	21.8	
	LSD[f]	24.8	5.5	2.3	
Weight%[g]	E77	24.1	27.1	48.9	
	Dal	86.1	14.2	NA	
	L996	5.8	59.4	34.9	
	LSD	6.2	8.8	3.3	
Mole%[h]	E77	2.9	26.0	71.2	2.7
	Dal	62.3	37.7	NA	NA
	L996	0.7	46.7	52.8	1.1
	LSD	10.0	6.8	5.1	0.3

[a] Data taken from Wang and White 1994b.
[b] Values are the mean of two separate determinations.
[c] F$_1$, F$_2$, and F$_3$ = high, intermediate, and low molecular weight fractions, respectively.
[d] Weight average chain length, expressed as weight of glucose units.
[e] Not available.
[f] Least significant difference at a significance level of $P < 0.05$.
[g] Percentages of the F$_1$, F$_2$, and F$_3$ fractions within the intermediate material portion as measured by peak area.
[h] Percentages of the F$_1$, F$_2$, and F$_3$ fractions within the intermediate material portion as calculated from weight% and CL$_w$.

TABLE VI
Correlations Among Selected Structural Characteristics and Functional Properties of Oat Starches[a]

	Characteristics[b]	T_o	ΔH	ΔH_r	%r	Firmness[c]	Stickiness[d]
Amylopectin	CLF$_1$	−0.97**[e]	NS[f]	−0.93**	−0.87*	0.99**	−0.97**
	CLF$_3$	NS	NS	NS	0.97**	−0.81*	NS
	WF$_1$	NS	0.86*	NS	NS	NS	NS
	WF$_2$	0.90*	NS	NS	0.84*	−0.93*	0.89*
	WF$_3$	−0.94**	NS	−0.86*	NS	0.95**	−0.94**
	M%R	−0.98**	NS	−0.91*	−0.88*	0.99**	−0.97**
Intermediate materials	WF$_3$	−0.98*	NS	−0.96*	−0.96*	0.99**	−0.99**
	M%R	−0.99**	NS	NS	−0.95*	0.99**	−0.88*
Amylose	DP$_w$	NS	NS	NS	−0.92**	NS	NS

[a] T_o = onset temperature of gelatination; ΔH = enthalpy of the phase transition of gelatination; ΔH_r = enthalpy of the transition of retrogradation; and %r = retrogradation percentage as determined by differential scanning calorimetry.
[b] Peak CL$_w$ of F$_1$, peak CL$_w$ of F$_3$, weight% of F$_1$, weight% of F$_2$, weight% of F$_3$, and mole % ratio (F$_3$/F$_2$), and peak DPw (From Tables III–V).
[c] Firmness of gel at 4°C for 168 hr, as determined by texture analysis.
[d] Stickiness of gel at 4°C for 168 hr, as determined by texture analysis.
[e] * and ** = Significant at $P < 0.05$ and $P < 0.01$ levels of probability, respectively.
[f] Not significant at $P < 0.05$.

(T_0) and enthalpy (ΔH) were significantly lower for oat starches than they were for corn starches (Table II). The T_0 values of oat starches increased with increased AM ($r = 0.97$, $P < 0.01$) and starch-lipid content ($r = 0.92$, $P < 0.01$) (Wang and White 1994a). E77 starch had significantly lower T_0 than did Dal and L996 starches, which were not significantly different from each other. The ΔH of Dal starch was significantly higher than that of E77 and L996 starches, which were not significantly different from each other. The low ΔH and T_0 values for oat starches may be due to the high lipid content in oat starch (Biliaderis et al 1986, Doublier et al 1987, Paton 1987). Also, Paton (1987) reported a lower ΔH value (2.2 cal/g) for oat starch than that previously reported for rice starch (2.7 cal/g) and suggested that oat starch may be more amorphous or less ordered than rice starch. Hoover and Vasanthan (1992) found wheat starch to have a lower T_0 (57°C) than that of oat starch (61°C). On the basis of T_0 and X-ray diffraction, they suggested that wheat starch had a lower degree of order in the crystalline structure than did oat starch. In the present study, the lower T_0 and ΔH of oat starches, when compared with corn starches, suggests less order in the crystalline structure of the oat starches. Among the oat starches, Dal may have the greatest order in the crystalline structure because Dal had the highest ΔH value. These results are consistent with our previous study, in which the Dal starch structure was probably more compact than the structure of the other oat starches, as indicated by the low limiting viscosity number $[\eta]$ of its AP (Wang and White 1994b).

