Effects of Flour Components and Dough Ingredients on Starch Gelatinization[1]

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Cereal Chem. 60(1):58–61

ABSTRACT

In high-water systems, starch and flour gave the same endotherm initiation temperatures. In low-water systems, however, the second (higher temperature) differential scanning calorimeter peak was much smaller with starch than with flour. As the level of gluten or xanthan gum mixed with starch was increased, the size of the second differential scanning calorimeter peak increased. We speculated that in a starch system, water migrates during starch gelatinization. In dough, gluten severely limits such migrations. That phenomenon and the fact that some areas within each starch granule require a higher temperature to gelatinize explains the effects noted in limited-water systems. As the level of sucrose was increased in a dough, the transition temperature increased, and the gelatinization temperature range decreased. At the level found in bread doughs, both sugar and salt increased starch gelatinization temperature. The two ingredients have an additive effect on gelatinization temperature, whereas shortening shows no effect.

The gelatinization properties of starch are of paramount importance in baked foods. The setting of the product and its texture are determined by the temperature at which starch gelatinizes and by the degree of gelatinization. Both water and energy are necessary to gelatinize starch. All baked products are limited-water systems.

The fact that sugar increases the temperature at which starch gelatinizes has been documented by many authors (Bean and Osman 1959; Bean and Yamazaki 1978a, 1978b; D'Appolonia 1972; Derby et al 1975; Hester et al 1956; Koepsel and Hoseney 1980; Miller and Trimbo 1965; Savage and Osman 1978). Some believe that sugar limits the water available to the starch and thereby increases starch gelatinization temperature (D'Appolonia 1972, Derby et al 1975). However, as noted by Donovan (1979) and Spies and Hoseney (1982), decreased water does not alter gelatinization temperature; lower water reduces the size of the first differential scanning calorimeter (DSC) peak and leads to the production of a second peak.

Small solutes such as sugar and salt lower water activity (Labuza 1975) and thereby increase starch gelatinization temperature (Spies and Hoseney 1982). Spies and Hoseney (1982) showed that water activity is not the only factor by which sugar increases starch gelatinization temperature; the interaction of sugar with starch chains in the amorphous areas of the starch granules also appears to be a factor in increasing starch-gelatinization temperature. Lelievre (1976) has thermodynamically treated a three-component system of starch-water-solute.

We used the DSC to study the effect of flour components and dough ingredients on the water available to starch for gelatinization in dough systems.

MATERIALS AND METHODS

Differential Scanning Calorimetry

A Perkin-Elmer DSC-2 with an Intracooler II system was used.

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0009-0352/83/010058004/$03.00/0

The starch was weighed in the DSC pans and water added with a syringe. The pan was sealed and reweighed to determine the amount of water added. Bread flours with and without various ingredients were mixed in a mixograph to optimum mixing time. The water content of the doughs was adjusted so that a water to starch ratio of 0.70 (w/w) was obtained for all samples. Mixtures of wheat starch with gluten or xanthan gum were mixed in a mixograph; water to starch ratios were the same as for the doughs. Because of the difficulties in transferring doughs into the DSC pans, the pans were cooled by being placed on an aluminum plate on dry ice so that the dough would freeze to the pan. Dough samples that had not been frozen and identical samples that were frozen gave identical thermograms. Samples were heated in the DSC at a rate of 10°C/min, sensitivity of 0.5 m cal/sec, and chart speed of 10 mm/min. An empty pan was used as the reference. The gelatinization temperature range obtained from thermograms was defined as the final temperature of the curve peak (Tf) minus the initial deviation temperature the instrument can detect (Ti).

RESULTS AND DISCUSSION

Thermal Transitions of Starch and Flour in High-Water Systems

Figure 1 shows the thermograms of starch and flour heated in an excess of water. A major endotherm (I) was obtained at a high water to starch ratio (2:1). The minor endotherm (III) is from the lipid-amylose complex reported by Kugimiya et al (1980). The Ti of the endotherms are essentially the same. A sample of flour with the water-solubles removed also gave essentially the same endotherm.

