

Structure and Pasting Properties of Oat Starch

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ABSTRACT

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Following a period of declining food use, oats are now increasing in importance because of perceived nutritional benefits. The pasting properties of oat starch were regarded as similar to those of other cereal starches until the development of instruments with a more rapid mixing system than the amylograph showed characteristic differences in oats.

These differences in pasting properties offer opportunities for novel products in both food and industrial areas. The structure, composition, and pasting properties of oat starch are reviewed, with particular emphasis on methods of measurement. Future directions of research in this area are suggested.

Oats are widely cultivated in temperate regions with a total world production in 1989 of 42.6 Mt (Kent and Evers 1994). However, only a very small proportion is for human food use, and as little as 5% of the oat crop enters world commerce (FAO 1990). Nevertheless, human consumption of oats is increasing, and this trend can be expected to continue as consumer demand for healthy nutritious products increases and as processors respond to this demand by producing new varieties of oat-derived products (Wilhelm et al 1989, Yiu et al 1991, Peterson 1992, Lapveteläinen et al 1994).

The oat grain comprises the hull (25%), pericarp, testa and aleurone (9%), starchy endosperm (63%), and embryo (3%). Variation in the composition of oats has been reported by various authors (Table I). The dehulled grain or groat contributes ≈75% to the entire grain mass but varies within the range 65–80%, also due to both varietal and environmental differences. Compared to other cereals, oats are characterized by lower carbohydrate content, with higher protein and fat contents. Thus, protein values of 10–12% in the whole oat grain are typical (Zarkadas et al 1995) and similar to wheat. Oat groats have the highest lipid concentration of all the common cereals (Acker and Becker 1971, Youngs 1974, Youngs et al 1977, Morrison et al 1984, Gudmundsson and Eliasson 1989, Becher 1992); it is two to five times as high as that of wheat. The lipid content, which is distributed throughout the kernel, may be as high as 10% of total oat mass, although measured values are very dependent on the method of analysis and, in the case of solvent extraction, vary considerably with the nature of the extracting solvent (Matz 1991). Lipid values obtained by extraction with ethoxyethane are termed “free lipids” to distinguish them from those lipids more or less strongly bound to other saccharide or protein components. Normalizing the material extracted with ethoxyethane to 100%, the equivalent figure for material extracted by ethanol was 128%, which equated to values obtained by acid hydrolysis methods. A distinctive feature of oats is the remarkable lipase activity in ungerminated seed (Youngs 1986).

Reducing sugars in oats are quite low, usually <0.1%, while total sugars are often ≈1% (Henry 1985). However, the monomers are of extreme importance as components of polysaccharides, both in their contribution to structural and storage components and, of more interest here, to the behavior of the grain during processing. The 1,3- and 1,4-β-glucans contribute ≈2–6% to the total groat mass and as much as 7% to the starchy endosperm of the oat grain

(Fincher and Stone 1986, Bhatti 1992). With water, β-glucans form viscous gums (Autio et al 1987) and contribute significantly to water retention and processing behavior. The higher content of gums, especially β-glucans, in the wet-milled oat bran has a marked effect on the viscosity of heat- and α-amylase-treated bran slurries (Jaskari et al 1995). Nonetheless, in common with other grains, starch remains the most abundant component in oats; it constitutes ≈60% of the dry matter of the entire oat grain. The iodine affinity of oat starch at ≈19.5 g/100 g is similar to that of wheat, barley, and rye (Banks and Greenwood 1967b).

The renewed interest in oats (Peterson 1992) has been accompanied by a similar increase in the study of oat starch. This article reviews the morphology and composition of the starch granule of oats and examines their combined effects on pasting properties.

THE STARCH OF OATS

Starch is found in the endosperm of the oat granule with trace amounts in the embryo and other organs; the oat starch granules are not embedded in a continuous protein matrix, as the protein is localized in discrete structures. Traditionally, the starch of oats has been of little interest to cereal chemists because, in contrast to most other cereals, it cannot easily be separated from the other components of the grain. Thus, there is no starch industry using oats as feedstock that is analogous to those based on maize in the United States or on wheat in Australia. As a consequence, relatively few references are found in cereal chemistry literature on the functionality of oat starch. Nevertheless, an understanding of the morphology and functionality of oat starch is essential to achieving maximum use of this cereal. Very little investigation of the differences between cultivars has been published, and many of the studies have been based on examination of a high-protein mutant, Hinoat (Paton 1981, 1986). Little work has been reported (Paton 1977) on the variation in the pasting characteristics of starch in oat cultivars that are important for its use for human consumption.

Morphology

Starch occurs in cereal grains as discrete granules which are solid, optically clear bodies, but oat starch differs from that of other cereals. The granules are only weakly birefringent, irregular in shape (often polyhedral but sometimes ovoid or hemispherical), tend to exist in clusters, and do not fall into discrete size distributions (i.e., A and B types) as in wheat and barley. The surfaces of the granules appear smooth with no evidence of fissures (Hoover and Vasanthan 1992). The average size of individual oat starch granules varies from 3 to 10 μm (Reichert 1913, Matz 1969, Lineback 1984, Paton 1986, Gudmundsson and Eliasson 1989, Hartunian-Sowa and White 1992, Hoover and Vasanthan 1992, Wang and White 1994b), which is much smaller than starch

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granules of wheat, rye, barley, and corn (Hoseney et al 1971). The average granule size of oat starch was positively correlated with percent of light transmittance and negatively correlated with lipid content, iodine affinity, blue value, amylose percent, and the wavelength of maximum absorption (λ_{max}) (Wang and White 1994b). As the groat oil content increased from 6.2 to 15.5% and the amylose content increased from 30.3 to 33.6%, the average size of the oat starch granules decreased from 6.3 to 3.8 μm (Hartunian-Sowa and White 1992). Mäkelä and Laakso (1984) conducted detailed studies on the size distribution of oat starch granules. The maximum number of granules appeared at a diameter range of 1.9–2.4 μm and, on the basis of the high reproducibility of the technique, it was concluded that no aggregation of individual granules occurred at concentrations <1 mg/mL. Two different average granule sizes, 3.0 and 6.4–7.4 μm , were obtained depending on whether the sizings were based on estimation of the granule's cross-sectional areas or directly on the effective volumes (Mäkelä and Laakso 1984).