The M_1 of the oat starches had a higher R and a lower PHI than that of the M_1 of the corn starches (Table II). Although the R were slightly different, the PHI values were similar among the three oat starches. The PHI value gives the relative shape of the endotherm (Krueger et al 1987). A tall, narrow endotherm has a high PHI and a short, broad endotherm has a low PHI. All oat starches had short, broad endotherms, whereas the corn starches had tall, narrow endotherms (Fig. 5).

High-temperature endotherm (*M_2*). The T_0 and R values of the M_2 transition (amylose-lipid complex) were not significantly different among all oat and corn starches (Table II). This observation was also reported by Sowa and White (1992).

All ΔH values of M_2 for oat starches were significantly different ($P < 0.05$) from each other and significantly higher than values for corn starches (Table II). Among the three oat starches, M_2 of the Dal starch had the highest ΔH value, followed by L996 starch and E77 starch. The high ΔH values observed in oat starches is related to the amount of lipid in oat, which is greater than that in corn starches (Wang and White 1994a). Also, Doublier et al (1987) showed that removing the internally bound starch lipids from oat resulted in an absence of any starch-lipid endotherm (M_2).

Refrigerated-Storage Retrogradation

The DSC parameters of the starch samples stored at 4°C for seven days (retrogradation) are reported in Table II. Representative thermograms are shown in Figure 6. The endothermic transitions for all stored oat and corn starches had lower T_0, ΔH, and PHI values and higher R values than the same parameters for gelatinization ($P < 0.01$), as expected (Donovan and Mapes 1980). The weaker molecular structure formed from recrystallization of the starches during storage after gelatinization had a lower T_0, decreased ΔH, and broader transitions (higher R and lower PHI) than did the native starch structure, as described by Donovan and Mapes (1980).

The T_0 of oat starches were not significantly different from each other or from that of PFP corn starch, but the T_0 of Dal starch was significantly different ($P < 0.05$) from that of B×MO starch. The ΔH of oat starches were significantly lower ($P < 0.05$) than those of the corn starches. Furthermore, the ΔH of E77 starch was significantly lower ($P < 0.05$) than the ΔH of the other oat starches. The %r was significantly lower for oat starches than it was for corn starches, and the %r was significantly different ($P < 0.05$) among all oat starches. The greater starch-

