Differential Scanning Calorimetry of Whole Grain Milled Rice and Milled Rice Flour[1]

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ABSTRACT

The thermal properties of whole grain milled rice and milled rice flour were investigated by differential scanning calorimetry. Thermal curves were obtained on representative long, medium, short, and very low amylose varieties over the temperature range of 20 to 110°C. All whole grain samples showed two endothermic transitions associated with starch gelatinization whereas comparable flour samples exhibited only one endotherm. The gelatinization temperatures for all long, medium, and short varieties decreased with decreasing grain length. Gelatinization onset temperatures for all samples were similar within each variety, but peak gelatinization temperatures were 13–17°C higher in the whole grain samples. Gelatinization enthalpies were about 40% greater in whole grain rice compared to rice flour for each variety. Heating rate studies conducted on the long-grain variety (Lemont) at rates of 0.17–1.33°C/min (10–80°C/hr) continued to show two gelatinization endotherms, although some thermal parameters changed with heating rate. The results show that the thermal curves for whole grain rice are considerably different from comparable flour samples, and these results are discussed in terms of the structural integrity of whole grain rice in determining its thermal properties.

Thermal analysis of rice starch and milled rice flour by differential scanning calorimetry (DSC) has been carried out by several investigators to study gelatinization phenomena of these starch- or flour-water systems (Biliaderis et al 1980, 1986a,b; Maurice et al 1985; Nakazawa et al 1984; Russell and Juliano 1983). Their studies showed that varying the water content of the starch or flour significantly alters the thermal properties. To account for the multiple-melting thermal profiles, Biliaderis et al (1986a,b) proposed a process of partial melting followed by recrystallization and final melting during the DSC scan.

In heating rate studies on rice starch by Nakazawa et al (1984), gelatinization onset temperature decreased as the heating rate was reduced below 1°C/min. Studies by Biliaderis et al (1986b) suggest that at slow heating rate there is a greater opportunity for chain rearrangement in the crystallites and thus a smaller fraction will melt at a low temperature.

Whereas these reports were concerned mainly with the thermal properties of rice starch or milled rice flour, no studies relating to the thermal properties of whole grain milled rice (head rice) have been reported.

Because most cooking applications involve the use of whole grain rice, ideally the thermal properties of rice components (starch, protein, lipid) that relate to its cooking quality should be studied in situ, that is, directly in the whole grain.

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The present investigation was undertaken to examine the thermal properties of whole grain milled rice and to compare them with the thermal properties of milled rice flour, using representative long-, medium-, and short-grain, and very low amylose rice varieties.

MATERIALS AND METHODS

Materials

Rough rice samples of Lemont (long-grain) and Mars (medium-grain) were obtained from the Louisiana State University Rice Experiment Station, Crowley, LA. Rough rice samples of S-201 (short-grain) and Calmochi (very low amylose) were procured from the California Cooperative Rice Research Foundation, Inc., Rice Experiment Station, Biggs, CA. All samples were dehulled in a McGill sheller and milled in a McGill miller no. 3, according to recognized laboratory methods (U. S. Agricultural Marketing Service 1974). To prepare the flours, milled rice was ground to a fine powder in a Udy cyclone mill.