Phase Transitions of Starch and Flour in Low-Water Systems

Bread doughs were mixed in a mixograph; water to starch ratio was 0.70. Wheat starch was weighed in DSC pans and water added to adjust the sample to the same water to starch ratio (0.70) as was used in dough. After the pans were sealed, the samples were equilibrated for at least 1 hr before heating in the DSC. Gelatinization phase transitions of the dough and starch samples are presented in Fig. 2. At that water to starch ratio, the baseline is difficult to determine. However, the ratio of the area of peak II to peak I for the starch sample was obviously much smaller than the same ratio for the flour sample. As shown by Donovan (1979), this indicates that less water is available to the starch for gelatinization in the flour sample.

Effects of Gluten and Xanthan Gum on Wheat Starch Gelatinization

Mixtures of starch with gluten (9.0%) or xanthan gum (9.0%) were heated in the DSC (water to starch ratio of 0.70). Thermograms such as those shown in Fig. 3 were obtained. The ratio of the area of the second peak (II) compared to the first peak (I) is greater for the starch-gum system than for the starch-gluten system. As the concentration of gluten or xanthan gum was decreased from 9 to 4.75% in the mixture, the size of the second peak also decreased (data not shown).

A single endotherm is observed in high-water systems because an excess of water is readily available to each starch granule. In a population of starch granules, the loss of birefringence occurs over a temperature range. In a limited-water system, those granules starting to gelatinize first take all the available water. Evidence to support that concept is shown in Fig. 4. A starch-water system (1:1) was heated to 85°C in a water bath; because of their increased temperature, those granules near the outer edge of the tube gelatinized and pulled water from the starch in the interior of the tube. Polarization microscopy showed that the granules in the center of the tube were birefringent.

In doughs, water is held by the gluten and therefore cannot migrate as readily as in a starch-water system. With less water available to the starch granules, the size of peak I is decreased. Continued heating of the starch-water mixture to a higher temperature will gelatinize the starch and give the second endotherm peak II. Ghiasi et al (1982) examined the starch obtained from the DSC pan and found that gelatinization (loss of birefringence) occurs over a wide temperature range at low water levels. Further evidence to support that phenomenon was obtained by mixing wheat starch with an excess of water, centrifuging the mixture to remove the excess, and dispersing the hydrated starch in mineral oil. The dispersion was then heated on the hot stage of a polarizing microscope. In that system, each starch granule gelatinized over a wide temperature range. Clearly, under conditions of low water, each individual starch granule loses birefringence over a wide temperature range (20–30°C). In dough, water does not migrate rapidly; thus, every starch granule must gelatinize by using the water in or near the granule.

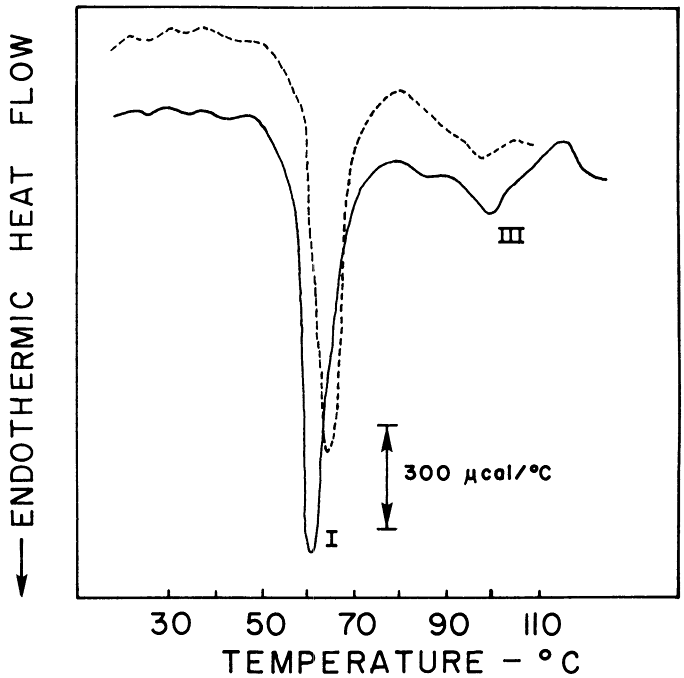

Fig. 1. Thermograms of flour (5.6 mg, solid line) and starch (3.8 mg, dotted line) both at a water to flour or water to starch ratio of 2.