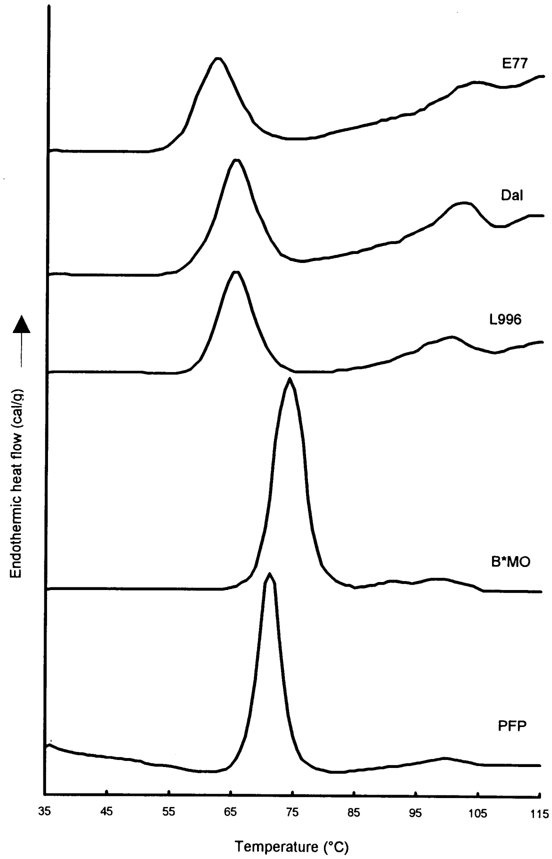

Fig. 5. Differential scanning calorimetry thermograms of gelatinization of oat and corn starches.

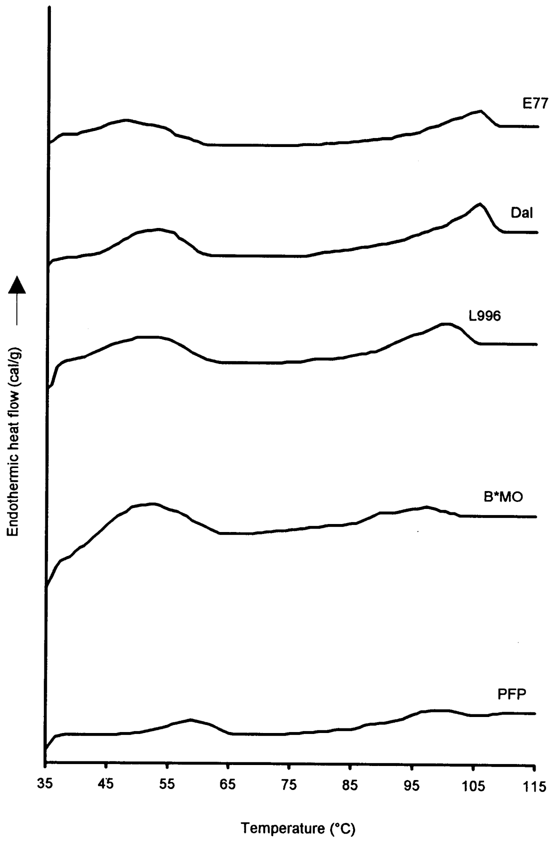

Fig. 6. Differential scanning calorimetry thermograms of retrogradation of oat and corn starches.

lipid content in oat than in corn starches may reduce the retrogradation in the oat starches. Among oat starches however, the %r decreased with decreased starch-lipid content. The E77 starch, with the least starch-lipid content, had the lowest %r, whereas L996 starch, with the highest starch-lipid content, had the highest %r.

Correlations were determined among the functional properties and previously measured physicochemical properties of starch granules (Wang and White 1994a). No significant correlations ($P < 0.05$) between thermal and pasting properties were found. The T_o of M_1 was negatively correlated with gel firmness ($P < 0.05$) and positively correlated with gel stickiness ($P < 0.05$) at all storage periods, meaning that as the T_o decreased, a firmer and less sticky gel resulted.

Correlations also were determined among the functional properties and previously measured structural data (Wang and White 1994b), as reintroduced in Tables III–V. Selected correlations are shown in Table VI. T_o was negatively correlated with several structural values, including increased percentage of low MW fraction (WF_3) in the AP and IM, and the M%R for AP and IM. These results suggest that, as the amount of low MW fraction and the ratio of F_3/F_2 for both AP and IM increased, the starch began gelatinizing at a lower temperature. The logic that shorter chains with increased branching are more easily gelatinized than longer chains with less branching makes sense. It follows that the percentage of fraction 2 (WF_2) within the AP was positively correlated with T_o. The MW dependence of the temperature of gelatinization and its likely relation to interchain entanglement has been cited elsewhere (Slade and Levine 1987).