Methods

DSC was conducted using a Hart Scientific model 7701 thermal analyzer (Hart Scientific, Provo, UT) equipped with a Hart Scientific 707 cell base designed for a system that includes a reference and one to three samples. Thermal curves were obtained from 20 to 110°C with heating rates of 0.17–1.33°C/min (10–80°C/hr), depending on the particular experiment. The sensitivity of the apparatus was 21 μJ/°C and corresponds to the minimum detectible change in heat capacity. Water as the reference and samples of about 800 mg (water + head rice) or 400 mg (water + flour) were sealed in 1-ml tantalum ampoules. Sufficient water was added to the rice kernels and flour to obtain approximately 70% moisture, which is the moisture content of fully cooked rice (Juliano et al 1981). The weight of material in all ampoules varied less than 10 mg. All samples were subjected to a presoak period for approximately 45 min (Hogan and Planck 1958) at room temperature, and the cells were equilibrated to 20°C. Separate studies indicated that 45 min was the minimum time required to soak our milled rice varieties in order to reach an equilibrium moisture content of 38–40% at room temperature. Thermal curves for milled rice samples presoaked for 45 and 270 min were compared, and no significant difference between the curves was seen (data not shown). A 45-min presoak was then chosen to expedite data acquisition. After the first heating run to 110°C, the sample cells were cooled to 20°C and rescanned almost immediately to determine the completion of gelatinization and the reversibility of the transitions. The second heating established a baseline for each run, since in all cases, no thermal transitions appeared during the second heating. Baseline subtractions were made on all thermal curves and only corrected curves are shown. The space surrounding the sample cells was flushed with dry nitrogen at a rate of 20 ml/min for all runs in order to prevent condensation on the outside of the cells during the run. Thermal transitions of head rice and flour were defined in terms of temperature at T_o (onset), T_p (peak gelatinization), and T_c (conclusion). The symbol ΔH refers to the enthalpy associated with gelatinization of starch. This gelatinization enthalpy corresponds to the area enclosed by drawing a straight line between T_o and T_c and is expressed in joules per gram on a dry weight basis of head rice or rice flour.

Amylose contents were determined according to the method of Juliano (1971). Moisture contents were determined by oven drying at 105°C for 24 hr.

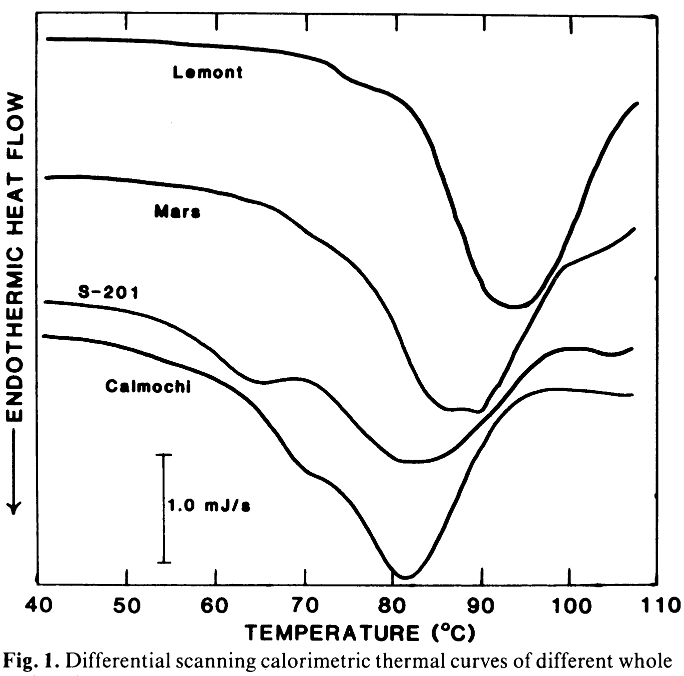

Fig. 1. Differential scanning calorimetric thermal curves of different whole grain milled rice varieties at 70% water content (w/w). The heating rate was 1.0°C/min.

RESULTS AND DISCUSSION

DSC of Whole Grain Milled Rice

DSC scans for four varieties of head rice are shown in Figure 1. At a scan rate of 1.0°C/min, the thermal curves were characterized by the appearance of two endotherms: a large, higher temperature transition and a small, lower temperature transition that appeared in each variety. The small endotherm was most prominent in S-201, where it could be considered a discreet thermal transition (T_p = 64.5°C), and least prominent in Mars, where it was a small shoulder on the main endotherm. The appearance of the shoulder or low-temperature endotherm was unusual. Two endotherms have been observed in rice starch samples with water contents of 65% and lower, but the second endotherm was located on the high-temperature side of the major transition (Nakazawa et al 1984). Another unusual feature of Figure 1 was the relatively high T_p values for the large endotherm in whole kernel samples, which we attribute to starch gelatinization, compared to the T_p values of flour samples of the same varieties (Table I). The onset and peak gelatinization temperatures decreased with decreasing grain size for Lemont, Mars, and S-201, but there was no correlation among T_o, T_p, and amylose contents as the medium-grain variety (Mars) had a lower amylose content than either the long-grain variety (Lemont) or the short-grain variety (S-201) (Table I). T_o values (Table I) were calculated to commence with the initiation of the low-temperature endotherm. The conclusion temperatures (T_c) are listed in Table I except for Lemont, which could not be calculated from Figure 1 because no final baseline was observed. The absence of a final baseline in our scan also precluded a calculation of the gelatinization enthalpy (ΔH) for this variety. However, for the other three varieties, ΔH is given in Table I.