The individual granules develop in compact spherical bundles or clusters, known as compound granules, $\approx 60 \mu\text{m}$ in diameter (Reichert 1913, Matz 1969, Hoover and Vasanthan 1992). The compound granules, which fill most of the central space within the endosperm cells, are usually broken as the kernel is processed, revealing the individual granules that are irregular in shape (Reichert 1913, Matz 1969, Hoover and Vasanthan 1992). Many of the granules are round on one side and polygonal on the opposite side, indicating the growth of the granules in clusters, where they acquire the shape of the neighboring starch granules (Hartunian-Sowa and White 1992).

Under crossed polarizers, granules of oat starch exhibit weak birefringence in the form of a Maltese cross, suggesting a high degree of order within the structure. The molecules are organized in a radial

direction as indicated by the positive sign of the birefringence (French 1984). Furthermore, a degree of crystallinity is suggested by the X-ray patterns corresponding to one of two limiting crystalline polymorphs (A,B) or the intermediate C form (Sarko and Wu 1978). X-ray diffraction studies indicate that both polymorphs are composed of ordered arrays of double helices, most likely left-handed with parallel strands (Imberty and Perez 1988). The X-ray spectra of native oat starch was of the A-type representative of cereal starches, with spacing at 0.38, 0.48, 0.52, and 0.58 nm (Gudmundsson and Eliasson 1989, Hoover and Vasanthan 1992), without any evidence of amylose-lipid complex in the native starch at room temperature. This may indicate that formation of the complex does not occur until gelatinization has commenced or, alternatively, it may be due to a too low concentration of crystalline domains.

It is now accepted that many of the physical characteristics of the starch granules' structure and behavior can be attributed to the crystalline regions of the granule, which are due to the amylopectin component. At approximately the same moisture content, the relative crystallinity of oat starch (0.90) was higher than that of wheat starch (0.67). This suggests a closer packing of double helices (formed from adjacent branches of amylopectin) in oat starch granules (Hoover and Vasanthan 1992). Nevertheless, the crystalline regions comprise less than half the total starch present; some 70% is amorphous, including all of the amylose and also much of the amylopectin. Furthermore, in comparison to wheat starch, the amylose chains of oat starch appear to be more loosely arranged in the amorphous regions but more compactly packed in crystalline regions (Hoover and Vasanthan 1992).

Starch Granule Composition

Amylose-amylopectin. The main variation in composition of oat starch is due to the relative proportions of amylose and amylopec-

TABLE I
Proximate Composition (%) of Oats

Variety	Moisture	Protein	Lipid	Starch	Fiber	Ash	Monosaccharides	β -Glucans	Reference
121 Swedish varieties	Oats	11.6	5.7	46.2	32.3	3	1.2		Åman 1987
19 Canadian cultivars	Groats			60.3				2.3	Bhatty 1992
101 Canadian cultivars	Groats							4.6	Bhatty 1992
3 Australian cultivars	Oats	10–13	9–11	7–10					Glennie-Holmes et al 1992
4 Swedish cultivars	Oats		5–7						Gudmundsson and Eliasson 1989
Line (U.S.) E77	Groats	18.3	6.2	57.8				4.1	Hartunian-Sowa and White 1992
Line (U.S.) DAL	Groats	21.4	8	50.8				4.6	Hartunian-Sowa and White 1992
Experimental line (U.S.) MO42017	Groats	21.2	15.5	39.3				5.7	Hartunian-Sowa and White 1992
3 Norwegian cultivars	Oats	11.2	7.6–8.6 ^a 8.8–10.1 ^b						Molteberg et al 1995
18 Canadian cultivars	Groats	14 - 25		44 - 61					Paton 1977

^a Ether extraction.

^b Ether extraction following acid hydrolysis.

TABLE II
Chemical Composition (%) of Oat Starch

Variety	Amylose	Lipid	Protein	Total Phosphorus	Ash	Moisture	Reference
3 U.S. cultivars	25–28	0.7–1.1	0.4–0.6				MacArthur and D'Appolonia 1979
3 Polish cultivars		1.1–1.7	0.28–0.39	0.06–0.07			Gibiński et al 1993
4 Swedish cultivars	27–29	1.8–2.3					Gudmundsson and Eliasson 1989
Various lines (U.S.)	30.3–33.6	2.1–2.5	0.85–0.95	0.15–0.19			Hartunian-Sowa and White 1992
AC Hill (Canada)	19.4	1.13	0.31		0.03	9.4	Hoover and Vasanthan 1994a
3 Canadian cultivars	25–29	1.35					Morrison et al 1984
Canadian cultivars		<0.3–0.4	<0.4–0.5	0.06–0.08			Paton 1977
Finnish commercial oats	29.2	1.3					Shamekh et al 1994
6 German cultivars	27–30	1.0–1.1 ^a					Tester and Karkalas 1996
3 Canadian cultivars	21–25 ^b 2–27 ^c	1.08–1.18					Wang and White 1994b

^a Corrected to total lipid.

^b By iodine affinity.

^c By blue value.

tin in the starch granules and this, together with the chain length distribution (Hoover et al 1994) and the frequency and spacing of branch points within the amylopectin molecule, has a profound influence on the properties of the starch. The iodine affinity of oat amylose ranged from 18.4 to 19.5 g/100 g and that of amylopectin from 0.30 to 0.58 g/100 g (Banks and Greenwood 1967b, Wang and White 1994a), reflecting the ability of the amylose to form a complex with iodine. Reports of the content of amylose in oat starch (Table II) ranged from a low of 18% (Paton 1979) to a high of 26–29% (MacArthur and D'Appolonia 1979, Morrison et al 1984, Doublier et al 1987, Gudmundsson and Eliasson 1989). However, in 1992, amylose contents of 30–34% were measured (Hartunian-Sowa and White 1992) by iodine affinity. Tester and Karkalas (1996) compared the structure and physicochemical properties of starches extracted from five normal and one naked oat cultivar. The molecular size or polydispersity of the native amylose and amylopectin determined by gel-permeation chromatography showed minimal differences. Total, apparent and δ -amylose (the difference between apparent and total amylose due to lipid complexing) (Morrison et al 1993) contents ranged from 27.5 to 29.8%, 19.7 to 22.0% and 7.1 to 8.1%, respectively, with lipid content, as fatty acid methyl esters, ranging from 0.66 to 0.75% on a dry basis.

