Differential Scanning Calorimetry of Sugar Cookies and Cookie Doughs[1]

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ABSTRACT

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Thermoanalytical studies with a differential scanning calorimeter showed three endotherms of cookie dough. Endotherms are identified as shortening-melting, sucrose-dissolving, and starch gelatinizing. Initiation of starch gelatinization was at temperatures above 100° C. Baked cookies also showed the gelatinization endotherm. Comparisons of endotherms of raw cookie dough and baked cookies indicated that only a small portion of starch was gelatinized during baking.

The question, What determines cookie-flour quality? has always intrigued cereal chemists. Transformation of a semifluid mixture of flour, sugar, shortening, water, milk solids, sodium bicarbonate, ammonium bicarbonate, and salt into cookies undoubtedly has a biochemical basis. Unfortunately, how those changes are accelerated and modified by heat is unknown.

The differential scanning calorimeter is useful in the study of transitions that occur when starch and water are heated (Donovan 1979). This technique has been used to follow the changes that occur in cake batter as it is heated (Donovan 1977, Huang et al 1982). The effect of various dough ingredients on starch gelatinization has also been reported (Ghiasi et al 1983, Spies and Hoseney 1982). The objective of this study was to use differential scanning calorimetry (DSC) to explain the transitions of cookie dough during baking.

MATERIALS AND METHODS

A commercial cookie dough flour obtained from Mennel Milling Company, Fostoria, OH, was used. The flour had 8.7% protein and 0.46% ash. Cookies were baked by the procedure of Finney et al (1950). The standard cookie formula was based on flour (40 g), 60% sugar, 30% shortening, optimum water (about 22.75%), 1.0% sodium bicarbonate, 0.75% ammonium bicarbonate, 3.0% milk solids, and 1.0% salt.

Differential Scanning Calorimetry

A Perkin-Elmer DSC-2 with Scanning AutoZero and Intra Cooler II was used. The calorimeter had been previously calibrated with distilled water and indium. For cookie dough, we omitted the leavening agent (NH_4HCO_3) from the standard formula, but retained the sodium bicarbonate to control pH. The gas produced by the leavening might have forced open the hermetically sealed sample pans. In certain tests in which the cookie formula was varied, shortening was omitted and sugar and water contents were altered.

Cookie dough (approximately 12 mg) was transferred to previously weighed aluminum DSC pans. The pans were sealed and then reweighed. The sample was placed in the calorimeter, and an empty pan was used as a reference. The samples were cooled to 7° C and then heated to 157° C at a rate of 10° C/min. A sensitivity of 1 mcal/sec and a chart speed of 10 mm/min were used.

Thermograms were used to determine the transition temperature and the enthalpy of gelatinization or dissolving of the sugar. The area under the curve was determined by means of a compensating polar planimeter. An indium standard was used as a standard for enthalpy calculations.

Heat of transition, ΔH, was calculated from the equation:

$$\Delta H \text{ sample} = \Delta H \text{ indium} \times \frac{W \text{ indium}}{W \text{ sample}} \times \frac{A \text{ sample}}{A \text{ indium}} \times \frac{R \text{ sample}}{R \text{ indium}} \times \frac{S \text{ indium}}{S \text{ sample}}$$

where ΔH = heat of transition (cal/g), W = weight (mg), A = area under curve, R = range sensitivity (mcal/sec), and S = recorder chart speed (mm/min).

Cookie Defatting

Baked cookies were lyophilized, ground in a coffee grinder, and defatted with petroleum ether in a Goldfisch fat extractor for 4 hr.

RESULTS AND DISCUSSION

Thermal Properties of Cookie Dough

A typical DSC thermogram for cookie dough is shown in Fig. 1. The thermogram has three endothermic peaks. The low-temperature peak was caused by melting of fat. The uppermost curve in Fig. 1 is a cookie dough prepared without fat. The onset temperature (T_o) of fat melting was 29°C. Samples of the cream (sugar and fat alone) in the DSC also gave this low-temperature endotherm.