Inspection of the ampoule contents at the end of the DSC run revealed that all of the water had been absorbed by the rice grains and that rice of every variety was completely cooked; that is, there was no evidence of hard centers when the grains were pressed between two glass slides or when the cooked grains were tested by chewing.

DSC of Rice Flour

The thermal curves for rice flour of each variety are given in Figure 2. Moisture values between whole kernels and flours were kept as close as possible in order to minimize this variable. The thermal curves for the flours (Fig. 2) were considerably different than the curves for the whole grain samples (Fig. 1). The most striking difference was the absence of two gelatinization endotherms in the flour samples. Besides the one gelatinization endotherm, there were distinct, small, higher temperature endotherms in the Lemont, Mars, and S-201 varieties but not in the Calmochi sample (Fig. 2). These higher temperature endotherms may be attributed to melting of an amylose-lipid

TABLE I
Amylose Content[a] and Thermal Curve Data[a] of Whole Grain Milled Rice and Milled Rice Flour[b]

Rice Variety	Amylose Content (%)	Whole Grain Milled Rice: Gelatinization Temperatures (°C) T_o	T_p	T_c	Enthalpy (ΔH) (J/g)	Milled Rice Flour: Gelatinization Temperatures (°C) T_o	T_p	T_c	Enthalpy (ΔH) (J/g)
Lemont	25.0 ± 0.1	72.7 ± 0.2	93.5 ± 0.5	ND[c]	ND	70.3 ± 0.1	75.9 ± 0.0	83.8 ± 0.1	10.3 ± 0.1
Mars	15.8 ± 0.1	65.4 ± 0.4	86.4 ± 0.7	98.6 ± 0.2	15.8 ± 0.4	65.3 ± 0.4	72.9 ± 0.4	82.2 ± 0.2	10.5 ± 0.1
S-201	20.6 ± 0.8	55.4 ± 0.7	82.6 ± 0.4	97.6 ± 0.8	13.3 ± 0.1	59.2 ± 0.2	66.6 ± 0.1	77.1 ± 0.1	9.5 ± 0.1
Calmochi	6.6 ± 0.0	60.5 ± 0.5	81.7 ± 0.3	93.5 ± 0.5	14.9 ± 0.4	61.0 ± 0.1	68.8 ± 0.1	78.8 ± 0.1	11.2 ± 0.4

[a]Values given are means ± SEM of triplicate determinations.
[b]Moisture content of all samples was 70%.
[c]ND = Not determined due to absence of concluding baseline.

complex formed during heating in the calorimeter or already present in the flour (Biliaderis et al 1986a). The fact that Calmochi has a very low amylose content (Table I) lends support to this argument. In fact, two high-temperature (100–140°C) endotherms have been attributed to an amylose-lipid complex (Biliaderis et al 1986b). Their finding indicates that organization of amylose-lipid complexes occur during gelatinization. Milled rice has been shown by Hogan and Deobald (1961) to contain approximately 0.5% total lipids. Observation of a second amylose-lipid complex was beyond the temperature range of our calorimeter.

The onset temperatures for both flour and kernel (Table I) were similar within each variety, but the peak gelatinization and conclusion temperatures were much lower in the flour. Gelatinization enthalpies were consistently lower in the flour, but the enthalpies for the head rice samples included the low-temperature endotherm in the calculations. In fact, ΔH values were about 40% greater for head rice than for flour samples. This large difference in ΔH, found in all varieties examined, means that more thermal energy is required to gelatinize starch in head rice than in rice flour and may reflect cell wall disruption during grinding.