A relatively large amount of a starch fraction with properties of both amylose and amylopectin has been reported over many years (Lansky et al 1949, Banks and Greenwood 1967a, Banks and Greenwood 1975, Paton 1979). These fractions were called anomalous amylose and anomalous amylopectin, respectively. In a series of articles, Wang and White (1994a–c) examined the structure and properties of starches isolated from oat cultivars containing a range of lipid contents (6.2, 8.0, and 11.2%). The isolated starches were fractionated into amylose, amylopectin, and intermediate materials by using butan-1-ol precipitation (Wang and White 1994a). The starch fractions were debranched and further fractionated by high-performance size-exclusion chromatography (SEC). The weight average degree of polymerization (DP_w) and apparent DP_w distribution of amylose ranged from 939 to 1,208 and from 392 to 2,920 glucose units, respectively. These values tended to be smaller than those of corn and rice starches reported elsewhere. The SEC profiles of debranched amylopectin showed three fractions: high, intermediate, and low molecular weight (HMW, IMW, and LMW, respectively); these fractions corresponded to chain lengths ranging from 181 to 204, 31 to 32, and 17 to 20, by weight of glucose units, respectively. The average chain length of oat amylopectin was slightly lower than that of other cereal starches (Banks and Greenwood 1967b). Differences in chain length and chain-length distribution of amylopectin also were noted among oat starch types, with the chain length of amylopectin increasing with increased amylose and starch-lipid contents. The results further suggested that the intermediate material contained longer, less highly branched molecules than did amylopectin (Wang and White 1994a). Hartunian-Sowa and White (1992) reported a large amount of the LMW starch fraction by SEC, a fact implying the existence of IMW starch. However, the most recent work (Tester and Karkalas 1996) suggested that the presence of so called "intermediate material" claimed by various authors is very much in doubt, since the intermediate material may be contamination of the amylose fraction with native or hydrolyzed amylopectin due to coprecipitation. Furthermore, the minor components of oat starch, and particularly those at the granule surface, also contribute to its properties.

Care must be exercised to distinguish nonstarch materials that are inherent components of the granule from those that arise due to the process of isolating the starch. The main nonstarch components of starch granules are protein and lipid. The protein content of isolated starches ranged from 0.3–1% (Table II). Small amounts of protein are probably the result of residual protein attached to the surface of the starch granule. The most significant proteins, in terms of their effects on starch behavior, are enzymes. Traces of

α -amylases can significantly affect pasting properties through hydrolysis of starch polymers, and the lipases are relevant to the stability of oats following milling.

Lipids. Isolated oat starches, in contrast to those of wheat and maize, contain greater amounts of lipid, ranging from 1 to 3%, presumably as a relatively large amylose-lipid complex (Acker and Becker 1971, Youngs 1974, Morrison et al 1984, Gudmundsson and Eliasson 1989, Hartunian-Sowa and White 1992, Gibiński et al 1993, Hoover and Vasanthan 1994a, Shamekh et al 1994, Wang and White 1994b, Tester and Karkalas 1996). From the perspective of starch functionality, the formation of a starch-lipid complex in which a saturated fatty acid chain occupies the core of the amylose helix is significant. Morrison (1981, 1988) identified three categories of lipid that are distinguishable experimentally. The internal lipids residing inside native starch granules either in the cavity of the amylose helix or in the spaces between amylose and amylopectin were considered the only true "starch lipids". Such lipids are composed exclusively of monoacyl lipids (free fatty acids and lysophospholipids). Starch surface lipids are artifacts derived from the surrounding proteinaceous matrix of the endosperm, and it was hypothesized that these compounds, which are also monoacyl lipids, formed inclusion complexes with amylose in the surface regions of the granule. The remaining lipids derived from endosperm (aleurone and germ) are termed nonstarch lipids. The majority are fully acylated (triacylglycerols, diacylglycerolipids, and phospholipids) and can reside either in a free state or bound with proteins on the granule surface. Free fatty acids and monoglycerides may also be present from lipolysis on isolation and storage of starch (Molteberg et al 1995).

Surface and nonstarch lipids, and internal granular lipids probably each contribute to the pasting characteristics of the starch granules, but the effect of the granular lipids is only apparent in pasting characteristics of isolated granules. The two groups are readily separated by extraction with propan-1-ol and water at ambient temperature or cold water-saturated butan-1-ol (to recover nonstarch and surface lipids), or by refluxing using a Soxhlet apparatus to recover internal lipids (Morrison 1981). Starch (internal) lipids are extracted very slowly and incompletely with polar solvents at ambient temperatures. Similarly, negligible quantities of the starch lipids are extractable with traditional low-polarity fat solvents such as chloroform or ethoxyethane (Morrison 1988). Alternatively, cold extraction with chloroform-methanol-water (3:2:1) followed by hot extraction with propan-1-ol has been used (Gibiński et al 1993) to separate the two groups. Hot extraction was significantly more effective in lipid removal as only 6% of the original lipid remained in the starch following hot extraction, whereas 52% remained after cold extraction. Hoover and Senanayake (1996) distinguished between the free lipid obtained by cold extraction with chloroform-methanol (2:1) at 25°C and the free plus bound lipid extracted by hot propan-1-ol and water (3:1). Room temperature washing of oat starch with the latter solvent did not alter the corresponding differential scanning calorimetry (DSC) thermogram, whereas refluxing in the same solvent reduced the endotherm at 66°C and completely eliminated the one at 102–104°C, suggesting the effectiveness of the latter approach in removal of internal lipids (Paton 1987).

