

# Effect of Sugars on Starch Gelatinization<sup>1</sup>

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## ABSTRACT

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As the concentration of sugar in sugar-flour-water solutions was increased, the gelatinization temperature of the starch also increased. The gelatinization-delaying characteristics of a sugar solution were shown to be related to the water activity of the solution and to the molecular size of the sugar. As the water activity of a sugar solution decreased, gelatinization temperature of starch in the solution increased. But at equal water activities,

not all sugars delayed gelatinization to the same extent. Sugars with longer chain lengths delayed gelatinization more than did shorter-chain sugars. Starch-sugar interactions may play a role in delaying starch gelatinization. Interaction of sugar with starch chains in the amorphous regions of the starch granule stabilizes those regions, thus increasing the energy required for gelatinization.

The rising cost of sugar and the increased availability of corn syrups have raised interest in the substitution of corn syrup for sucrose in bakery items, especially in such high-sugar items as cakes. To satisfactorily replace sucrose in cakes, corn syrup must perform most of the same functions as sucrose in the cake system. An important function is the control of starch gelatinization.

Sucrose delays the start of the gelatinization process (Bean and Osman 1959, Bean and Yamazaki 1978a, D'Appolonia 1972, Derby et al 1975, Miller and Trimbo 1965). At the concentration used in cakes (55-60%), sucrose delays gelatinization of starch from 57 to 92°C (Bean and Yamazaki 1978a). The effects of different sugars on gelatinization vary (Bean and Osman 1959, Bean and Yamazaki 1978b, Koepsel and Hosney 1980, Savage and Osman 1978). In general, monosaccharides delay gelatinization less than disaccharides, except maltose, which acts like a monosaccharide (Savage and Osman 1978). Sugar's ability to limit the water available to the starch is thought to delay gelatinization (D'Appolonia 1972, Derby et al 1975, Hosney et al 1977), although Wootton and Bamunuarachchi (1980), who compared enthalpy values of starch gelatinization in sugar solutions, think other factors may be involved. The exact mechanism by which sugar delays starch gelatinization is unclear, so we studied some of its possible mechanisms.

## MATERIALS AND METHODS

### Flour

Pillsbury's "Supercake," a chlorinated soft wheat flour (8.9% protein, 0.42% ash, pH 4.6) was used.

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### Sugars

Reagent grade sugars were used in all chemical studies.

### Gelatinization Temperature

The gelatinization temperature was determined with a Kofler hot-stage microscope. To prevent moisture loss during heating, we placed a single drop of the desired sugar solution (0.5% flour) under a coverslip having edges coated with Vaseline. The temperature was raised at approximately 2°C/min. The gelatinization temperature was designated as the temperature at which 50% of the granules had lost birefringence.

### Water Activity

Water activity (*A<sub>w</sub>*) was measured with a Beckman water activity meter, with a 75-100% rh module. For the measurements at 25°C, the sensor was covered with a cardboard box to prevent airflow from changing the temperature of the sensor too rapidly. The sensor was placed in a laboratory oven for the measurements at 50°C. In both cases, at least 1 hr elapsed before the sensor equilibrated, after which readings were taken.

### Differential Scanning Calorimetry

A Perkin-Elmer DSC-2 with an Intracooler II and Scanning Autozero was used for bound-water and certain gelatinization measurements. In both methods, a heating rate of 10°C/min was used. A sensitivity of 1 mcal/sec and a chart speed of 20 mm/min were used in the determination of gelatinization phase transitions. For the bound-water determinations, the sugar solutions were placed in aluminum pans, sealed, weighed, cooled to -60°C, and then heated from -60 to 10°C. The  $\Delta H$  was compared with that of pure water to determine the free (freezable) water. Bound water was calculated by subtracting the free water content from the total water content of the system. A sensitivity of 10 mcal/sec and a chart speed of 80 mm/min were used to determine freezable water. In both cases, an empty pan was used as the reference.

For the gelatinization measurements, the flour-water-sugar

samples were mixed in vials beforehand; a slurry was transferred to an aluminum pan and the pan sealed to prevent moisture loss. The pan was weighed after sealing to determine sample weight and was heated from 17 to 107°C.

