Wheat Flour and Defatted Milk Fractions Characterized by Differential Scanning Calorimetry. II. DSC of Interaction Products[1]

N. ERDOGDU[2], Z. CZUCHAJOWSKA[2], and Y. POMERANZ[2]

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ABSTRACT

Wheat flour prime starch, tailings starch, and gluten were blended (each) in a 1:1 ratio with lactose, commercial and laboratory acid and sweet whey, and acid and sweet casein. Their interactions were measured by differential scanning calorimetry (DSC). Lactose interacted with starches and gluten. It increased the endotherm temperatures of gelatinization and enthalpy (ΔH) of the prime and tailings starches. Gluten reduced the melting temperatures and ΔH of lactose. Caseins did not interact with starches. The enthalpy peak of the amylose-lipid complex of prime starch was eliminated or reduced by most of the dairy ingredients. In tailings starch, the complex had a significantly reduced onset temperature. In contrast to commercial or simulated (dialyzed) whey protein concentrates, laboratory nondialyzed whey powders interacted with wheat flour components. Thus, both the isolation and the processing conditions affected the mode of interaction of wheys with wheat flour components.

A previous report (Erdogdu et al 1995) noted that the processing of whey into a protein concentrate caused pronounced changes in differential scanning calorimetry (DSC) diagrams. The objective of this study was to use DSC to investigate the interaction patterns of dairy fractions with wheat flour components in a model system. Wheat flour fractions included prime starch, tailings starch, and gluten; dairy fractions included lactose, acid and sweet whey, and acid and sweet casein prepared in the laboratory or commercially. Some laboratory preparations were dialyzed or heat-treated (at 80 or 95°C). A comparison of the interaction patterns of laboratory versus commercial fractions was made to gain a better understanding of the effects of whey processing conditions on their functionality.

MATERIALS AND METHODS

Wheat Flour and Dairy Fractions

The preparation of wheat flour and dairy fractions were described previously (Erdogdu et al 1995). Abbreviations used here include: PS (prime starch), TS (tailings starch), GL (gluten), C (commercial), L (laboratory), D (dialyzed), La (lactose), SWP (sweet whey powder), SWPC (sweet whey protein concentrate), AWP (acid whey powder), AWPC (acid whey protein concentrate), SC (sweet casein), and AC (acid casein). Interactions were studied by DSC on 1:1 blends of wheat flour and dairy fractions. In addition, the effects on thermograms of lactose present in various dairy products or in blends of up to 50% prime starch and tailings starch were determined.

DSC assays were described previously. For each endotherm curve, onset (T_o) and peak (T_p) temperatures and transition enthalpies (ΔH) were computed. Standard deviations of temperature values were <1.0°C. Standard deviations of enthalpy values were <10% of the mean. Water (20 μl) was added to 10-mg samples (water-free basis) and kept in the capsules for 20 min to 4 hr (depending on the nature of the material and rate of water absorption). Increasing the equilibration time from 2 to 4 hr did not affect enthalpy curves.

Statistical Analyses

All separations, fractionations, and analyses were done at least in duplicate. All results were averaged. Data were analyzed using the statistical analysis system of the SAS Institute (1985).

RESULTS AND DISCUSSION

Several assumptions were made in the interpretation of the DSC thermograms to explain the interactions between wheat flour components and dairy ingredients.

In the presence of whey, an increase of ~10°C occurred in the endotherm temperatures of starch gelatinization. This increase was considered to be an effect of lactose, which is a whey constituent.

In analyzing mixtures, whenever the individual ingredients were blended in a 1:1 ratio, a 50% reduction in ΔH was expected. This reduction in ΔH was not caused by an interaction but by the dilution of individual ingredients. According to Eberstein et al (1980), ΔH of starches is linearly related to amount at a 1:2 starch-to-water ratio, which was used in this study.

And, finally, the disappearance of an original peak was considered indicative of an interaction. On the other hand, unless there was a significant change in ΔH when the original endotherm appeared in blends at the same temperature, we assumed that there was no interaction between the ingredients.