A positive correlation has been found between the lipid content in groats and the amylose content in isolated oat starches (Morrison et al 1984, Hartunian-Sowa and White 1992). Gudmundsson and Eliasson (1989) reported a similar relationship between the amylose and lipid contents in different varieties of oat starch. Morrison (1988) has suggested that the explanation for this correlation, which holds for all nonwaxy cereal starches, may lie in the regulation of starch biosynthesis by lipids. Furthermore, the internal starch lipid content (1.3%) was considerably higher than the free extractable lipid value of 0.3% (Doublier et al 1987). The internally bound lipid renders as much as 60% of the amylose inaccessible to iodine in native oat starch.

Others. Phosphorus is an important minor constituent of oat starch where it occurs as a component of lysophospholipids, including lysophosphatidyl choline, lysophosphatidyl ethanolamine and lysophosphatidyl glycerol. The proportion of lysophospholipids to free fatty acids in internal starch lipids varies with species but in oats 30% typically occurs as free fatty acids (Morrison 1985). Phosphorus contents of 0.15–0.19% (by mass) have been reported (Hartunian-Sowa and White 1992), although values of 0.06–0.08%, which are still higher than other cereal starches (Paton 1977, Gibiński et al 1993), appear more typical. The fact that these starches also contained less lipid (<0.3%) may have accounted for the smaller phosphorus contents (Hartunian-Sowa and White 1992).

The effects of processing on oat composition, including trace components such as phytin and phenolic compounds, have been investigated (Liukkonen et al 1992, Yiu 1986). Most endospermic cell walls in rolled oat samples were fractured (Yiu 1986) due to the impact of mechanical processing, and the proteins and lipids appeared as aggregated masses after processing, with destruction of the distinct structural units found in unprocessed groats. Further aggregation was induced by cooking, which also resulted in many starch granules losing original structural organization and anisotropic characteristics.

PASTING

From the consumer's point of view, the pasting properties of the whole oat product are critical to its acceptance. However, most

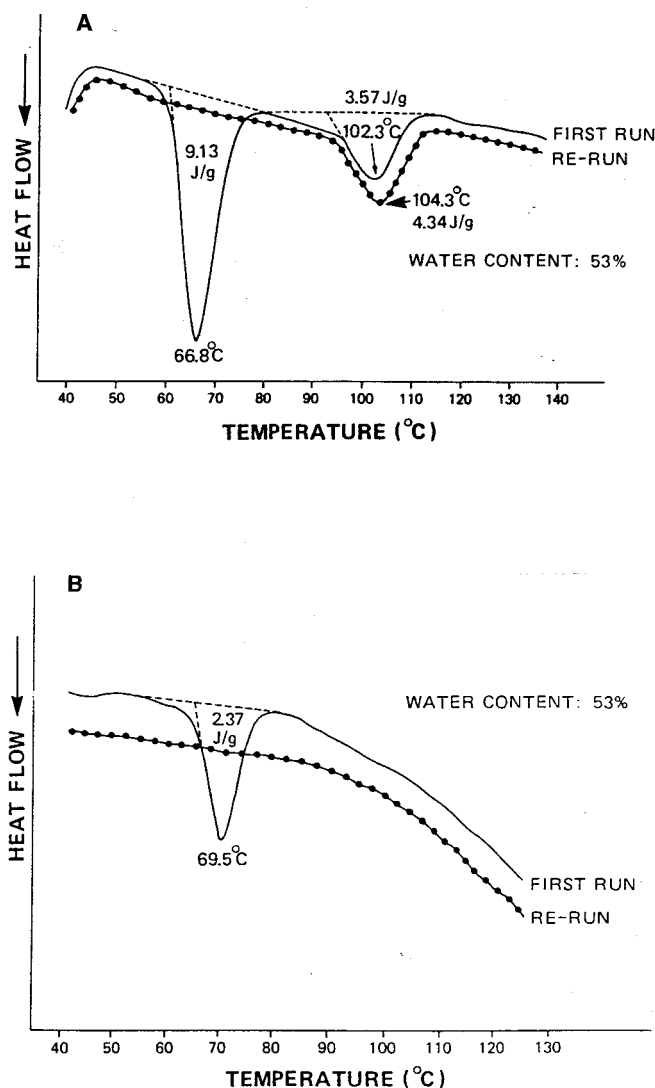


Fig. 1. Differential scanning calorimetry thermograms of native oat starch (A) and lipid-free oat starch (B). Reprinted from Doublier et al (1987).

studies have concentrated on isolated starch because of the problems of separating the effects due to starch, glucans, and other components. This is associated with the usual difficulty of valid analytical measurement, namely, limited specificity of test methods, although there are some important distinctions between measurement of the performance characteristics of a product and determination of a specific chemical molecule.

Instrumentation

The process of gelatinization is well documented (Paton 1986), having been studied with pasting apparatus, microscopic examinations of granule swelling and loss of birefringence, light transmittance, and DSC (Collison 1968, Biliaderis et al 1980). Only the salient features of the process in oats will be presented here.

DSC has provided valuable insight into the order-disorder phenomena of granular starches (Biliaderis et al 1986). Data obtained from the DSC thermograms are the enthalpy of gelatinization and the various temperatures associated with the gelatinization phenomena (T_o , T_p and T_c) (Tester and Karkalas 1996) that correspond to the onset, peak, and conclusion gelatinization temperatures, respectively (Muenzing 1991). Low temperature endotherms in the DSC thermogram of oat starch have been attributed to the disorganization of starch crystallites and a higher temperature endotherm has been attributed to the melting of the amylose-lipid complexes (Fig. 1). The existence of a strong amylose-lipid complex is evident from the higher temperature endotherm of Fig. 1A. The reversibility of this complex formation and melting is shown by the re-run thermogram, whereas the lower temperature endotherm (associated with melting of starch crystallites and gelatinization) was irreversible. Despite the convenience and precision with which these measurements can be made, they are frequently of secondary importance to the pasting and rheological properties of the swollen starch granules.

