Differential Scanning Calorimetry of Oat Starch Pastes[1]

DAVID PATON[2]

ABSTRACT

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Oat starch (variety Sentinel) was examined by differential scanning calorimetry over a range of moisture contents. Two endotherms were observed, one around 66° C and a second at 102–104° C. Washing the granules at room temperature with *n*-propanol-water (3:1, v/v) did not alter the thermogram, whereas refluxing in the same solvent reduced the endotherm at 66° C and completely eliminated the one at 102–104° C. This result is evidence for the existence of amylose-lipid complexation in oat starch. Treatment of the data according to the Flory-Huggins equations showed that oat starch exhibits a higher temperature of melting of most perfect starch crystallites (T_{mo}) and a slightly lower enthalpy of fusion of the repeating glucose unit (ΔH_u) when compared with other cereal starches. The amylose-lipid endotherm exhibits a slightly lower value for T_{mo} but a higher value for ΔH_u when compared to corresponding data for other starches. Storage studies conducted with 30% w/w oat starch pastes showed that the rate of retrogradation was reduced by around 50% and that this was a function of the bound lipid. These results are discussed in terms of providing further explanation for previously observed anomalies in oat starch paste and gel behavior.

Oat starch has been reported to display anomalous cooked paste and cooled gel behavior when compared to other cereal starches of normal (24–27%) amylose content (Paton 1977, 1979). In particular, when cooked pastes are cooled from 95° C to 70–80° C, they develop almost all of the consistency that they display at a final cooled temperature of 30° C. The cooled, rested gels are clearer than wheat or corn starch gels, are semi-rigid, and do not severely retrograde when stored at 5° C for up to two weeks.

Previously published data on the amylose content of oat starches suggest values in the 16–18% range based upon iodine binding following 85% methanol treatment by Soxhlet extraction (Paton 1979). Morrison and Laignelet (1983) showed that the Soxhlet treatment is inappropriate for starches whose total lipid content, determined by chemical analysis, exceeds that which can be removed by the Soxhlet procedure. Morrison et al (1984) subsequently examined numerous wheat, maize, barley, and rice cultivars and clearly showed that there is a considerable discrepancy between the true and apparent amylose content. These authors presented some limited information on oat starches of Canadian origin, illustrating that of all of the cereal starches, oat displays the highest lipid content and the largest discrepancy in values obtained for true and apparent amylose content. Recently, Doublier et al (1986) confirmed the results of Morrison et al (1984) and showed that between 1.2 and 1.5%, w/w, of lipids are present within oat starch granules.

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[2]Food Research Centre, Agriculture Canada, Research Branch, Ottawa, Ontario K1A 0C6.

The technique of differential scanning calorimetry (DSC) has in recent years been extensively applied to the study of starch/water systems. Several comprehensive reviews on this topic have been presented by Biliaderis (1983), Donovan (1979), Biliaderis et al (1980), and Hoseney (1984). Of particular interest has been the widespread use of this technique to examine the thermal events associated with the swelling of starch granules in aqueous environments and the relationship of these events to starch gelatinization.

A limited number of studies have been published on the use of DSC to examine the thermal characteristics of starch gels as a result of storage over time. Nakazawa and co-workers (1985) studied retrogradation of potato starch. Their results showed that 30% w/w starch dispersions, which had been precooked in the calorimeter pans and subsequently subjected to storage at 5° C, display a reappearance of an endotherm in the same temperature region as the original endotherm for granular potato starch. However, this "second-run" endotherm is much broader in temperature range than the original endotherm and exhibits maximum heat of transition values approximately 60–80% of the original. Zeleznak and Hoseney (1986) have shown that retrogradation of wheat starch gels is controlled by the amount of water present during the aging process and is independent of the amount of water involved in the gelatinization step. The starch in bread that had been baked with various antistaling agents also exhibited a similar behavior. These results indicate that antistaling agents do not operate by a mechanism that alters moisture availability to the starch during the baking process, thus affecting retrogradation.

Miles et al (1985) measured the rate of development of an endothermic (M1 type) peak and also the rate of change in shear modulus (G′) of 20% solids gels made from smooth-seeded, leafless pea starch. When the shear modulus of the starch gel was compared with that of a heated and cooled solution of the equivalent amount of solubilized amylose (4.2%, w/w), G′ for the starch gel continued to increase slowly with time, whereas G′ for the amylose gel remained constant after two days of storage. Over a seven-day storage period, the development of the M1 type endotherm also increased. These data also point to a major role for amylopectin in the starch retrogradation process.