Prime Starch Interactions with Dairy Ingredients

The T_p of lactose was 88.5°C (Table I and Fig. 1g). This is in good agreement with the melting temperature of 78°C and 87°C at water-to-lactose ratios of 1.7:1.0 and 1.0:1.0, respectively, that were reported by Kim and Walker (1992).

The endotherm temperatures of prime starch gelatinization were significantly increased by increases in lactose (Table I, Fig. 1). T_o, T_p, and ΔH for lactose alone were 56.5°C, 88.5°C, and 65.45 J/g, respectively. As the concentration of lactose in the mixture increased from 10 to 50%, for each 10% lactose increase, T_o and T_p increased by an average of 1 and 2°C, respectively. The increase in the lactose concentration was positively correlated with T_o ($r = 0.89$) and T_p ($r = 0.97$) (Fig. 2). Lactose might compete

TABLE I
Differential Scanning Calorimetry of Prime Starch (PS) and Lactose (La) Mixtures

	Starch Gelatinization			Amylose-Lipid Complex		
Materials	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
PS (100%)	57.8	64.1	10.47	97.9	102.6	1.47
PS:La (90:10)	59.1	64.7	7.88	96.3	101.9	0.91
PS:La (80:20)	61.4	66.4	7.34	95.9	101.7	0.71
PS:La (70:30)	62.4	68.2	7.67	95.5	101.3	0.51
PS:La (60:40)	61.2	70.2	12.41	95.3	101.0	0.34
PS:La (50:50)	63.0	74.3	25.56	—	No peak	—

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[2]Department Food Science and Human Nutrition, Washington State University, Pullman, WA 99164-6376.

with prime starch for water and decrease water activity or interact with the starch chains and thus raise the gelatinization temperatures (Kim and Walker 1992).

The possibility that the large increases in enthalpy at high lactose concentrations (40 and 50%) were, in part at least, due to melting of lactose crystals cannot be excluded. In addition, the relatively small changes in T_o and T_p temperatures, as well as ΔH, in the amylose-lipid complex results indicated, at least in part, a dilution effect.

The origin and type of whey governed changes in the DSC thermograms of prime starch. Lactose, which was the major component of both commercial and laboratory wheys, caused an increase of about 10°C (or more) in the gelatinization temperatures of starch (Tables II and III and Fig. 3).

Interaction of L-AWP with prime starch was most pronounced. The T_p of the endotherm of prime starch at 64.1°C increased to 83.4°C when blended with L-AWP (Table II and Fig. 3c). The 19.3°C increase is more than twice as high as expected from the lactose effect. Therefore, another L-AWP component seems to have caused an additional increase of 10°C in the gelatinization temperature of prime starch. This increase in the gelatinization temperature, which was accompanied by a ΔH decrease, implied an interaction between L-AWP and prime starch. This interaction was overcome by dialysis. L-DAWP did not interact with prime starch, probably because of the removal by dialysis of a low molecular weight component of whey (Fig. 3d). Heat treatment of the L-DAWP had no effect on additional changes in the transition endotherm (Fig. 3e). Similarly, commercial C-WPC showed no interaction (in addition to lactose) with prime starch (Table III). The endotherms of prime starch and commercial WPC mixtures were biphasic in character, showing overlapping peaks of the individual components (Fig. 4b,c). The production of commercial WPC involves ultrafiltration. L-DAWP resembles commercial WPC in that a low molecular weight component responsible for the interaction is removed. The amylose-lipid complex endotherm of prime starch practically disappeared in all prime starch-whey blends. This implies that lipids may have high affinity for some whey components.