Most research on gelatinization has been performed with several types of viscosity apparatus. Small changes in starch structure

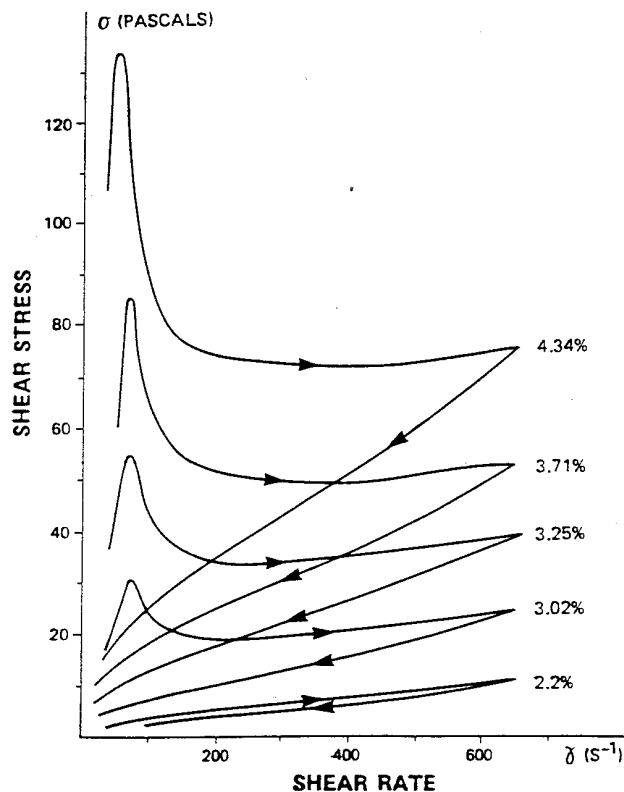


Fig. 2. Flow curves of oat starch pastes at different concentrations. Pasting conditions: high heating rate and low shear. Measuring temperature: 70°C. Reprinted from Doublier et al (1987).

result in large changes in viscosity of the slurry on heating, which gives thermoviscometric methods high sensitivity. Myrback and Gjorling (1945) calculated that the rupture of 0.10% of bonds in the starch molecule depressed the viscosity of the resultant slurry by 50%, whereas 7% of the linkages must be opened before the remaining dextrans fail to give a blue color with iodine (Myrback and Lundberg 1943). As the viscosity of a starch paste depends on the rate of shear, the material represents a non-Newtonian system. Starch pastes are also thixotropic, exhibiting gel characteristics when quiescent and fluid properties when a shearing force is applied (Shuey and Tipples 1982). Thus, the most rigorous analysis can only yield, at best, an apparent viscosity. Hence, to study the complex changes in starch pasting, it is essential to heat the paste under standardized conditions while continuously recording the changes.

Three instruments, the amylograph, the Ottawa Starch Viscometer (OSV), and the Rapid ViscoAnalyser (RVA) have been the main instruments used. The RVA is characterized by a faster and stronger mixing action than the OSV, which, in turn, has a stronger mixing action than the amylograph. These characteristics of the RVA lead to both more rapid peak development and more rapid breakdown than in the amylograph. This has important implications for the non-Newtonian gelatinizing-gelatinized starch systems discussed below (Figs. 2 and 3).

The viscograms produced by all three instruments have several common features. The original instrument, the amylograph, gives an amylogram consisting of four distinct phases: 1) pregelatinization, 2) the gelatinization peak, 3) drop-off, as stirring (and enzymes, if present) degrade the structure of the gelatinized starch, and 4) "setback", the increase in viscosity that follows cooling (Table III). Apart from a stronger mixing action, the OSV of Voisey et al (1977) had the advantages of small sample size, variable bowl speed, and electronic sensing and recording of results. Its method of heating is based on a boiling water bath, which has a number of disadvantages, however it produces viscograms similar to the those of the amylograph.

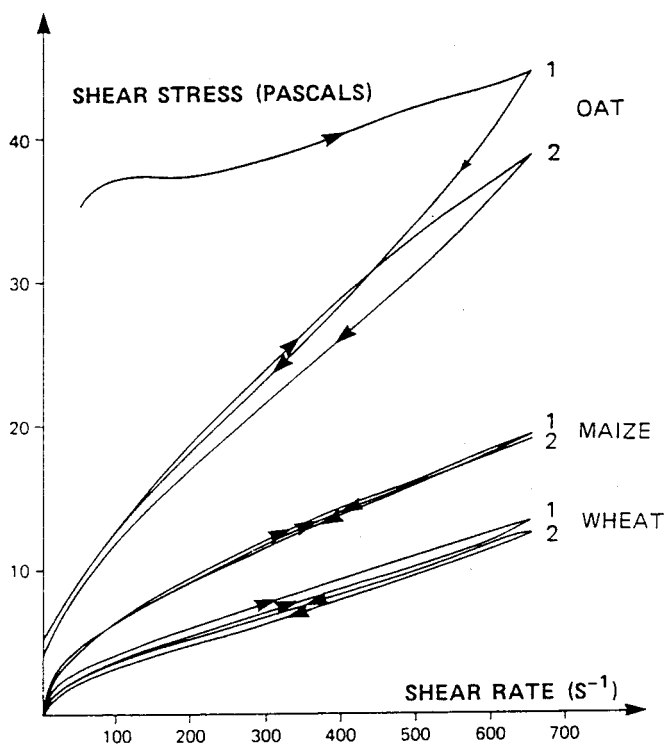


Fig. 3. Comparison of flow curves of oat, maize, and wheat starch pastes. Concentration: 3.4%. Pasting conditions: high heating rate and low shear. 1 = first run, 2 = second run. Reprinted from Doublier et al (1987).