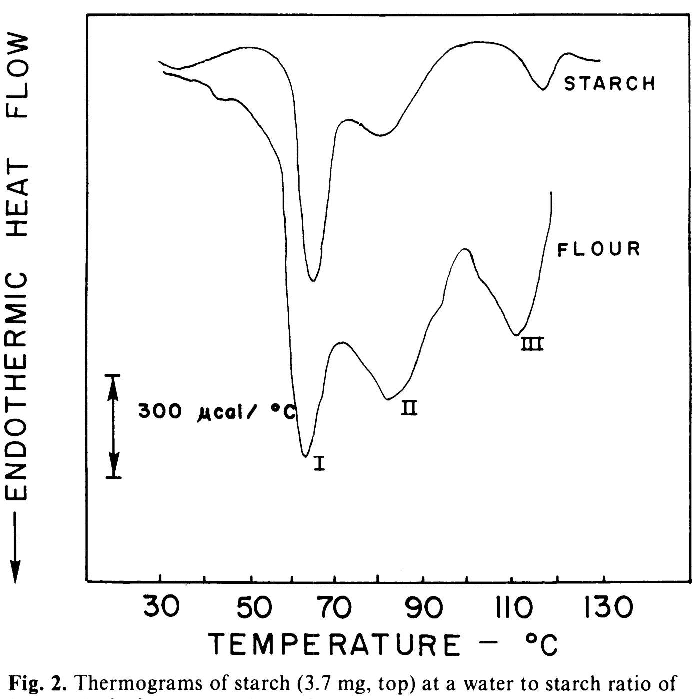

Fig. 2. Thermograms of starch (3.7 mg, top) at a water to starch ratio of 0.70, and of a flour-water dough 21.8 mg (10.14 mg starch, bottom) with a water to starch ratio of 0.72.

Gluten or xanthan gum act as water-binding agents. Some of the water held by gluten or xanthan gum is available to gelatinize starch granules; however, some of the water is not available for starch gelatinization. Thus, we observe a decrease in the area of the first peak (I) relative to that of the second peak (II) with flour, starch-gluten, or starch-xanthan gum compared with starch alone. Increasing the concentration of gluten or xanthan gum further decreases that ratio.

The above discussion shows clearly that the relative area and the temperature of the endotherm peaks are controlled by many factors. As Donovan (1979) noted, the amount of water has a great effect. It is important whether the water can migrate freely, as in a pure starch system, or whether it is held by gluten or a gum. It does appear that the thermogram (particularly the relative area and position of the two peaks) is a sensitive measure of the availability of water for starch gelatinization.

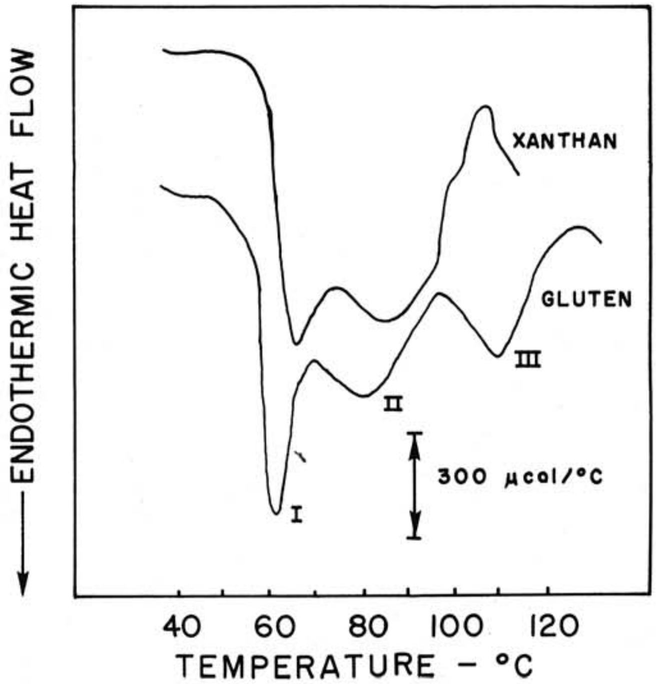

Fig. 3. Thermograms of starch-gluten mixture (9% gluten, bottom line) and a starch-xanthan gum mixture (9% xanthan, top line), water to starch ratio 0.70.