## RESULTS AND DISCUSSION

### Sugars and Gelatinization Temperature

The effects of several sugars on the gelatinization temperature (50% loss of birefringence) of starch are shown in Fig. 1. Various sugars delay gelatinization to different extents. At low concentrations, little difference is found between the effects of the various sugars. At high concentrations, however, the gelatinization-delaying effects of various sugars differ significantly.

No clear-cut pattern is apparent in the sugars' effect on starch gelatinization. For example, the effect is not based on molecular size; maltotriose (a trisaccharide) delays gelatinization less than sucrose does but more than maltose (both disaccharides). Chemical composition does not appear to be the factor governing gelatinization; gentiobiose and maltose exhibit different gelatinization-delaying characteristics although they differ only in the linkage of their glucose units (maltose,  $\alpha$ -1:4; gentiobiose,  $\beta$ -1:6).

### Gelatinization and Bound Water

The delay of starch gelatinization in sugar solutions has been attributed to sugar's ability to limit the availability of water to starch (D'Appolonia 1972, Derby et al 1975, Hosoney et al 1977). When sugar is placed in water, it binds some of the water and thus lowers the amount of free water in the system.

The bound (unfreezable) water of sugar solutions was measured with differential scanning calorimetry (DSC). Plotting bound water in a sugar solution versus the solution's gelatinization temperature (Fig. 2) shows that as the amount of bound water increases, the gelatinization temperature of starch also increases. The curves, however, are almost identical to those for sugar concentration versus gelatinization temperature in Fig. 1. Thus the increase in gelatinization temperature with the increase in bound water may be simply coincidental, with some other property of the sugar solution controlling starch gelatinization.

DSC curves of starch in sucrose solutions seem to indicate that bound water in sugar solutions is not directly involved in

controlling the temperature at which starch gelatinizes. When starch is heated in excess water, DSC shows a single, sharp peak. When the water level is reduced, the height of the peak diminishes, but the peak still occurs at the same temperature. As the peak height diminishes, its base broadens and a second peak forms. If the

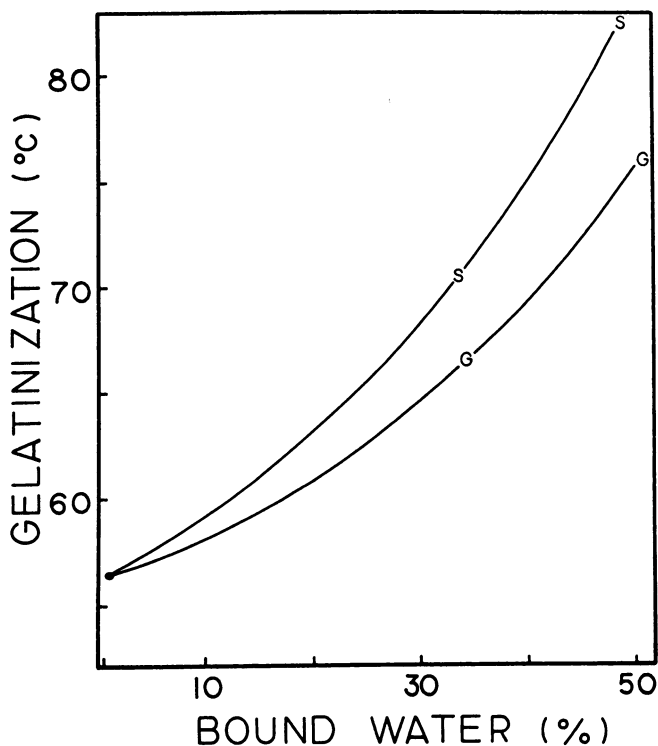


Fig. 2. Bound water versus gelatinization temperature. S = sucrose, G = glucose. Bound water was calculated by subtracting free (freezable) water from the total water of the system and converting to percentage.