The purpose of the present study was to examine the thermal transitions occurring in oat starch, to compare these data to previously published data on other cereal starches, and further to seek a basis for the explanation of anomalies in oat starch paste behavior.

MATERIALS AND METHODS

Oat starch was prepared by mild sodium carbonate extraction of ground clean oat groats as previously described (Paton 1977). Waxy maize and wheat starches were obtained respectively from Nacan Products and Ogilvie Mills, Montreal, Québec, Canada. Surface-adhering lipid was removed from oat starch by copious washing of the starch in *n*-propanol/water (3:1) at room temperature, followed by acetone treatment and air-drying.

Oat starch was defatted by refluxing a unit amount of starch in a minimum of 20 volumes of a 3:1 mixture of *n*-propanol and water under a nitrogen stream for 1 hr. Following a second exchange of solvent, the starch was recovered by filtration, washing in acetone, and air-drying (Morrison and Coventry 1985).

In certain instances, the previously bound oat starch lipids were readsorbed onto the extracted starch by combining the damp filtered starch with all of the extract in a large round bottom flask and rotary evaporating the mixture to dryness at 50° C under 730 mm of vacuum.

Differential scanning calorimetry (DSC) of starches was performed using a Dupont 910 cell base fitted with a pressure cell and a Dupont 1090 analyzer. An operating pressure of 1,400 kPa of N_2 was used to eliminate the problem of moisture loss due to pan failure at temperatures above 120° C. Starch was mixed with sufficient water in sealed vials to give the appropriate volume fraction of water and stored at room temperature overnight. Sufficient moisture-tempered starch equivalent to 3–5 mg (dmb) was weighed into a coated DSC pan, tamped down with a fine Teflon-coated rod, and sealed with a pan lid. A second pan was sealed containing 3–5 mg of pure silica sand as a reference. Starch samples were analyzed at a heating rate of 10° C/min over the temperature range 40–140° C. The onset temperature of gelatinization, T_o, the temperature of the endothermic peak, T_p, and the final endotherm temperature, T_m, were noted from the chart. The area under each endothermic peak, based upon drawing baseline tangents to the peak, was computed by the instrument software to give an enthalpy value (ΔH) in joules per gram (J/g). M1 and M2 were used to designate the endotherms associated with the melting of starch crystallites and the melting of an amylose-lipid complex, respectively.

In calculating the volume fraction of water (ν_i), the densities of water and starch were taken as 1.00 and 1.55, respectively (Lelievre 1973). The volume fraction of water is taken as the total volume of water divided by the total volume of water plus starch. T_m, the upper temperature limit for each endotherm, was expressed in ° K. The variation of T_m with the volume fraction (ν_i) was obtained by applying the Flory-Huggins equation (1953):

$$\frac{1}{T_m} - \frac{1}{T_{mo}} = \frac{R}{\Delta H_\mu} \cdot \frac{V_\mu}{V_i} (\nu_i - X_i \nu_i^2) \qquad (1)$$

where R = gas constant, ΔH_μ = enthalpy of fusion per repeating glucose unit, V_μ/V_i = ratio of the molar volume of the repeating unit to the molar volume of the diluent (water), X_i = Flory-Huggins polymer diluent interaction parameter, T_{mo} = melting point of the most perfect crystallites (° K). An estimate of ΔH_μ was obtained by arranging equation 1 to give:

$$\frac{\frac{1}{T_m} - \frac{1}{T_{mo}}}{\nu_i} = \frac{R}{\Delta H_\mu} \cdot \frac{V_\mu}{V_i} \left(1 - \frac{BV_i}{RT_m} \cdot \nu_i\right) \qquad (2)$$

and plotting the left-hand side expression as a function of ν_i/T_m. In order to compare data for oat starch with previously published data for other starches, results are reported at different values for ν_i. In applying the Flory-Huggins equation, the assumption is made that the interactive parameter $X_i = 0$. In point of fact, Maurice et al (1985) and Biliaderis et al (1986) stressed that the "melting" of the starch-water system is a nonequilibrium process and as such applying the Flory-Huggins equation presents some difficulty in interpreting the findings. While this limitation is recognized, the Flory-Huggins approach is still considered useful within the context of making relative comparisons of the behavior of different starches examined under the same analytical conditions.