Effect of Dough Ingredients

Sugar. Thermograms of doughs heated in the DSC with 25, 50, and 100% sucrose (based on flour weight) are presented in Fig. 5. Starch-free gluten shows no endotherm, so changes in the starch are responsible for the observed endotherms. The effect of sucrose on Ti and the gelatinization temperature range is shown in Table I. Sucrose increased the Ti of starch in the doughs. Although we used a much lower water to flour ratio than did Jacobsberg and Daniels

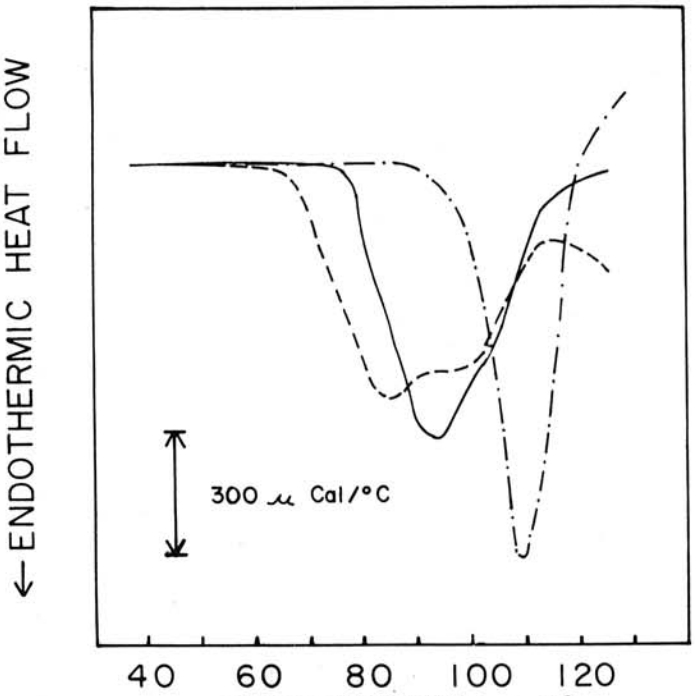

Fig. 5. Thermograms of flour-sugar mixtures containing 4:1 flour to sugar (12.1 mg dough, -----), 2:1 flour to sugar (13.4 mg dough, _____), and 1:1 flour to sugar (16.2 mg dough, -·-·-). In all cases the water to starch ratio was held at 0.70.

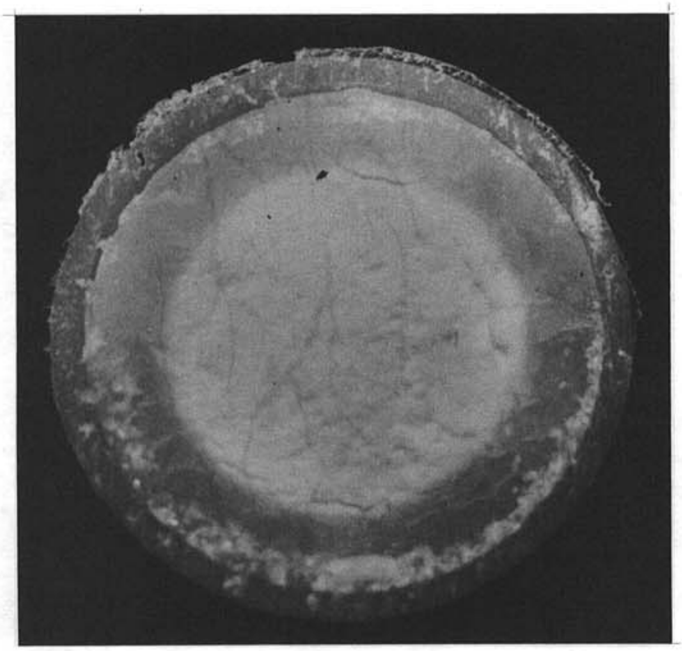

Fig. 4. Cut centrifuge tube containing starch:H_2O (1:1) and heated in a water bath (85° C). Microscopic examination of starch in the opaque center of the tube showed them to be birefringent.