Chungcharoen and Lund (1987) also characterized the gelatinization endotherm of Lemont flour, and their values for T_o, T_p, and T_c were consistently higher than our values, but their gelatinization enthalpy (ΔH) was slightly lower than ours. These discrepancies may be due to their using a higher scan rate and a much smaller sample size.

The similar onset temperatures for whole grain and flour samples within each variety lead us to believe that the same process, namely starch gelatinization, was initiated in both sets of samples at similar temperatures. However, as heating progressed, gelatinization of another, larger population of starch granules was initiated in the head rice, with the peak gelatinization and conclusion temperatures displaced to higher values.

A possible explanation for these observed differences in starch gelatinization could be attributed to one of three different mechanisms: 1) the existence of two populations of starch granules with distinct gelatinizing characteristics, 2) the presence of heat transfer effects that inhibit equilibration between whole grain rice in water and the water reference in the calorimeter, or 3) the existence of two separate compartments within the kernel—one easily accessible and one less readily accessible to water—that physically separate a small and large population of starch granules. The compartments may be separated by a natural barrier, possibly the cell walls between the subaleurone and central endosperm layers (Bechtel and Pomeranz 1978), which may retard water penetration into the center of the kernel.

The first mechanism noted above is the least likely. If two different populations of starch granules existed, they should also exist in the flour samples as well. However, only one endotherm attributed to starch gelatinization was observed in all flour samples.

The second mechanism represents a more likely possibility and was the subject of a detailed study described below.

Heating Rate Studies

The presence of low-temperature endotherms, broad thermal transitions, high gelatinization temperatures, and large (800 mg) total sample size of the whole kernel samples, led us to determine whether heat transfer effects were contributing to the thermal curves depicted in Figure 1. The size and geometry of our ampoules were such that a relatively low heating rate (e.g., 1.0°C/min) is required to insure thermal equilibration of the sample at the time of data collection.

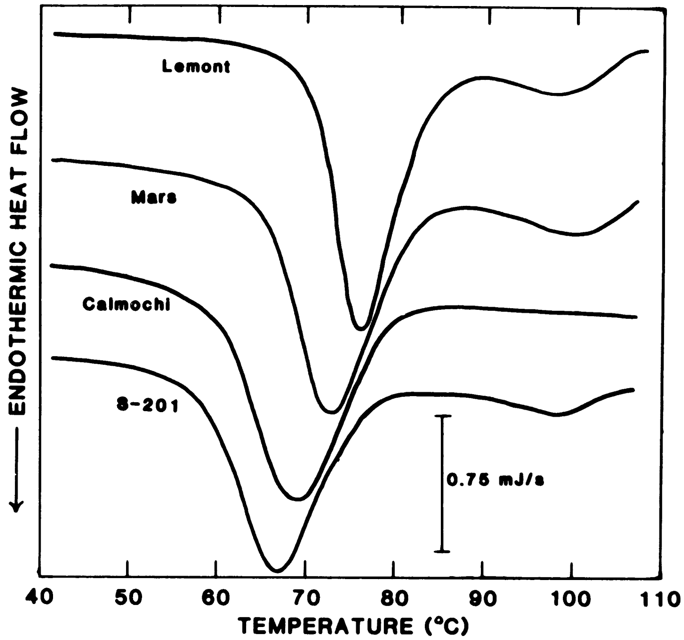

Fig. 2. Differential scanning calorimetric thermal curves of different milled rice flour varieties at 70% water content (w/w). The heating rate was 1.0°C/min.

TABLE II
Enthalpy Values[a] at Different Heating Rates for Lemont Milled Rice

Heating Rate (°C/min)	ΔH (J/g): Whole Grain	Flour
0.17	14.9 ± 0.2	11.6 ± 0.1
0.33	14.7 ± 0.2	11.1 ± 0.1
0.67	14.6 ± 0.3	10.8 ± 0.0
1.00	ND[b]	10.3 ± 0.1
1.33	ND	...