The gelatinization temperature of prime starch increased in the presence of caseins in proportion to their lactose content. Lactose (~20%) was present in laboratory caseins but practically

TABLE II
Differential Scanning Calorimetry of Prime Starch (PS) and Laboratory (L) Dairy Ingredient Mixtures (1:1)

	Starch Gelatinization			Amylose-Lipid Complex		
Materials	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
PS	57.8	64.1	10.47	97.9	102.6	1.47
+L-sweet whey protein	66.5	73.3	5.52	—	No peak	—
+L-acid whey protein	72.0	83.4	2.67	100.0	105.5	0.40
+L-dialyzed acid whey protein	67.3	73.3	4.92	—	No peak	—
+L-dialyzed acid whey protein (at 80°C)	68.8	73.7	4.53	—	No peak	—
+L-sweet casein	61.8	67.7	5.03	92.0	100.3	0.63
+L-acid casein	63.8	69.4	5.12	91.9	99.9	0.33

TABLE III
Differential Scanning Calorimetry of Prime Starch (PS) and Commercial (C) Dairy Ingredient Mixtures (1:1)

	Starch Gelatinization			Amylose-Lipid Complex		
Materials	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
PS	57.8	64.1	10.47	97.9	102.6	1.47
+C-sweet whey protein concentrate	65.9	73.1	5.51	—	No peak	—
+C-acid whey protein concentrate	67.6	74.8	4.35	—	No peak	—
+C-sweet casein	58.5	64.1	4.91	93.5	98.9	0.32
+C-acid casein	58.7	63.8	4.59	92.4	99.1	0.31

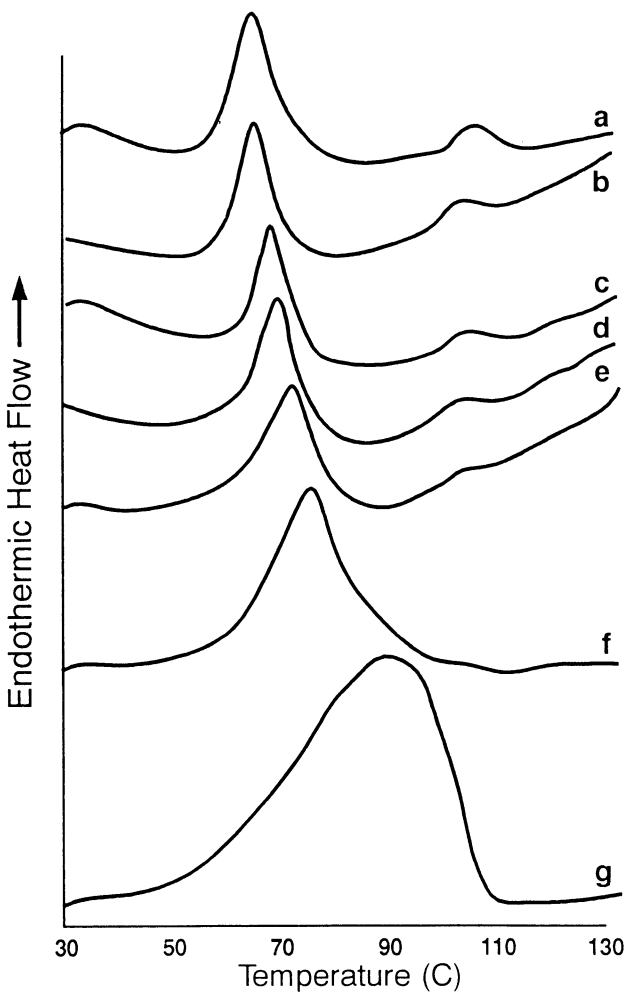

Fig. 1. Differential scanning calorimetry thermograms of prime starch and lactose mixtures: a) 100:0, b) 90:10, c) 80:20, d) 70:30, e) 60:40, f) 50:50, and g) 0:100.