Cookie doughs contain 60% sugar (based on flour weight) and have a very limited water content (22.75%, based on flour weight). Thus, only part of the sugar dissolves during dough mixing (Yamazaki 1971, Kissell et al 1973). The second endothermic peak is sugar dissolving as dough is heated. If the sugar is dissolved

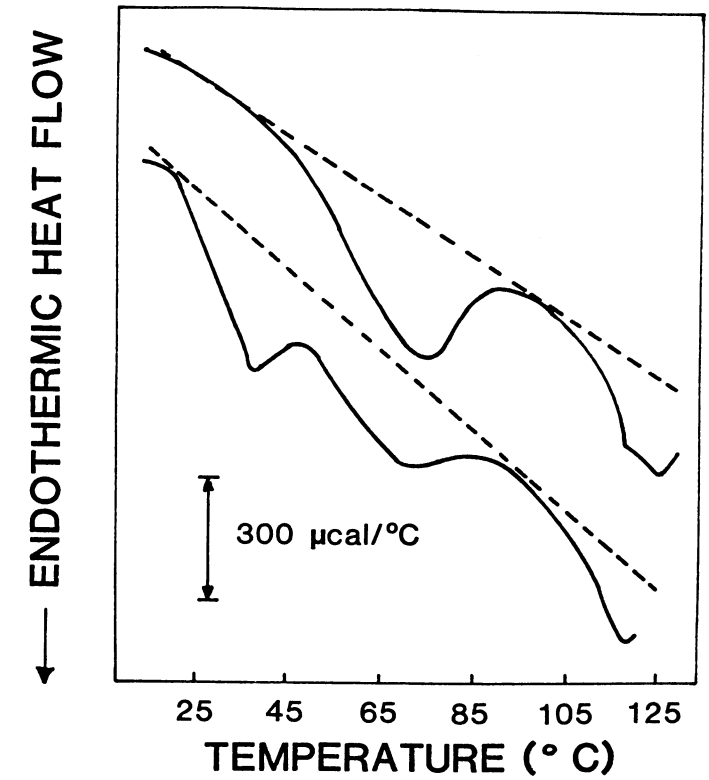

Fig. 1. Thermogram of a standard cookie dough (bottom curve). --- = the baseline. The top curve represents a dough that contains no fat.

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before the cookie dough is mixed, the second peak does not appear (Fig. 2).

Samples of various sugar–water ratios were prepared and heated in the calorimeter. As the ratio of sugar to water increased, the enthalpy increased (Fig. 3). Enthalpy at lower sugar–water ratios than those shown could not be determined.

The third endotherm is the gelatinization of starch. The onset temperature of this endotherm was 117°C (Fig. 1). At slightly higher temperatures exotherms were obtained, presumably, from sugar caramelization. Sugar has been shown by many researchers to increase the gelatinization temperature of starch (Bean and Osman 1959, Miller and Trimbo 1965, Derby et al 1975, Bean and Yamazaki 1978, D'Appolonia 1972, Koepsel and Hoseney 1980). Some researchers attribute the increase in starch gelatinization temperature to the ability of sugars to limit the availability of water to starch (D'Appolonia 1972, Derby et al 1975). However, as reported by Donovan (1979) and Spies and Hoseney (1982), decreased amounts of water did not increase starch gelatinization temperature but only reduced the size of the first peak and produced a second peak.

Amount of Water and Gelatinization Temperature

The effects of different water levels on gelatinization temperature of cookie dough are shown in Fig. 4. Cookie doughs were made without fat because fat complicates the curves and does not affect gelatinization temperature (Ghiasi et al 1982). The size of the second peak (sugar dissolving) was smaller as the level of water was increased. This is additional evidence that the second peak is sugar that is dissolving. When comparing Figs. 3 and 4, we presumed that much of the water in cookie doughs is bound and not available to act as a solvent for sugar. If that is true, then the ratio of sugar to water is higher than one would calculate. When the amount of water in the cookie dough was doubled, the sugar endotherm completely disappeared. Moreover, the onset temperature of starch gelatinization decreased as compared to the control (Fig. 4, Table I). The gelatinization thermograms show that as the water was increased, the size of the first starch gelatinization peak increased, and the size of the second peak (shoulder) decreased. If the water level is increased enough, the second peak will disappear, and one single sharp peak will occur. These results are in agreement with those reported in the literature (Donovan 1979, Ghiasi et al 1982).