Storage studies of starch pastes were conducted by heating replicate DSC pans containing starch at a $\nu_i = 0.78$ (30%, w/w solids), at a heating rate of 10° C/min, from 40 to 140° C, cooling to 20° C, removing the pan from the calorimeter, and storing in a refrigerator at 5° C for up to 30 days. Sufficient samples were processed to allow for duplicate analysis at each storage period interval. After each storage period, samples were allowed to come to room temperature prior to rerunning in the calorimeter from 40 to 140° C as already described. The reappearance of a low-temperature endotherm and the size of its enthalpy value were noted and calculated. This enthalpy value was expressed as a percentage of the enthalpy value of the original lower temperature endotherm (M1) for the starch, and this value was then plotted as a function of the number of storage days at 5° C.

RESULTS AND DISCUSSION

Washing oat starch granules with *n*-propanol/water (3:1) at room temperature did not result in any alternation of the thermogram of the starch. Refluxing the starch in the same solvent resulted in a reduction of the enthalpy value (ΔH) associated with

the low-temperature endotherm M1 and a complete elimination of the higher temperature endotherm M2 (Table I). The reduced value of ΔH for the M1 endotherm is likely as a result of partial gelatinization of the starch granules during refluxing in the solvent. Lipids associated with starch granules are of two types: those adhering to the granule surface and considered to arise from residual contamination of the starch by endospermic lipids during the starch isolation procedure, and those which are within the granule itself, either imbedded in the starch matrix or in the form of an amylose-lipid complex. Soxhlet extraction procedures have been universally employed to defat starches prior to further analysis. Recently, Morrison and Coventry (1985) critically appraised the use of a variety of water-miscible aliphatic alcohols as suitable extractants for starch-bound lipids. They concluded that, in each case examined, water was required to be present to cause the granule to swell and to at least partially loose crystallinity if internally bound lipids were to be efficiently removed. Lipid yields were found to decrease if the proportions of alcohol and water were not kept within well-defined limits. Further, each solvent system required a slightly different molar volume of solvent per gram of starch. It was also necessary to reflux the starch at temperatures close to 100° C in order to obtain maximum extraction of bound lipids. It is therefore reasonable to conclude that refluxing oat starch in 20 volumes/g of *n*-propanol/water (3:1) at 100° C would result in partial loss of granular structure and a reduction in the value of ΔH for the M1 thermal transition.

Figure 1 illustrates the effect of running the heated samples a second time. Although the M1 endotherm is eliminated, the second (M2) endotherm is still present, and in fact the enthalpy is increased. Further multiple reruns did not increase this enthalpy value. The results of Table I and Figure 1 clearly demonstrate in oat starch the presence of the melting of an amylose-lipid complex. Similar types of complexes have previously been demonstrated for other starches (Kugimiya and Donovan 1981, Biliaderis et al 1986). Further, the increase in the enthalpy value of the M2 endotherm is consistent with previously reported data by Kugimiya and Donovan (1981), which showed that the maximum complexation of lysolecithin with amylose could only be attained if the mixture were heated a second time. This increase in enthalpy was believed to be associated with the time required for proper dispersibility of the lipid in the aqueous starch phase during the conditions of the test. Oat starch has been examined in this laboratory under lysolecithin-saturating conditions, and the maximum enthalpy associated with this reaction was found to be approximately 9.0 J/g. Because Figure 1 shows that the enthalpy value for the M2 endotherm upon rerunning is 4.34 J/g, it may be calculated that almost 50% of the oat starch amylose is complexed with the internally bound starch lipids when an aqueous mixture of oat starch is heated to beyond the boiling point of water.