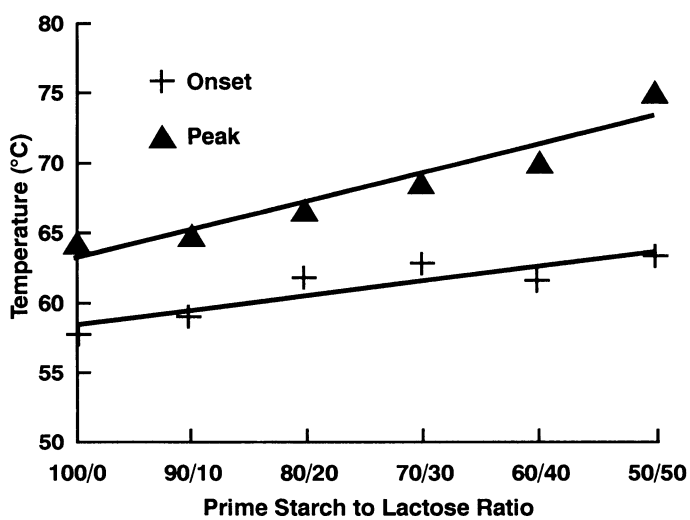

Fig. 2. Relationship between prime starch-to-lactose ratios and differential scanning calorimetry onset and peak temperatures in the gelatinization range.

absent from commercial caseins (Erdogdu et al 1995). As a consequence, the gelatinization temperature of prime starch was raised by 4–5°C with laboratory (Table II, Fig. 3f,g), but not with commercial, caseins (Table III, Fig. 4d,e). The temperature of the amylose-lipid complex enthalpy of prime starch was less affected by caseins than by wheys.

Tailings Starch Interactions with Dairy Ingredients

The gelatinization temperature of the tailings starch was also (as with prime starch) positively correlated with the lactose concentration (Table IV). For each 10% increase in lactose up to 40%, T_o and T_p of the tailings starch increased, on average, by ~1°C (r = 0.99). The T_o at 50% is probably reduced due to a relaxation in chain flexibility of tailings starch at high sugar concentrations (Spies and Hoseney 1982). The tailings starch is highly diverse in composition when compared to the relatively homogenous prime starch.

Lactose did not affect (except for dilution) the amylose-lipid complex of tailings starch. Lactose did not consistently interfere, as prime starch did (Table I, Fig. 1), with the formation of the amylose-lipid complex of tailings starch (Table IV).

Neither laboratory nor commercial wheys interacted with the gelatinization endotherm of tailings starch (Tables V and VI). The temperature of the amylose-lipid complex of tailings starch was reduced by both laboratory and commercial whey preparations. However, the precise interaction effect is difficult to quantitate because of the small ΔH values for the second peak.

As observed for prime starch, the lactose concentrations of casein preparations governed the raise in the gelatinization temperatures. Otherwise, caseins showed no evidence of interaction with tailings starch (Tables V and VI).

Gluten Interactions with Dairy Ingredients

Gluten, per se, showed no distinct DSC peaks. The interactions

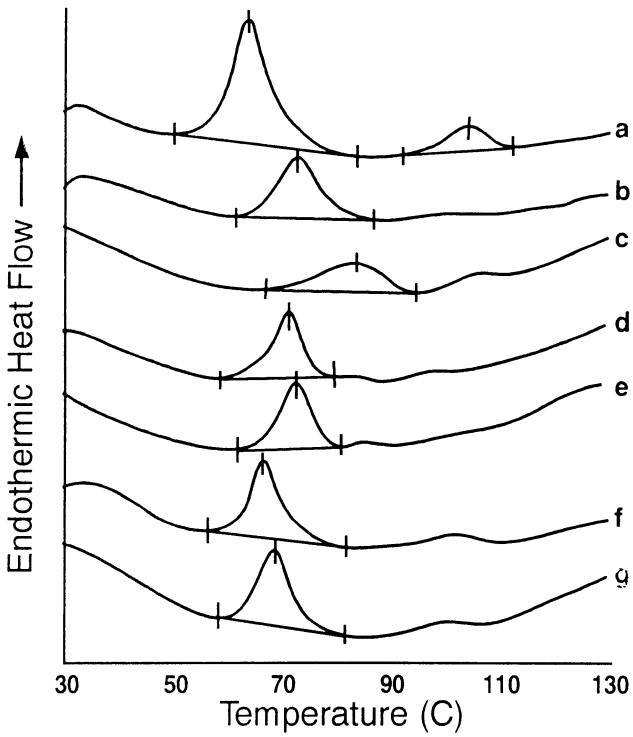

Fig. 3. Differential scanning calorimetry of 1:1 mixtures of prime starch and laboratory dairy fractions: a) prime starch, b) sweet whey powder, c) acid whey powder, d) dialyzed acid whey powder, e) dialyzed and heated (80°C) acid whey powder, f) sweet casein, and g) acid casein.