Sugar Concentration and Gelatinization Temperature

Thermograms of cookie doughs prepared with 30, 40, 50, and 60% sucrose (based on flour weight) are given in Fig. 5. At low sugar concentrations, the second peak (dissolving sugar) was absent. Also, at the low sugar level, starch gelatinization occurred at a low temperature compared to the starch gelatinization temperature of the control (60% sucrose). At the lowest level of

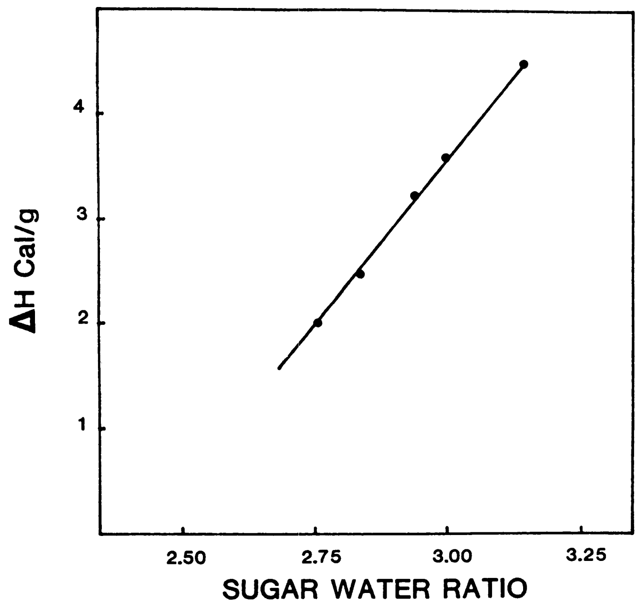

Fig. 3. Change in enthalpy as a function of the sugar–water ratio.

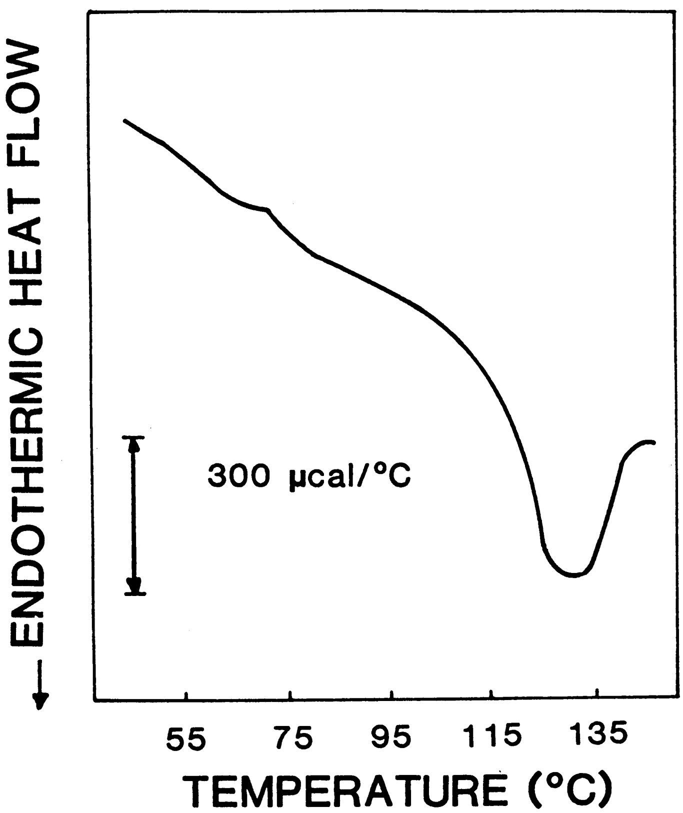

Fig. 2. Thermogram of cookie dough containing no fat and with the sugar dissolved in water before the dough was mixed.