As the volume fraction of water (ν_i) in a starch-water mixture varies, so too does the value for T_m. When T_m is expressed in °K and its reciprocal is plotted as a function of ν_i, the relationship illustrated in Figure 2 results. As suggested by the application of the Flory-Huggins equation, extrapolation of the curve to the zero value for ν_i gives an intercept that allows the calculation of a value for T_{mo}, the melting point of the most perfect crystallites. The deviation of the M1 endotherm data from linearity above a value for $\nu_i = 0.70$ is similar to that observed by Biliaderis and co-workers (1986) for certain rice starches. These authors demonstrated that both T_p and T_c (T_m) are dependent on moisture content. As ν_i increases up to a value of 0.7, both T_p and T_c (T_m) decrease but individually assume a constant value for values of $\nu_i > 0.7$. This causes the plot of $1/T_m$ against ν_i for the M1 endotherm to deviate from linearity. The enthalpy of fusion of the repeating polymer unit may be deduced through further manipulation of the data of Figure 2 by plotting the left hand side of equation 2 against ν_i/T_m (Fig. 3). Extrapoliation to $\nu_i/T_m = 0$ allows the limit value to be inserted into equation 2 and ΔH_μ to be calculated. Table II compares these results with results previously obtained for other starches. Also included in this table are the data for the second endotherm (M2) associated with the amylose-lipid complex. For the first endotherm (M1), oat starch shows a higher T_{mo} and lower ΔH_μ value than those found previously for other starches, except for the values for wheat published by Donovan et al (1983). It might be inferred that oat starch is more amorphous or less ordered, but this does not seem to be supported by X-ray diffraction data, which shows that oat and wheat starches have similar spectra. This does not preclude some other type of noncrystalline granule modification from existing as Doublier et al (1986) showed that as oat starch swells, amylose and amylopectin are co-leached, whereas amylose is preferentially leached in most

TABLE I
The Effect of Organic Solvent Treatment on Thermal Transitions in Oat Starch[a,b]

	M1		M2	
Treatment	**ΔH(J/g)a**	**T_p(°C)**	**ΔH(J/g)**	**T_p(°C)**
None				
First run	9.13 ± 0.4	66.8 ± 0.2	3.57 ± 0.3	102.3 ± 0.5
Rerun	...	...	4.34 ± 0.4	104.3 ± 0.2
Surface washed	9.13 ± 0.3	66.6 ± 0.1	3.60 ± 0.4	102.5 ± 0.2
Refluxed	2.37 ± 0.3	65.2 ± 0.2	...	...

[a] All samples examined at $\nu_i = 0.63$.
[b] Average of two determinations.

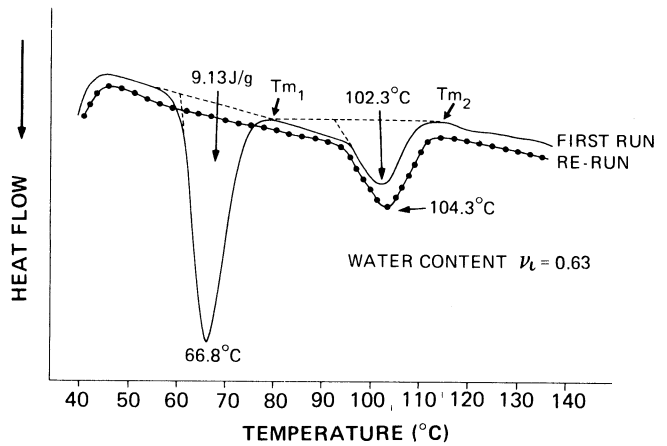

Fig. 1. Differential scanning calorimetry thermograms of native oat starch (variety Sentinel) showing the amylose-lipid complex.

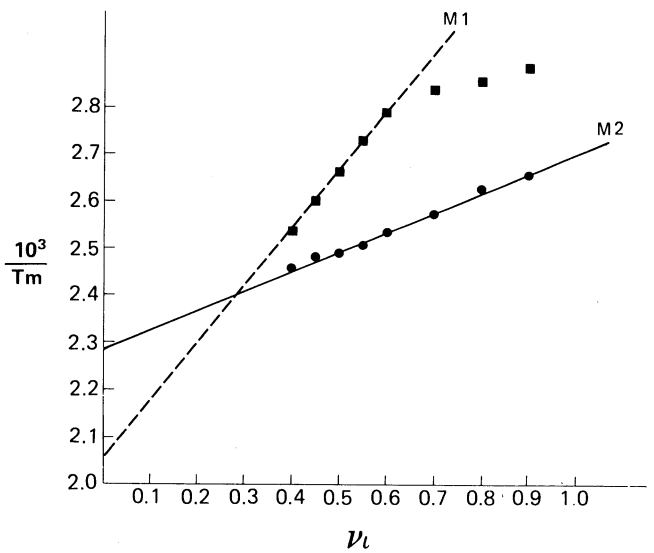

Fig. 2. Flory-Huggins plots of the reciprocal melting temperature, T_m (° K) as a function of the volume fraction of water (ν_i) for the first (M1) and second (M2) transitions of native oat starch.

other cereal starches. The enthalpy of fusion for the higher order oat endotherm (M2) is greater than those of the other starches in spite of the temperature of melting of the most perfect of these crystallites being just slightly lower. This higher enthalpy value suggests a stronger amylose lipid complex. The lower T_{mo} could be a function of the nature and composition of the complex, being dependent upon the composition and binding characteristics of the lipids trapped within the oat starch granule.