[a]Values given are means ± SEM for triplicate determinations.
[b]ND = Not determined due to absence of concluding baseline.

Lemont head rice and flour were chosen to study the effect of heating rate on the thermal curves for this variety. Varying the scan rate from 0.17 to 1.33°C/min did not eliminate the low-temperature endotherm in the thermal curves of the head rice samples (data not shown). Decreased heating rate caused a narrowing of the gelatinization endotherms in both sets of samples (data not shown).

Enthalpy values for both sets of samples decreased with increased heating rate (Table II). These results are in contrast to the findings of Hendrickx et al (1987), who found the enthalpy

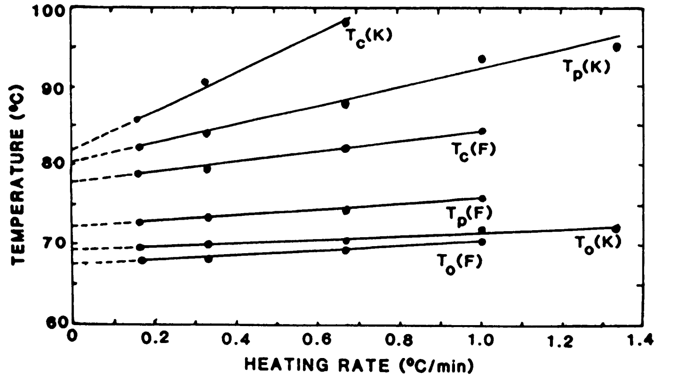

Fig. 3. Onset temperature (T_o), peak temperature (T_p), and conclusion temperature (T_c) of Lemont milled rice kernels (K) and flour (F) as a function of heating rate.

TABLE III
Slope Values[a] of the Gelatinization Parameters as a Function of Heating Rate for Lemont Whole Grain Rice and Rice Flour

Gelatinization Parameters	Slope (min) Whole Grain	Flour
T_o	1.8	2.9
T_p	12.2	3.6
T_c	24.6	6.6

[a]Data taken from Figure 3.

of gelatinization to be independent of heating rate for waxy maize starch. Head rice showed a slight but consistent decrease in ΔH with increased scan rate, but the flour samples exhibited a significantly larger decrease in ΔH.

The relationships for T_o, T_p, and T_c as a function of scan rate for both Lemont head rice and flour are given in Figure 3. They are linear relationships in which the data have been extrapolated to zero heating rate. Hendrickx et al (1987) also found linear relationships between T_o, T_p, and heating rate for waxy maize starch. Slope values (i.e., the gelatinization temperature divided by the heating rate in degrees Celsius per minute), which are a measure of the change in individual gelatinization temperatures with heating rate, are presented in Table III. The changes in temperature with scan rate for both whole kernel and flour samples were lowest for the onset temperature and highest for the conclusion temperature. Not only was T_o essentially independent of the scan rate, but it was also similar for kernel and flour, where the difference at zero scan rate was about 2°C (Fig. 3). The change in heating rate had a greater effect on the gelatinization temperature of the head rice, but at zero heating rate, the T_p for whole kernels was still almost 9°C higher than for flour (Fig. 3). The T_c for head rice was most affected by heating rate, and at zero scan rate the difference between kernels and flour was only 4°C (Fig. 3). The heating rate studies indicate that heat transfer effects may be responsible for broadening the thermal curves, especially for head rice samples.

When heat transfer effects were eliminated at zero heating rate, peak gelatinization and conclusion temperatures were still significantly higher in the kernels, and the lower temperature endotherm persisted, even at the lowest heating rate. Apparently, the heat transfer mechanism does not completely explain the differences in thermal curves between kernel and flour. The most likely mechanism appears to be compartmentalization of the starch granules as described earlier. Compartmentalization is dependent upon kernel integrity, and since this integrity is largely destroyed by conversion to a flour, the larger, higher temperature endotherm is absent in the flour samples.

Identification and location of these compartments, and hence barrier(s) that restrict water diffusion, will form the basis of future studies.

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