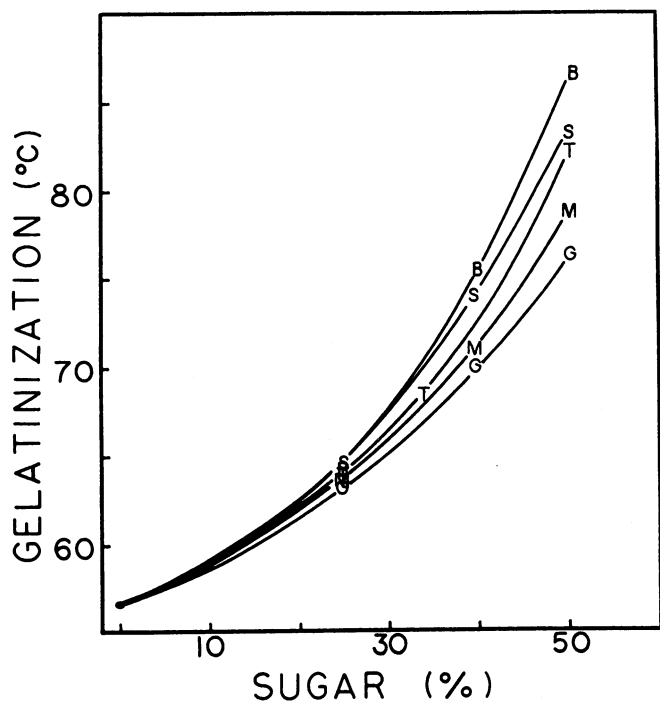


Fig. 1. Sugar concentration versus gelatinization temperature. B = gentiobiose, S = sucrose, T = maltotriose, M = maltose, G = glucose.

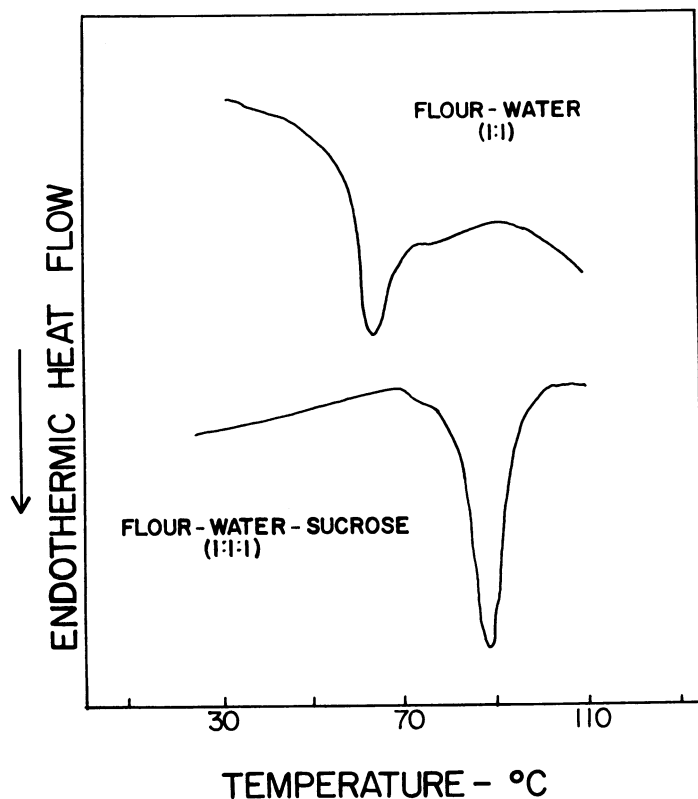


Fig. 3. Differential scanning calorimetry of flour:water and flour:water:sucrose.

water level is reduced further, the first peak eventually disappears. While that is happening, the second peak continues to grow, and shifts to a higher temperature (Donovan 1979). Thus, reducing the amount of free water by binding part of the total water to sugar should not delay starch gelatinization.

In addition, if the higher gelatinization temperature of starch in sugar solutions results from the sugar binding the water and the resulting limitation of available water, then DSC curves should show the second peak emerging when sugar is added. But that does not occur (Fig. 3); instead, the first peak shifts to a higher temperature. In fact, instead of broadening, the base of the peak narrows somewhat when sucrose is added. That indicates more available water, rather than less. Perhaps the water binding by the sugar increases the amount of water available to the starch during the gelatinization process.

#### Aw and Gelatinization

If sugar's ability to delay starch gelatinization does not result from its water-binding capacity, then why does it delay gelatinization? When sugar, or any small solute, is added to water, it affects the thermodynamic properties of the water. This, in turn, affects the water's ability to interact with other components in the system (Labuza 1975). If the reactivity of the water is lowered, then chemical and physical reactions involving water will require more energy. Thus, the higher gelatinization temperatures of starch in sugar solutions may result from the lower reactivity of the water in the solutions.