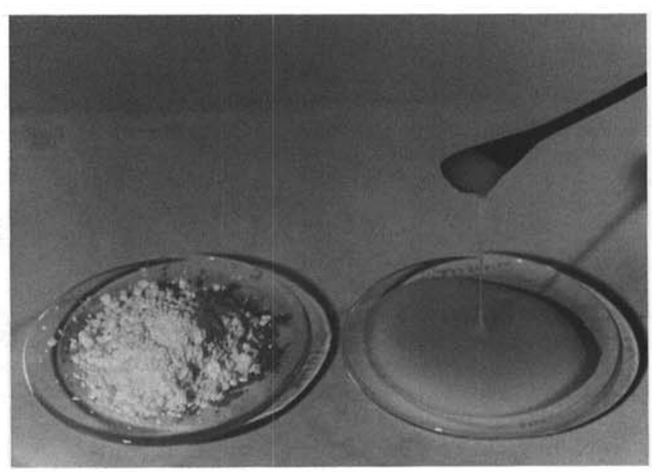

Fig. 6. Starch-H_2O mixture (1:1, **left**) and a starch-H_2O-sugar mixture (1:1:1, **right**).

TABLE I
Effect of Sucrose Concentrations on the Initial Deviation Temperature (Ti) of Doughs

Percent Sucrose	Ti (°C)	Gelatinization Range (°C)
25	67	46
50	78	32
100	98	22

TABLE II
Effect of Salt on Initial Deviation Temperature (Ti) of Doughs

Percent Salt	Ti (°C)
2	62
6	65
10	62
25	51
50	51

(1974), the gelatinization temperature agreed well. As the level of sugar was increased in the dough, Ti increased, and the gelatinization temperature range decreased. The second peak also gradually disappeared. At 100% sugar level (1:1 ratio of sugar and flour), the second peak completely disappeared and gelatinization occurred over a relatively narrow temperature range (Table I). The values reported here do not agree with those reported by Wootton and Bamunuarachchi (1980). They reported that sugar did not affect either Ti or Tf.

Sugar also competes for water with gluten and other flour constituents. Gato and Isemura (1964) showed that the hydration (mol H_2O/mol of solute) of sucrose decreases greatly as the temperature increases from 20 to 40°C. So, even though it may initially bind more water at room temperature than other dough ingredients, sucrose loses its ability to bind water as the temperature increases. Apparently, that water is available to the starch for gelatinization and may help to explain the narrowing of the gelatinization range in dough with high sugar levels.

When a starch-sugar (1:1) mixture was heated in the DSC with the same water to starch ratio as in doughs (60%), the thermogram was essentially the same as that found with flour-sugar, indicating that gluten does not play a major role in lowering the gelatinization temperature range of starch in high-sugar doughs.

More water seems to be available to the starch when high sugar levels are present in the system. The starch-water mixture containing high sugar also appears to have more water (Fig. 6). The total volume of solution increases as sucrose is dissolved in water. Because starch has a defined volume, there is more solution outside the starch granule to give the mixture its flow properties. Donovan (1979) showed that 1.5 g of water per gram of starch is necessary to obtain a single endotherm. Calculation of the total volume of solution per gram of starch in the 1:1:1 flour-sugar-water dough gives a value of 1.66 ml. Thus, increasing the volume of solution with solute apparently is just as effective as adding more water to obtain the single endotherm. The reason for this is not clear.

Salt. Table II shows the effects of salt on Ti. When salt is added to a flour-water system, it lowers the water activity and increases the starch gelatinization temperature. Ti increases as the concentration of salt increases up to 6%; levels higher than that lower Ti (Table II). The Ti is lower in doughs containing 25% salt than that of starch-water alone. Similar results were reported by Wootton and Bamunuarachchi (1980) and by Sandstedt et al (1960).

TABLE III
Effect of Bread Dough Ingredients on Initial Deviation Temperature (Ti) of Doughs

Sample	Ti (°C)
Flour-water dough	56
Flour-water + 2% NaCl	62
Flour-water + 6% sucrose	61
Flour-water + 2% NaCl + 6% sucrose	66
Flour-water + 2% NaCl + 6% sucrose + 3% shortening	67

Effect of Bread Dough Ingredients on Starch Endotherm

Thermograms of dough with 2% salt and 6% sugar show that both increase Ti (Table III). The effects of salt and sugar are additive. Clearly, Ti is not affected by adding shortening to doughs containing sugar and salt (Table III).

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[Received January 5, 1982. Accepted September 20, 1982]