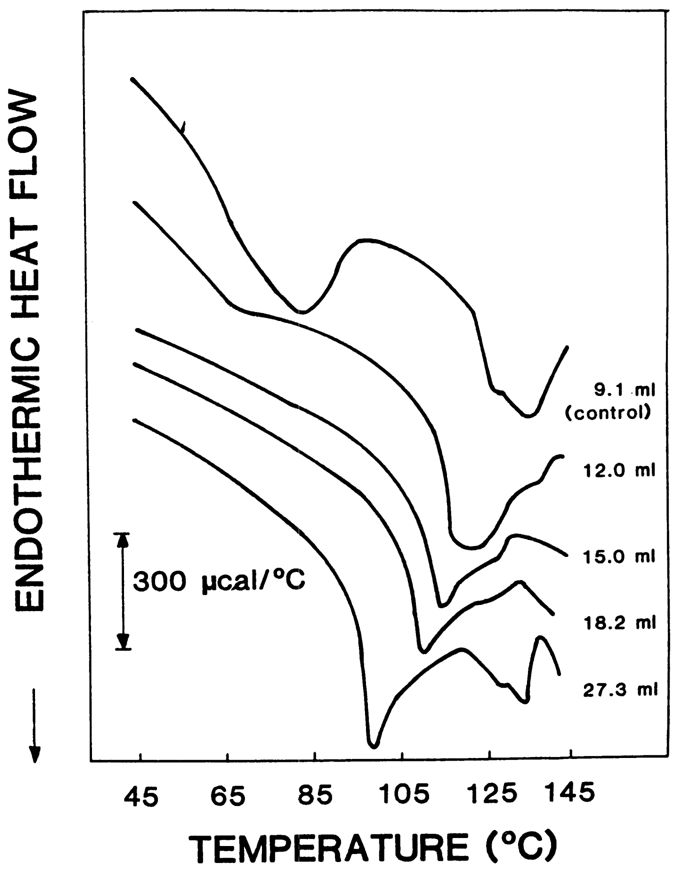

Fig. 4. Effect of water level on gelatinization temperature of starch in cookie doughs containing no fat and no NH_4HCO_3.

sugar (30%), there was more water per gram of sugar (sugar concentration was lower). At the lowest sugar concentration, starch was gelatinized at a lower temperature when compared to the gelatinization temperature for high sugar levels. Percent sucrose and onset temperatures, respectively, were: 30%, 98°C; 40%, 108°C; 50%, 111°C; 60%, 117°C.

The sugar–water ratios in both of the above experiments change in the same direction. The major difference in the two experiments is that the total amount of sugar to water in Fig. 4 is more than in Fig. 5. Clearly, although the sugar–water ratio (sugar concentration) is important, the total amount of sugar–water is not important in determining the temperature of starch gelatinization.

Thermal Transition of Cookies Before and After Baking

To determine the amount of starch gelatinized during baking, cookies were ground, lyophilized, and analyzed by the DSC with an excess of water. Two endotherms were obtained as shown in Fig. 6. Defatting cookies with petroleum ether caused the fat-melting peak to disappear. After the endotherms were obtained, the sample was cooled and reheated. The sample no longer showed a gelatinization transition. These observations indicate that the two peaks were fat-melting and starch-gelatinization endotherms.

Cookies made from flours milled from seven wheat cultivars were mixed with excess water and evaluated by DSC (data not shown). Similar thermograms (at the same water–flour ratio) were obtained from raw cookie dough prepared from the same flours. Analysis of variance showed no significant difference in enthalpy of starch gelatinization between raw cookie dough and baked cookies. This finding agrees with previous reports of little or no starch gelatinization in sugar cookies (Hoseney et al 1977, Lineback and Wongsrikasem 1980, Varriano-Marston et al 1980).

TABLE I
Effect of Water Levels on the Onset Temperature of Cookie Dough

Water Level		Onset Temperature (0°C)
Percent	Milliliters	
22.75	9.1	117
30.00	12.0	109
37.50	15.0	107
45.50	18.2	101
68.27	27.3	91