One method of measuring the water's reactive ability in a solution is to determine the  $A_w$ , ie, the ratio of the vapor pressure of the solution to the vapor pressure of pure water, which indicates the chemical potential of the water. As  $A_w$  decreases, the chemical

potential of the water decreases, which should also cause the gelatinization temperature of starch to increase in that solution.

Figure 4 shows the relationships of  $A_w$  and gelatinization temperature for starch in various sugar solutions. In all the sugar solutions, as  $A_w$  decreases, gelatinization temperature increases, but not at the same rate. At equal  $A_w$ s, sucrose delays gelatinization more than glucose does and less than maltotriose does.

A small solute like salt (NaCl) would also be expected to decrease  $A_w$  and delay gelatinization (Fig. 5). At equal  $A_w$ s salt delays gelatinization much less than does sucrose. This provides additional evidence that some factor other than  $A_w$  controls starch gelatinization in sugar solutions.

Two possible reasons for the difference in the abilities of various sugars to delay gelatinization are: 1) changes in  $A_w$  with increasing temperature and 2) some factor, other than  $A_w$ , also affecting starch gelatinization.

$A_w$ s of the sugar solutions were measured at 25°C. As the temperature is increased, the  $A_w$ s of the sugar solutions may change, at different rates for different sugar solutions. If the  $A_w$ s of the sugar solutions change at different rates, as the temperature approaches the gelatinization temperature of starch, perhaps the various sugar solutions have the same  $A_w$ .

To determine if such changes do occur, we also measured the  $A_w$  at 50°C. The results (Table I) show that even though  $A_w$  changes slightly with temperature, it changes by the same amount in both sugar solutions.

#### Starch-Sugar Interactions

$A_w$  affects starch gelatinization but does not appear to be the only factor delaying starch gelatinization in sugar solutions. Brown and French (1977) have shown that starch oligosaccharides are bound in the gel phase of starch granules. Such binding between starch chains by sugars in the amorphous regions of the granule may stabilize those areas and delay gelatinization.

#### Sugar-Bridge Effect on Starch Gelatinization

Perhaps sugar's ability to link starch chains together affects the gelatinization temperature of the starch granule. The formation of bridges between starch chains in the amorphous regions of the granule may stabilize those areas and delay gelatinization.

Donovan (1979) described the gelatinization process as "stripping" the crystalline regions of the starch granule. The chains in the amorphous areas exhibit limited flexibility when the granule

TABLE I  
Effect of Temperature on Water Activity of Sugar Solutions

Sugar Solution	Water Activity at	
	25°C	50°C
Sucrose		
50%	0.912	0.890
33%	0.945	0.931
Glucose		
50%	0.842	0.829
33%	0.928	0.910

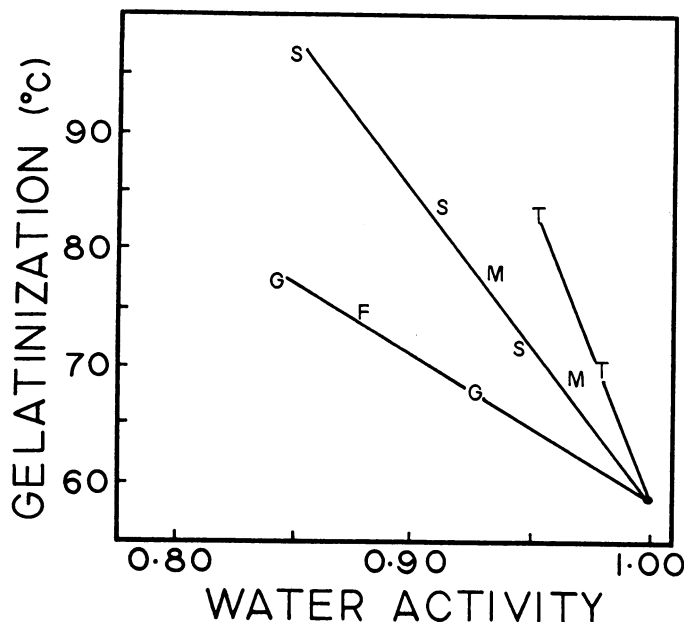


Fig. 4. Water activity of sugar solutions versus gelatinization temperature. F = fructose, G = glucose, M = maltose, S = sucrose, T = maltotriose.