Because the thermograms shown in Figure 1 represent the melting or dissociation of crystalline domains, the ordered structures associated with an amylose-lipid complex must be formed at a temperature lower than the melting temperature. It has also been observed that ΔH values of waxy rice starches are generally higher than those of their nonwaxy counterparts (Biliaderis et al 1986). It is possible that the lower values for nonwaxy starches are a result of the occurrence of two competing events—namely the endothermic melting of starch crystallites related to dissociation of the granule structure and the exothermic formation of an amylose-lipid crystalline state. Thus the observed thermogram shows a net endothermic heat flow. It is clear that the ΔH value (9.0–9.5 J/g) usually found for oat starch is considerably lower than typical values found for wheat (10.5–12.0 J/g), rice (10.2–13.6 J/g), and waxy maize (20.1–20.8 J/g). Indeed, Biliaderis et al (1986) showed that ΔH values for rice starches vary considerably depending upon the bound lipid content of the starch. The highest lipid content (1.65%, w/w) produced the lowest first transition endotherm (11.5 J/g) at a $\nu_i = 0.61$. Table III shows that oat starch produces an even lower value of ΔH (9.1 J/g) for the first endotherm (M1). A higher second endotherm (M2) value (3.57 J/g) was found for oat starch compared to a previously published value of 3.20 for the high-lipid-containing rice variety IR 480-5-9 (Biliaderis et al 1986). Thus, although both the rice starch variety IR-480-5-9 and the oat starch (variety Sentinel) have approximately the same bound lipid content (1.5%, w/w), the influence this lipid has on the starch under a thermal environment in the presence of water appears quite different. Unfortunately, Biliaderis et al (1986) did not describe the paste characteristics of the rice varieties under study. It is not therefore possible here to compare the paste properties of oat and a high-lipid rice starch.

Wheat starch shows an M1 endotherm enthalpy quite similar to that of the high lipid rice starch. However, the magnitude of the M2 endotherm is considerably less and is more in accord with the lower lipid rice variety IR 5, which has 1.11% bound lipid. Wheat starch has been shown by Morrison and Coventry (1985) to contain approximately 0.7% bound lipids with an M1 enthalpy value of 11.2 J/g. Here again, the quantity and differing nature of bound starch lipids may help to explain these differences in amylose-lipid complexation.

In one experiment, the influence of extracting the bound oat starch lipids was examined and, without isolation and drying of either fraction, reabsorbing the lipids onto the starch matrix by rotary vacuum evaporation of the refluxed starch-*n*-propanol-water mixture. The results of examining duplicate runs of this product by DSC are shown in Table IV. The lack of good agreement in ΔH values for each transition between duplicate samples A and B is likely a function of the random fashion by which the extracted lipid is reabsorbed onto the partially disrupted starch matrix. It is immediately obvious that two lipid-related starch transitions occur in the reabsorbed samples compared with the native starch and that the highest temperature endotherm, M3, has the largest enthalpy value. Upon cooling and reheating, some readjustment in physical state takes place, with the M2 endotherm now having the larger ΔH value. It appears from this result that reabsorption of extracted lipid causes the initial formation of metal-stable states, which upon cooling and reheating assume a more stable state approaching that of the M2 transition of the native starch. This double-transition behavior of amylose-lipid complexes when lipid is deliberately added to starch is similar but not identical to what takes place when single lipid species, e.g., C12 and C16 fatty acids, are added to pure amylose (Biliaderis et al 1985). Complex formation, melting, and process reversibility are very dependent upon moisture content and on the annealing and cooling rates. The defatted oat starch-reabsorbed oat lipid system is much more complex than the amylose-lipid systems described by Biliaderis et al (1985). However, the bimodal behavior observed in the thermograms is similar. This is in marked contrast to the apparent uniformity of melting, formation, and remelting behavior observed for native oat starch, which contains a high level of internally bound lipids of varying species. It has not been possible to induce the pasting curve and paste properties of the native oat granular starch as a result of lipid reabsorption. In contrast, a lipid-reabsorbed oat starch paste has properties similar to those exhibited by a starch treated with mono- and diglycerides—namely a higher pasting temperature, lower pasting peak, and a marked reduction in cold paste viscosity.