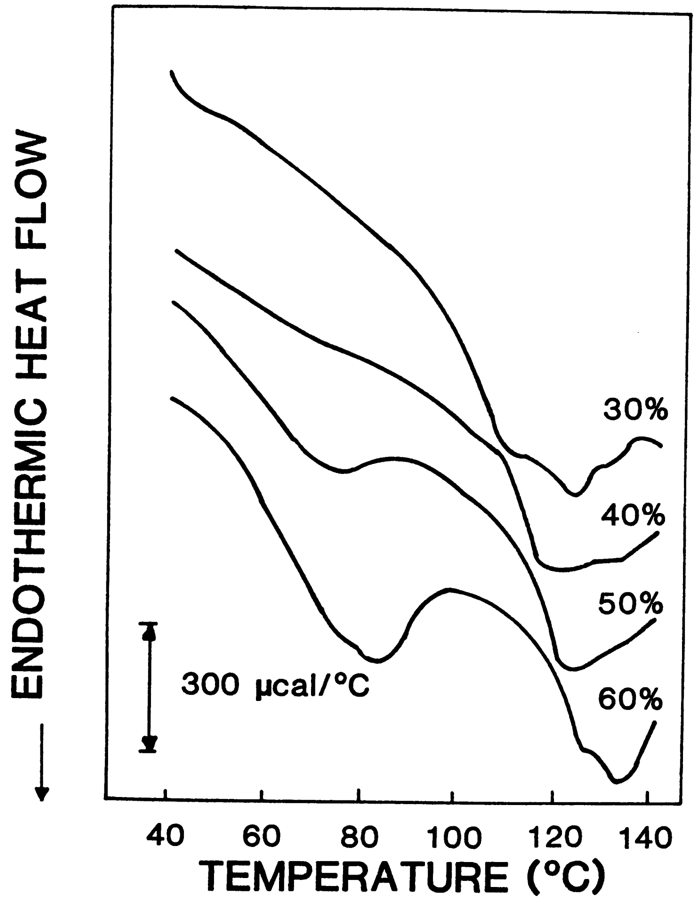

Fig. 5. Effect of sugar level (percent based on flour weight) on starch gelatinization of cookie dough.

Significance of the Findings

The discovery of a fat-melting peak was expected. The sugar-dissolving peak, which was also expected, emphasizes that only part of the sucrose dissolves during cookie dough mixing. The presence of crystalline sucrose in cookie dough during the early stages of baking appears to be important functionally, and is a major difference between sucrose and liquid sweeteners.

The finding that starch gelatinization occurs at temperatures well above 100°C also appears important. DSC measurements were made in sealed pans, so no water was lost; considerable water is lost, however, during baking of cookies. It is therefore not surprising that no starch gelatinization was found in this type of cookie.

From the data presented, the DSC appears to be a useful instrument in following certain changes that occur when cookie doughs are heated.

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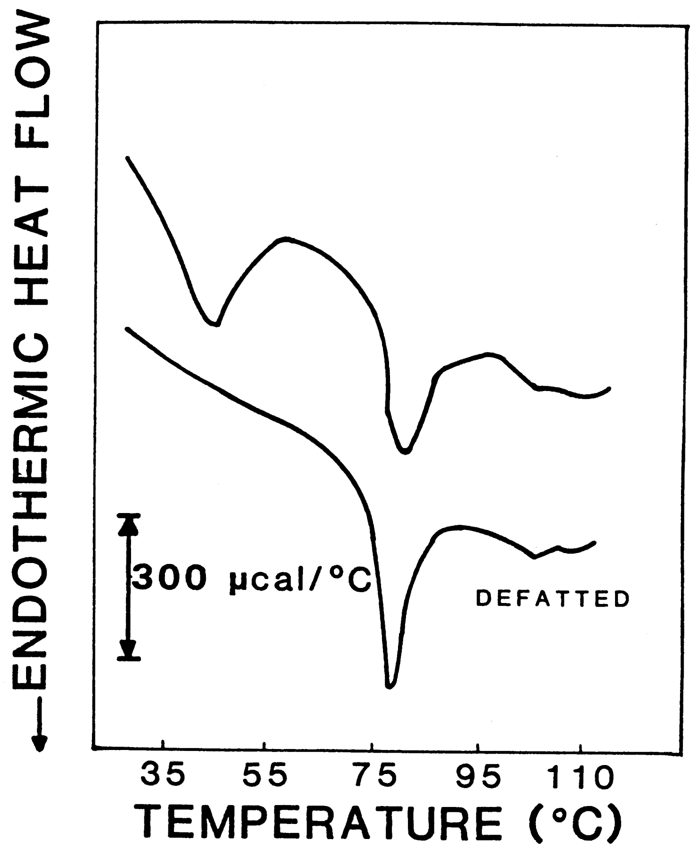

Fig. 6. DSC thermograms (excess water) of ground baked cookies. Top curve = nondefatted; bottom curve = defatted.

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