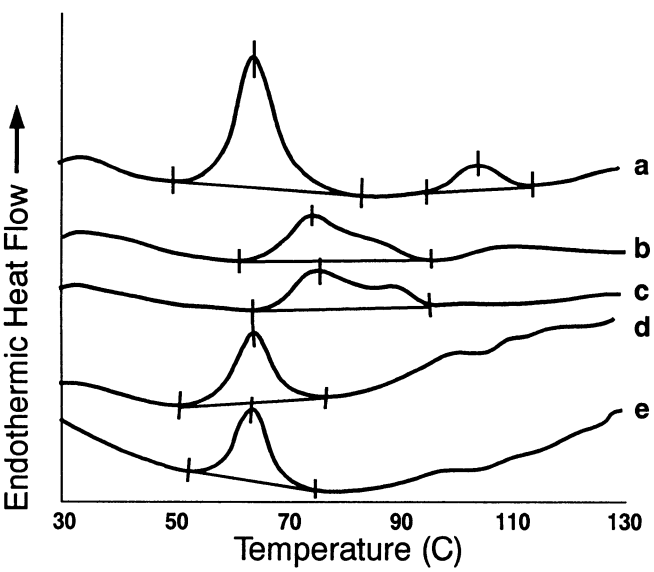

Fig. 4. Differential scanning calorimetry of 1:1 mixtures of prime starch and commercial dairy fractions: a) prime starch, b) sweet whey protein concentrate, c) acid whey protein concentrate, d) sweet casein, and e) acid casein.

TABLE IV
Differential Scanning Calorimetry of Tailings Starch (TS) and Lactose (La) Mixtures

	Starch Gelatinization			Amylose-Lipid Complex		
Materials	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
TS (100%)	54.5	64.6	5.02	91.7	102.9	2.47
TS:La (90:10)	55.2	64.7	4.49	92.6	100.7	1.38
TS:La (80:20)	57.2	66.0	4.06	91.9	100.6	1.33
TS:La (70:30)	58.1	66.9	3.34	90.3	100.1	1.44
TS:La (60:40)	60.3	68.1	2.86	92.2	101.0	1.19
TS:La (50:50)	43.0	69.0	10.64	91.9	100.5	1.27

TABLE V
Differential Scanning Calorimetry of Tailings Starch (TS) and Commercial (C) Dairy Ingredient Mixtures (1:1)

	Starch Gelatinization			Amylose-Lipid Complex		
Materials	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
TS	54.5	64.6	5.02	91.7	102.9	2.47
+C-sweet whey protein concentrate	65.3	73.7	2.14	93.9	102.1	0.23
+C-acid whey protein concentrate	64.8	73.6	2.76	93.2	99.3	0.31
+C-sweet casein	55.9	64.5	2.24	90.2	97.9	0.72
+C-acid casein	56.2	64.2	1.99	90.2	97.9	0.72

TABLE VI
Differential Scanning Calorimetry of Tailings Starch (TS) and Laboratory Dairy Ingredient Mixtures (1:1)

	Starch Gelatinization			Amylose-Lipid Complex		
Materials	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
TS	54.5	64.6	5.02	91.7	102.9	2.47
+L-sweet whey protein	63.6	71.9	2.82	89.5	97.7	0.93
+L-acid whey protein	67.1	73.7	2.40	91.6	99.5	0.69
+L-dialyzed acid whey protein	64.2	72.8	2.79	92.9	100.0	0.52
+L-dialyzed acid whey protein (at 80°C)	64.0	71.7	2.55	93.2	99.0	0.35
+L-sweet casein	59.4	67.2	2.07	89.0	98.1	0.98
+L-acid casein	61.4	71.6	2.75	89.4	101.1	0.91

TABLE VII
Differential Scanning Calorimetry of Gluten (GL) and Laboratory (L) Dairy Ingredient Mixtures (1:1)