The process of syneresis of starch gels is thought to result from the tendency of the polymer chains to reestablish their original thermodynamic crystalline state. As such, these chains ultimately lose their ability to hold water, and the gels "weep" or undergo

TABLE II
Comparative Data for Values of T_{m0} and ΔH_μ for the M1 and M2 Transitions of Selected Starches

	M1		M2	
Starch	T_{m0} (°C)	ΔH_μ(kJ/mole)	T_{m0} (°C)	ΔH_μ(kJ/mole)
Oat	214.0	39.0	164.0	117.0
Wheat	216.0	41.0	170.0	92.0[a]
	181.0	53.0	167.0	98.5[b]
Potato	166.0	58.0	...	...[a]
Maize	187.0	58.0	172.0	96.5[b]
Waxy maize	197.0	61.0	...	...[b]

[a] Donovan et al (1983).
[b] Donovan and Mapes (1980).

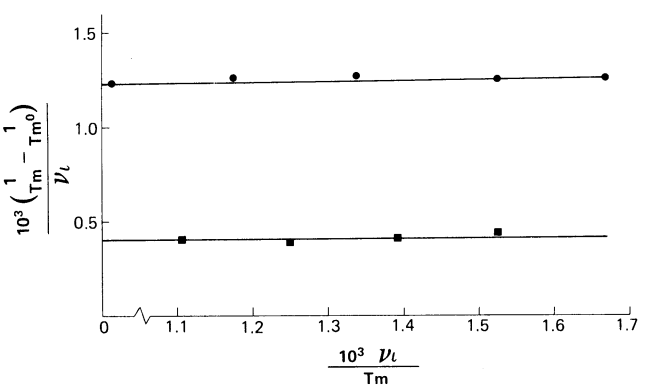

Fig. 3. Flory-Huggins plots used to calculate the value for ΔH_μ for the M1 and M2 transitions of native oat starch.

TABLE III
Comparative Differential Scanning Calorimetry Data for Oat, Rice, and Wheat Starch[a]

				Transition Enthalpy (ΔH, J/g)	
Sample	T_0	T_p	T_m	Starch	Amylose-Lipid Complex
Oat starch	61.1	66.8	82.0	9.13	3.57
Rice starch[b,d] (IR 480-5-9)	53.0	61.9	87.0	11.5	3.20
Wheat starch	58.7	64.2	87.0	11.2	1.95
Rice starch[c,d] (IR 5)	61.0	73.1	95.0	13.3	1.80

[a] All starches analyzed at $\nu_i = 0.63$.
[b] % Amylose = 28.7; % lipid = 1.65.
[c] % Amylose = 31.2; % lipid = 1.11.
[d] Biliaderis et al (1986).

TABLE IV
Effect of Reabsorbing Extracted Oat Lipids on the Thermal Behavior of Oat Starch[a]

	M1			M2			M3		
	T_0 (°C)	T_p(°C)	ΔH(J/g)	T_0 (°C)	T_p(°C)	ΔH(J/g)	T_0 (°C)	T_p(°C)	ΔH(J/g)
Sample A[b]									
First run	65.7	70.7	0.927	88.4	94.5	0.472	102.7	111.8	2.64
Rerun	...	...	...	87.3	98.9	4.02	113.7	117.6	0.22
Sample B[b]									
First run	65.0	72.3	1.42	86.5	95.4	0.877	103.7	114.8	3.55
Rerun	...	...	...	88.9	98.3	2.68	109.1	116.5	0.693
Native oat starch	61.0	66.1	10.0	87.9	100.5	3.52	...	...	...

[a] All samples analyzed at $\nu_i = 0.80$.
[b] A and B represent duplicate treatments of lipid add-back.