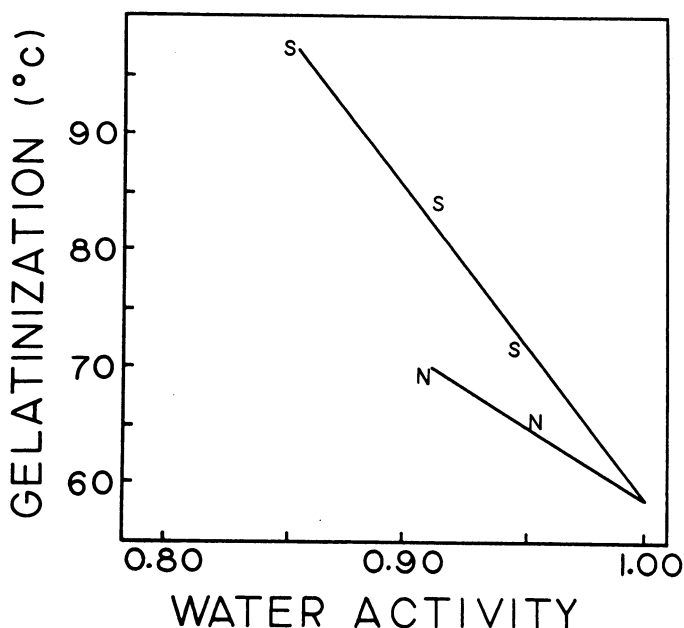


Fig. 5. Solution water activity versus gelatinization temperature. N = NaCl, S = sucrose.

is placed in water. If the system is heated, the chains become more energetic and move around more. Their movement in the amorphous regions imparts a strain on the points where they are tied together—the crystalline regions. If the temperature is raised enough, a point is eventually reached where the strain on the crystallites is great enough to pull them apart. That would be the gelatinization temperature of the granule.

In that model of the gelatinization process, flexibility of the chains in the amorphous areas would directly affect the gelatinization temperature of the granule. If the chains in the amorphous regions were tied together, their flexibility would be restricted. More energy would be required before the chains' movement could pull the crystallites apart, and that would increase the gelatinization temperature.

#### Effect of Sugar Chain Length

Figure 4 shows that the longer the sugar molecule is (up to a trisaccharide), the greater the delay in gelatinization is at a specific  $A_w$ . Also, within a specific molecular class (monosaccharide, disaccharide, etc.), all the sugars tested exhibited the same relationship between  $A_w$  and gelatinization temperature. Such a relationship would be expected if the only factor, other than  $A_w$ , governing the gelatinization of starch in sugar solutions were the size of the sugar molecule. Brown and French (1977) have shown that, of the oligomers they tested ( $G_3$  through  $G_7$ ), maltotetraose gave maximum absorption.

#### Proposed Role of Sugars in Controlling Starch Gelatinization

Sugar delays gelatinization through a combination of two independent mechanisms: 1) lowering  $A_w$  of the solution, and 2) interacting with starch chains to stabilize the amorphous regions of the granule.

When sugar is added to a starch-water system, it lowers the  $A_w$ , which decreases the chemical potential of the water in the system; then reactions involving water require more energy than they would in pure water. The increased energy requirement results in a higher gelatinization temperature for starch.

In addition, sugar delays gelatinization by interacting with starch. Sugar molecules will bond with starch chains in the amorphous regions of the granule, thus effectively producing interactions between the starch chains. Longer sugar molecules can bridge more gaps between chains and thus produce more links than shorter sugar molecules can. Kainuma and French (1972) have shown that X-ray patterns for potato starch are more crystalline after being dried with a starch syrup. Bridges between chains restrict the flexibility of the chains, thus requiring more energy to

“strip” the crystallites. As more links are formed, flexibility is more restricted, and more energy is required to pull the crystallites apart. The increased energy requirement results in an even higher gelatinization temperature for starch.

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