Although the average chain length of the high MW fraction (CLF_1) also was negatively correlated with T_o, the fact that only 7.3% of the AP (as indicated earlier) was contained in F_1 suggests that the correlation was meaningless. Similarly, the positive correlation between the enthalpy of gelatinization (ΔH_g) and the amount of high MW fraction (WF_1) probably was meaningless, as was the negative correlation between CLF_1 and the enthalpy of retrogradation (ΔH_r) and the %r.

The ΔH_r was negatively correlated with WF_3 and M%R of AP and with WF_3 of IM, suggesting less retrogradation with greater weight percentage of the low MW fractions (WF_3 of AP and IM) and with greater branching (M%R). Similarly, %r was negatively correlated with M%R of AP and with WF_3 and M%R of IM. It follows that CLF_3 and WF_2 of AP were positively correlated with %r.

Once again, correlations with CLF_1 of AP were probably useless. A negative correlation between %r and the weight-average degree of polymerization (DP_w) of the AM portion suggested that as the DP_w decreased, the percentage of retrogradation increased, indicating that shorter chains of the AM retrograded more easily than did longer chains. In general, this information seems to contradict the other findings listed in Table VI. However, it may be that, when shortened, the chain of AM, somewhat greater than of AP or IM, are indeed more easily retrograded than the very long chains associated with AM.

Gudmundsson and Eliasson (1989) reported that oat starch had the greatest lipid content among corn and wheat, and it also had the smallest retrogradation tendency. However, the oat starch cultivar Chicauhua, when defatted, showed a great increase in retrogradation when compared with the native starch. Another cultivar, Svea, showed a much smaller difference between native and defatted starch. Thus, there seemed to be other factors, besides oat lipid content, that influenced retrogradation in oat starches. These researchers suggested that the native lipids may complex, not only with AM, but also with some chains of AP, thus reducing retrogradation. The ability of AP to form with the lipid (and, thus, decrease retrogradation) might depend upon properties of the AP, such as chain length, chain-length distribution, and degree of multiple branching.

The recrystallization of AP during storage after gelatinization is, indeed, thought to be responsible for the retrogradation as measured by DSC (Gudmundsson and Eliasson 1990), inasmuch as the AM component in the starch recrystallizes very fast. The AP component changes much more slowly (Miles et al 1985). Other researchers have noted the link between retrogradation, AP concentration, and the fine structure of AP. Yuan et al (1993) noted that the chain length and chain-length distribution of AP from corn may affect retrogradation behavior by forming a mixture of crystallites of different sizes, with longer chain lengths forming longer double helices. They suggested that the more ordered structure created by longer chains may produce a higher %r than that of the shorter chains. The observations of Gudmundsson and Eliasson (1989) and Yuan et al (1993) are consistent with the correlations obtained in our study, which indicated relationships between %r, CL_w, and degree of multiple branching.

CONCLUSIONS

The functional properties of oat starches isolated from different oat types differed from each other and from corn starches. The oat starches differed from corn starches in showing a higher pasting temperature and a lower peak viscosity, as determined by a viscoamylograph, and in forming less firm starch gels as determined by a texture analyzer. Also, using DSC revealed oat starches had a lower T_o and %r and, generally, a lower ΔH for M_1 and a higher ΔH for M_2 than did corn starches. The differences between oat and corn starches may be attributed to greater quantities of starch-lipid and a more amorphous nature or less crystalline order in the oat starches. Among oat starch gels, the firmness was negatively correlated ($r = -0.79, -0.89, -0.93$, and -0.91 for 5, 24, 72, and 168 hr of storage, respectively) and the stickiness was positively correlated ($r = 0.71, 0.94, 0.94$, and 0.94 for 5, 24, 72, and 168 hr of storage, respectively) with the starch-lipid content ($P < 0.05$). Furthermore, the T_o of M_1 was positively correlated with AM ($r = 0.97$, $P < 0.01$) and starch-lipid content ($r = 0.92$, $P < 0.01$). The %r increased with increased CL_w of F_3 of AP ($P < 0.01$), decreased AP content ($P < 0.01$), and degree of multiple branching of AP ($P < 0.05$).

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