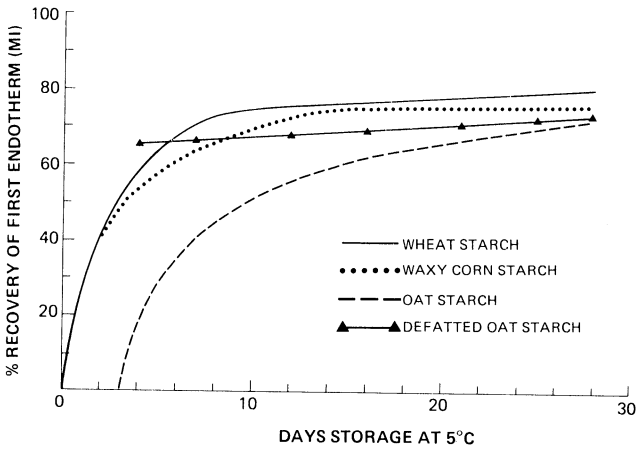

Fig. 4. Differential scanning calorimetry of cooked starch pastes ($\nu_i = 0.78$) as a function of the number of days aged at 5° C.

syneresis. Since the first noted endotherm of the DSC scan of a moistened granular starch is associated with the disorganization of the native crystalline structure, any substantial tendency of the cooked starch to reassume a crystalline state should result in the gradual reappearance of an endotherm upon examination of the sample by DSC. Figure 4 is a plot over a 30-day period of a reappearing endotherm. Although for each starch this endotherm does not reappear at precisely the same temperature as found for the native starch, it is convenient to present the results on the basis of the reappearing endotherm as a percentage of the enthalpy value displayed by the control starch in each case. Figure 4 indicates that a reestablishment of a crystalline states does indeed take place, although the enthalpy value reached for this endotherm does not exceed 80% of the value found for the native starches in each case. If the percentage recovery of the M1 type endotherm is plotted against the natural logarithm of the number of storage days for starch gels, a linear relationship exists with $r^2 = 0.88$ (wheat), 0.95 (waxy maize), and 0.98 (oat), respectively. It is interesting to note that waxy maize starch, which contains 1.0% amylose, behaves almost identically to wheat starch, which contains 27% amylose. This observation lends further strength to the hypothesis that starch granule crystallinity is more associated with amylopectin chains than with amylose chains. It also supports the contention of other workers that amylopectin is the operative starch fraction in the phenomenon of bread staling (Russell 1983a, Zeleznak and Hoseney 1986). Using DSC measurements on bread crumb, Russell (1983a) showed that the storage data could be fitted to an Avrami equation of the form $\phi = e^{-kt^n}$, where ϕ is the fraction of the total change in the measurement still to occur, n = Avrami exponent, and k = rate constant.

Applying the data of Figure 4 to an Avrami equation where $n = 1$, rate constants of approximately 2.8×10^{-1} and 1.25×10^{-1} per day were found for wheat and oat starches, respectively. It is interesting to note that Russell (1983b) showed that the addition of a monostearate to a bread dough caused the rate constant for staling to be reduced by 50%. The data shown here for oat starch suggest that the effect of the internally bound lipids upon the rate of retrogradation of oat starch is also around 50%. However, even this unusually high level of bound lipid (1.5%, w/w) is insufficient to prevent retrogradation, because it has been observed that 9% gels stored covered in a refrigerator begin to weep after 14 days. Thus, it appears that in practice starch gels will undergo syneresis at levels of polymer recrystallization considerably lower than is thermodynamically possible.

Oat starch gels prepared at a $\nu_i = 0.80$ exhibit a slower rate of recrystallization than is observed for wheat and waxy corn starches. After 10 days of storage, only a 50% recrystallization was observed for oat starch, whereas wheat and waxy maize had attained 70–75%. The interesting feature of Figure 4 is the result upon removal of bound lipid from the oat starch. Here, recrystallization was similar to wheat and waxy corn starches, indicating the important role that must be played by the internally bound starch lipids. Completely defatted oat starch has been reported to set up quickly into a very firm opaque gel in contrast to the native starch (Doublier et al 1986).

One remaining unresolved aspect is the location, nature, and role of the lipids bound within the oat starch granule. Unpublished preliminary data from this laboratory indicate considerable variability in lipid compositional data, which may be a function of the nature of the solution employed to remove protein during starch isolation. Notwithstanding these difficulties, and in light of the results presented here on attempted lipid add-back to defatted oat starch, the morphological location of these lipids is likely to be of significance in altering the behavior of swollen oat starch chains when these are cooled from a hot paste to ambient temperature.

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