Materials	1st Peak			2nd Peak		
	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)
GL	—	No peak	—	—	No peak	—
L-sweet whey protein	34.0	51.5	8.76	101.1	108.9	0.72
GL+L-sweet whey protein	—	No peak	—	—	No peak	—
L-acid whey protein	47.0	66.8	10.82	101.3	107.2	0.42
GL+L-acid whey protein	—	No peak	—	—	No peak	—
L-dialyzed acid whey protein	—	No peak	—	86.6	90.3	1.23
GL+L-dialyzed acid whey protein	—	No peak	—	82.2	86.7	0.37
L-dialyzed acid whey protein	—	No peak	—	87.2	90.6	0.95
GL+L-dialyzed acid whey protein (at 80°C)	—	No peak	—	83.4	87.3	0.44
GL+Caseins	—	No peak	—	—	No peak	—

between gluten and dairy ingredients, however, could still be followed by observing the changes in interacting dairy ingredient thermograms. Gluten and lactose interacted. This was confirmed by significantly reduced endotherm temperatures and ΔH of lactose melting (Table VIII).

Gluten did not interact with commercial WPC but interacted with laboratory-produced WPC unless they were dialyzed (Tables VII and VIII). The T_p of L-SWP (51.5°C) and L-AWP (66.8°C) disappeared when gluten was incorporated (Table VII). The interactions, insofar as enthalpy peaks are concerned, were overcome when wheys were dialyzed or ultrafiltered (Tables VII and VIII). This indicates that some low molecular weight component of wheys plays an important role in the interaction. Still, adding gluten lowered T_o and T_p of the second peak, indicating an additional residual interaction. It was not possible to follow the interaction of gluten with caseins by DSC because neither gluten nor caseins showed any pronounced peaks.

In summary, T_o and T_p of prime starch and tailings starch gelatinization are significantly increased by interaction with lactose. DSC thermograms of prime starch are affected by the origin and type of whey, mainly the lactose content of the latter. The amylose-lipid complex endotherm was reduced by prime starch or tailings starch and whey interactions. Caseins showed no evidence of interaction with starch. Lactose or dialyzable components in whey interacted with gluten.

TABLE VIII
Differential Scanning Calorimetry of Gluten (GL) and Commercial (C) Dairy Ingredient Mixtures (1:1)

Materials	Peak		
	T_o (°C)	T_p (°C)	ΔH (J/g)
GL	—	No peak	—
Lactose (La)	56.7	88.5	63.35
GL+La	42.5	66.3	13.13
C-sweet acid protein concentrate	81.0	93.0	1.82
GL+C-sweet acid protein concentrate	80.3	86.2	0.39
C-acid whey protein concentrate	87.6	92.0	1.85
GL+C-acid whey protein concentrate	85.6	90.3	1.11
Caseins	—	No peak	—
GL+C-Caseins	—	No peak	—

CONCLUSIONS

The in vitro study provides evidence of interactions occurring between the components of wheat and milk during heating in the presence of excess water. The DSC method provides information about the nature of those interactions. Their identification can be useful in formulations of food systems containing wheat and milk products.

Recognition of the size and pattern of interactions between the main components of flour and milk fractions can be helpful in selecting beneficial milk products for the baking industry. This will be the subject of further studies in our laboratories.

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LITERATURE CITED

EBERSTEIN, K., HÖPCKE, R., KONIECZNY-JANDA, G., and STUTE, R. 1980. DSC-Untersuchungen an Stärken. I. Möglichkeiten thermoanalytischer Methoden zur Stärkecharakterisierung. Starch/Staerke 32:397-404.

ERDOGDU, G., CZUCHAJOWSKA, Z., and POMERANZ, Y. 1995. Wheat flour and defatted milk fractions characterized by differential scanning calorimetry. I. DSC of flour and milk fractions. 72:70.

KIM, C. S., and WALKER, C. E. 1992. Effects of sugars and emulsifiers on starch gelatinization evaluated by differential scanning calorimetry. Cereal Chem. 69:212-217.

SPIES, R. D., and HOSENEY, R. C. 1982. Effects of sugars on starch gelatinization. Cereal Chem. 59:128-131.

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