The RVA (Ross et al 1987) has several substantial advantages over the amylograph (Walker et al 1988; Deffenbaugh and Walker 1988, 1989). These include small sample size, ability to set temperature profiles, and ability to report to computers. Results are commonly reported in Rapid Viscoanalyser units (RVU) which are approximately equal to $cP \times 10$, but may also be reported in cP. However, use of the latter method of reporting may give the incorrect impression that the measurement is an absolute viscosity. The viscogram consists of the high-speed mixing phase, a gelatinization peak, and drop-off as stirring (and enzymes, if present) degrade starch to less viscous products, as with an amylogram. Measurements include peak viscosity, peak area, time-to-peak, drop-off, and final viscosity, but there is only a short pregelatinization phase (Fig. 4) as compared to an amylograph. This shorter period reduces the opportunity for enzymic activity during the test. Care must be exercised in the use of temperature data from the RVA to allow for the lag time between the heated block temperature and the temperature of the sample (Hazelton and Walker 1996). A cooling phase following gelatinization allows the determination of the degree of setback.

The RVA differs from the amylograph in two important characteristics: a more rapid rate of heating and a stronger mixing action. Nevertheless, when the heating rate was controlled to 1.5°C/min, the results obtained on an RVA (using wheat meal) were similar to those obtained on the amylograph, with correlation coefficients of the order of 0.90 (Deffenbaugh and Walker 1988, 1989), as was also found with the OSV (Voisey et al 1977).

Starch Isolation

Much of the published data on oat starch has been obtained on isolated starch (Lim et al 1992) which requires a difficult and time-consuming procedure, even when employed on a laboratory scale. For example, oat starch can be fractionated by a neutral steeping process in the presence of mercuric chloride at low temperatures (Banks and Greenwood 1967b). Starch was extracted from the softened grain following maceration, fiber was removed without starch loss by careful screening of the crude product, while contaminating protein was removed by repeated sedimentation in water. Final traces of protein were coagulated by shaking an aqueous suspension of the starch in toluene. Advantages claimed for this approach were minimal degradation and chemical modification of the isolated starch. In other instances, oat starch has been isolated from ground groats using aqueous sodium carbonate (pH 10)

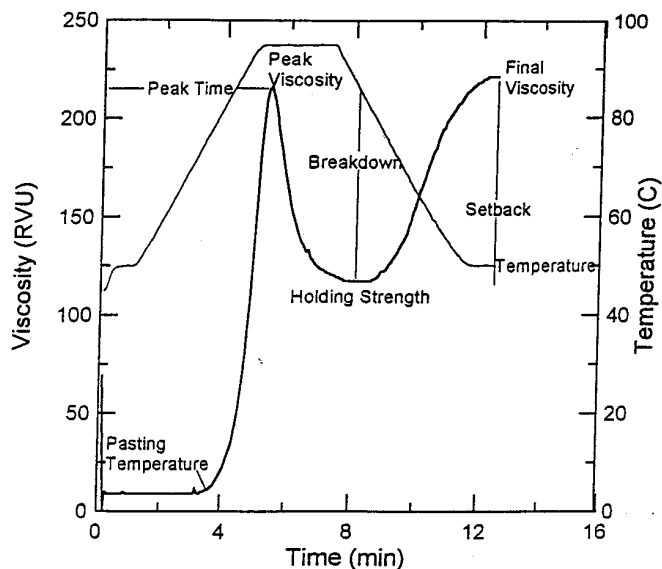


Fig. 4. Typical Rapid ViscoAnalyser pasting curve identifying characteristic features.

at 45°C (Doublie et al 1987). Oat starch isolated by the latter procedure contained 0.5% protein and 0.3% free lipid. The internal lipids in oat starches extracted with water and dilute alkali (Liukkonen and Laakso 1992) were practically identical, although starch obtained by the alkali method contained 21% less nonstarch lipids as total fatty acids, 63% less Kjeldahl N with a low level of nonstarch free fatty acids. The authors concluded that isolation of starch under alkaline conditions both reduces the content of nonstarch lipids and maintains a better composition in the residual starch lipids.

Recent investigations (Glennie-Holmes et al 1992) demonstrated the value of RVA measurements in the study of "green" groats in which no attempt was made to isolate the starch component so that pasting properties of the whole groat could be related to consumer acceptance. The typical rapid viscochrom is characterized by a relatively small initial peak due to gelatinization (peak viscosity), a small drop in viscosity due to mechanical damage (trough), followed by a substantial increase in viscosity on cooling. It is this latter increase, referred to as the setback, that characterizes both the amylograms (MacArthur and D'Appolonia 1979, Mua and Jackson 1995) and the viscochroms of oats.

Characteristics

In pasting behavior, oat starch was characterized with the amylograph by MacMasters et al (1947) as being very similar to that of maize. Paton (1977) found some differences in that cooked granules of oat starch appeared more shear-sensitive than those of corn, wheat, or rice starches, and when subjected to cooling, the hot starch paste viscosity increased rapidly in the 70–80°C range (Paton 1979). The cooled gels were clearer, less firm, more elastic, more adhesive, and less susceptible to retrogradation than those of other cereal starches (Paton 1977). Despite these differences, the generally accepted view was that oat starches differed little from other cereal starches until Paton (1979), using the OSV rather than the Brabender Amylograph, showed distinct differences from other cereals in the pasting of oat starches. Thus, oat starch pastes examined with the OSV developed unusually high initial setback viscosities (high hot paste consistency) within the first 30 sec of cooling, and a dramatic consistency increase on further cooling when compared to similar paste concentrations of corn and wheat starches (Paton 1977, 1979). Under greater shearing power and more rapid temperature changes, it was confirmed that oat starch had greater susceptibility to shear forces and greater increase in viscosity on cooling. Both these factors have relevance to the processors of oats for human-food use (Hoover and Vasanthan 1994b), as retention time in a typical vertical-column groat steamer is ~12–15 min (Paton 1986), whereas an amylograph run takes over 40 min. When cooked pastes were cooled from 95 to 70–80°C, they developed almost all of the consistency that they displayed at a final cooled temperature of 30°C. The cooled, rested gels were clearer than wheat or corn starch gels, were semirigid, and did not severely retrograde when stored at 5°C for up to two weeks (Paton 1987). Similar high setbacks have been found (Glennie-Holmes et al 1992) with the RVA on green groats.

Doublie et al (1987) compared the swelling power and solubility at 96°C of oat, corn, and wheat starches pasted under condi-

tions of low shear and either high or low heating rates. Whereas corn and wheat exhibited variability in both parameters according to the preparation procedure, oat starch was much less sensitive and showed much higher swelling power and solubility. The solubility of the oat starch molecules is increased markedly between 90 and 95°C. Heating to 95°C also induces considerable changes in the microstructure of oat starch pastes (Autio 1990), most of the granules being disintegrated. During cooling, the major starch component, amylopectin, forms a dense network structure (Virtanen et al 1993). Others have also found that oat starch granules swelled more and, therefore, were more deformable than wheat or maize starches (Gudmundsson and Eliasson 1989, Hoover and Vasanthan 1992). The deformability of starch granules affected the rigidity of starch gels; less swollen starch particles giving rise to more rigid gels. Both the rigidity and elasticity of oat and barley gels were greatly dependent on the preceding heating conditions (Autio 1990). Flow curves of shear stress versus shear rate for oat starch pastes are shown in Fig. 2 (Doublie et al 1987). It is evident that at a concentration >2%, oat starch displays strong thixotropic behavior that increases with starch concentration. Figure 3 compares flow curves of oat, wheat, and maize starches pasted by the high heating rate, low shear condition. There are marked differences between the three starches, with maize and wheat showing pseudoplastic flow. For oat starch, thixotropic flow is still apparent in the second run, although most of the structure of the paste has been destroyed in the first run. On the other hand, the first and second runs were very similar for both maize and wheat starches. In summary, comparison of the three starches indicated that the structural network of hot oat starch pastes was stronger than that of either wheat or corn when assessed at the same concentration. Furthermore, the stronger internal structural network of the hot oat starch pastes is magnified on cooling.

Gelatinization parameters for oat starch are similar to those of rye starch (Gudmundsson and Eliasson 1991) but differ from those for other cereals. The gelatinization temperature where optical birefringence disappears, indicating a loss of crystallinity, lies between 57 and 62°C for native oat starch (Paton 1987, Gudmundsson and Eliasson 1989, Tester and Karkalas 1996), although a somewhat lower value of 53–59°C has also been reported (Lineback 1984). The differences may be varietal or, alternatively, they may reflect the method used to determine the value. Nevertheless, Hartunian-Sowa and White (1992) reported that gelatinization onset differed significantly among starch types (varieties), ranging from 55.5 to 62.4°C, and was positively correlated with amylose ($r = 0.97$) and starch-lipid ($r = 0.92$) contents ($P < 0.01$) (Wang and White 1994c). Their results support the former view that the variation is a result of structural differences among starches from different oat varieties. Typical gelatinization enthalpies in J/g of dry starch were: wheat 11–20, maize 18.0, waxy maize 19.7, high-amylose maize 31.8, rice 10–14, and barley 10.2–10.5 (Paton 1987, Tester and Morrison 1990, Lauro et al 1993, Kent and Evers 1994, Tester and Karkalas 1996). The reported values for oat starch were somewhat lower at 8–12 J/g of dry starch (Paton 1986, Gudmundsson and Eliasson 1989, Hoover and Vasanthan 1994a, Wang and White 1994c, Tester and Karkalas 1996). These data suggest

TABLE III
Pasting Data from Oat Amylograms

Sample	Pasting Temp (°C)	Peak Height (BU)	Hold (BU)	Final Viscosity (BU)	Setback (BU)	Reference
3 cultivars	81–83.5	760–855		870–1,130		MacArthur and D'Appolonia 1979 ^a
Commercial cultivars	83	390	280	790		Mua and Jackson 1995 ^b
Hinoat		455	85	245		Paton 1981 ^c
3 U.S. cultivars	83.6–93.0	155–310	145–295	285–470	105–240	Wang and White 1994c ^d

^a Pasting conditions: 95°C for 30 min.

^b Pasting conditions: 95°C for 30 min, then cooled to 85°C (35 g, dry basis in 500 mL of water).

^c Pasting conditions: Holding time at 97°C, 30 min then cooled to 25°C (500 g, 9% dry basis).

^d Pasting conditions: 30–95°C at the rate of 1.5°C/min, maintained at 95°C for 30 min (6% w/w dry basis).

less order in the crystalline structure of oat starches than in other cereal starches. Native oat starch had a relatively low value of recrystallization enthalpy when compared to other native starches. The oat starch granules, in addition to different morphology, differed from barley and wheat starch in showing more leaching of amylopectin and less amylose in water dispersions (Doublier et al 1987, Mua and Jackson 1995), as well as larger amylose-lipid dissociation enthalpy and lower amylopectin recrystallization tendency (Shamekh et al 1994). Oat starches also showed a higher value for the transition enthalpy for dissociation of the amylose-lipid complex compared to the values for other cereals (Paton 1987, Gudmundsson and Eliasson 1989, Tester and Morrison 1992, Wang and White 1994c) supporting the presence of more complexed lipids in oat starch relative to the starch of other cereals.

Oat starches exhibit a lower percentage of retrogradation (%*r*) than other cereal starches including corn and maize (Gudmundsson and Eliasson 1989, Shamekh et al 1994, Wang and White 1994c). The %*r* was negatively correlated with amylopectin content ($r = -0.84$, $P < 0.01$) (Wang and White 1994c). Evidently, this property is related to the greater amount of internally bound lipids in oat starch, as lipids are one of the major factors in lowering the retrogradation (Gudmundsson and Eliasson 1989, Wang and White 1994c). Hence, the high lipid content in oat starches may play a role in decreasing both the rate and the amount of starch retrogradation inasmuch as the oat starches retrograded only 32–40% over a 28-day storage period (Hartunian-Sowa and White 1992). However, based on the results of Gudmundsson and Eliasson (1989) comparing various native and defatted oat starches other factors may also be operative.

Oat starch also differs from wheat starch in showing higher peak viscosity and setback, low gel rigidity, greater susceptibility toward acid hydrolysis, greater resistance to α -amylase action and a higher freeze-thaw stability.

Factors Affecting Pasting Properties

Pasting characteristics are influenced by a number of factors including starch granule size, starch composition, processing ingredients, and chemical pretreatment. Oat starch granules apparently do not exhibit the bimodal size distribution noted for some grains where large granules have been referred to as A-type and small (<10 μm) granules as B-type (following, among others, McDonald and Stark 1988). Nonetheless, questions relating to particle size (Meredith 1980, Bechtel et al 1990) may still be an issue. It is possible that there are differences in the temperatures of gelatinization and amylose contents depending on granule size.

Protein and lipid contents of starch exert a significant influence on the pasting properties. For example, the intrinsic viscosity of oat starch amyloses was negatively correlated with the protein content of the parent flour (MacArthur and D'Appolonia 1979). On the other hand, the intrinsic viscosity of the starch amylopectins decreased as the flour protein decreased. Amylose and starch lipid contents were positively correlated with the onset of gelatinization of oat starches (Hartunian-Sowa and White 1992, Wang and White 1994c). The long branch chain amylopectin and the intermediate molecular size amylose produced the greatest synergistic effect on viscosity (Jane and Chen 1992). Besides amylose and amylopectin, other components in starches may also have important roles in determining pasting properties. For instance, Hoover and Senanayake (1996) demonstrated significant differences in pasting properties between two oat cultivars despite similar amylose and total lipid contents. On the other hand, lipid removal from oat starch resulted in a marked reduction of swelling power and an increase in solubility (Doublier et al 1987, Shamekh et al 1994). The swelling power, solubility and nature of solubles of the defatted oat starch were quite similar to those of corn and wheat starches. An important distinction can be made however between the behavior of oat starch and other starches. In native oat starch granules, swelling proceeds with the coleaching

of amylose and amylopectin throughout the pasting process (Doublier et al 1987), whereas during heating of maize, wheat, and barley starches, amylose is solubilized first, and only after all the amylose has been leached from the granule will part of the amylopectin be leached, provided that a strong enough shear force is applied (Doublier et al 1987). Lipid removal from the oat starch evidently allowed amylose to leach selectively from the oat granules.

Figure 1B shows the effect of removing the internally bound starch lipids on the DSC thermogram. The main feature of both the initial and re-run thermograms is the absence of an endotherm associated with the starch-lipid complex. A comparison of the pasting curves for lipid-free and native oat starch (Doublier et al 1987) showed marked differences in the cooling portion of the pasting curve; the lipid-free oat starch more closely resembled corn and wheat starches. Similar results have been reported by Hoover and Vasanthan (1992) and Gibiński et al (1993), who noted that lipid removal from oat starch decreased the swelling factor, peak viscosity, set-back, gelatinization temperatures, freeze-thaw stability, and paste clarity ($\text{pH} > 4.0$), while increasing the thermal stability, amylose leaching, enthalpy of gelatinization, susceptibility toward α -amylase, and paste clarity ($\text{pH} < 4.0$). The results of such studies distinguish intrinsic differences in the granules rather than differences in the interactions between starch and lipids (mainly nonstarch) during pasting. While reconstitution experiments can be used to examine the effects of nonstarch lipids of differing quality on the pasting characteristics of starch with differing intrinsic characteristics, oat starch granules contain significant amounts of lipid, unlike other cereals; removal of these lipids without altering the granule is problematical if not impossible. Thus, the actual mechanism of the involvement of internally bound lipids on the pasting and rheology of oat starch pastes and gels remains unexplained at present. Nevertheless, starch-bound lipids seem to play quite a different role in oat starch than in wheat and corn. The spatial location of lipids within oat starch granules in relation to the disposition of amylose and amylopectin may be important in governing the leaching of amylose and amylopectin from the oat starch granule (Doublier et al 1987).

A number of processing ingredients can affect pasting properties. The main factors to consider here are additions of sugars and salts. Sugars, especially sucrose, have had marked effects on the gelatinization properties (Bean and Yamazaki 1976) of various starches. The RVA has been used to demonstrate the effect of pH or the presence of various salts on pasting characteristics of starch (Walker et al 1988). When sucrose was added to samples of acceptable and unacceptable cultivars of oats, the RVA curves were more widely differentiated and emphasized the differences between cultivars (Glennie Holmes et al 1992). Thus, it is suggested that additions of sucrose in the RVA testing of progeny from a breeding program could improve the differentiation between cultivars acceptable and not acceptable for human food use. Acid modification of oat starch granules caused substantial changes in the pasting behavior; viscosity decreased dramatically, amylopectin degraded to smaller molecules, and a more elastic gel structure based on amylose was formed (Virtanen et al 1993).

SUGGESTIONS FOR FURTHER STUDY

A number of techniques deserve closer investigation. For example, DSC, ^{13}C -NMR spectrometry, and X-ray diffraction have been used to examine wheat, maize, potato, and tapioca starches following defined thermal pretreatments to provide samples exhibiting degrees of structure loss (Cooke and Gidley 1992). As ^{13}C -NMR spectrometry is a short-distance range probe, detected order by this technique corresponds to double-helix content in contrast to X-ray diffraction, which detects only those double helices that are packed in regular arrays. The data reported from DSC studies as applied to oat starch has great potential.

Published studies on the pasting behavior of oats have been confined to few cultivars, with little consideration of the effects of environment or environment by genotype interactions. For example, the composition of oats grown in Australia differ substantially from those from the Northern Hemisphere. Characteristically, Australian oats are higher in lipid and lower in protein than those from Canada (V. D. Burrows, *personal communication*). It should be remembered that oats are grown in Australia under conditions of rising temperatures, increasing day-length but falling moisture, in contrast to most other oat-growing countries, where harvest is approached with falling temperatures, shortening day-length, and stable if not increasing moisture availability. The effects of these differences in agronomic practice on oat quality need to be determined if breeders and processors are to be guided in selection of progeny or parcels of grain suitable for human food use.

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