

Effect of Soluble Sugars on Gelatinization and Retrogradation of Sweet Potato Starch

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The effect of water-soluble sugars contained in sweet potato on gelatinization and retrogradation of starch was studied by means of differential scanning calorimetry. Gelatinization peak temperature T_p and gelatinization enthalpy increased with increasing sugar concentration. The shift of T_p to higher temperatures was attributed to the stabilization of the crystalline region in starch and the immobilization of water by sugar molecules. The effect is larger in the order sucrose, glucose, fructose. All these sugars prevent retrogradation of sweet potato starch paste, and the order of effectiveness is the same as in the case of increase in gelatinization temperature. The effect of sucrose concentration on T_p was explained by a zipper model approach.

INTRODUCTION

One of the important characteristics of sweet potato (*Ipomoea batatas*) in food processing and cooking is "sweetness", which comes from water-soluble sugars. Taira and Yasui (1987) examined the content of water-soluble sugars for eight varieties of Japanese sweet potatoes, and the results are shown in Table I. The content of soluble sugars was found to be about 20% starch. Sucrose is the main component of the sugars, while glucose and fructose are minor components (Taira and Yasui, 1987; Van Den et al., 1986). When sweet potatoes are processed or cooked, these sugars should have influence on gelatinization or retrogradation properties of starch. We have studied gelatinization and retrogradation properties from the viewpoint of effect of water-soluble sugars in the present work.

Since sugars influence strongly the quality of baked products such as cakes or breads, effects of sugars on gelatinization and retrogradation of wheat starch have been studied by many techniques: differential scanning calorimetry (DSC) (Wootton and Bamunuarachchi, 1980; Spies and Hosney, 1982; Slade and Levine, 1987), loss of birefringence (Bean and Yamazaki, 1978; Bean et al., 1978; Spies and Hosney, 1982), rheological studies including amylography (D'Appolonia, 1972; Bean and Yamazaki, 1978; Bean et al., 1978; Cheer and Lelievre, 1983), and nuclear magnetic resonance (NMR) (Hansen et al., 1989). Sugars are known to function as antistaling ingredients (Slade and Levine, 1987). It is well-known that sugar prevents staling of rice cake and shifts the gelatinization temperature to higher temperatures. Some researchers reported that enthalpy of gelatinization of starch decreased with the addition of sucrose (Wootton and Bamunuarachchi, 1979; Chungcharoen and Lund, 1987). These confectionery systems contain sugar of very high concentration. Such a system may not contain sufficient water, which is necessary for gelatinization of starch. Although the content of water-soluble sugars in sweet potato is about 10% in dry matter, it may change the properties of the starch, and so it is also important to study the effect of sugars of low concentration on gelatinization and retrogradation. Cheer and Lelievre (1983) reported that the viscosity, yield stress, and rigidity of a several percent wheat starch paste showed maxima at the sucrose concentration of about 20%. The viscosity maxima at 20% concentration of various sugars were also observed by Bean and Osman (1959). In the present study, DSC measure-

ment has been carried out to clarify the effect of sugars on the gelatinization and retrogradation of sweet potato starch in a wide concentration range of sugars. DSC study makes it possible to determine the gelatinization temperature and the heat of gelatinization (Shiotsubo and Takahashi, 1984) and also to analyze the retrogradation process at a molecular level (Roulet et al., 1988). Though there have been a few DSC studies on sweet potato starch (Wada et al., 1979; Kitada et al., 1988), the interaction between starch and other components of sweet potato has not yet been examined.

MATERIALS AND METHODS

Materials. Sweet potato starch and sugars were purchased from Wako Chemicals Industries Ltd. and used without further purification. Moisture content of the starch was determined as 16% by heating at 105 °C for 5 h at 10^{-2} mmHg. Water was distilled by using a glass apparatus.

Differential scanning calorimetry (DSC) measurement was carried out by use of a differential scanning calorimeter (SSC580 with DSC10 module, Seiko Electronics Co. Ltd.). Sweet potato starch and sugar solution were directly weighed into a silver pan of 70 μ L and the pan was sealed hermetically. A pan containing the equal amount of water was used as a reference. The temperature was raised from room temperature to 130 °C at the heating rate of 1.0 °C/min. The temperature and enthalpy of gelatinization were determined from the endothermic peak temperature and the peak area, respectively. After the first run heating, the pan was quenched immediately from 130 to 5 °C and then stored at 5 °C for various periods. The temperature was raised from 5 to 120 °C at the same heating rate in the second run.

The peak temperature (T_p) and the area of the gelatinization peak/mg of starch (ΔH) were found independent of starch concentration for lower starch concentrations (<40 w/w %) in a preliminary work. A similar tendency was found for rice starch at lower concentrations (<50 w/w %) (Biliaderis et al., 1986). The retrogradation might proceed faster in the system with high starch concentration. Sweet potato starch (20 mg) and about 40 mg of sugar solution were put in a DSC pan, so that starch concentration might become 33 w/w % in the present work.

RESULTS AND DISCUSSION

Typical heating DSC curves of 33 w/w % sweet potato starch in sucrose solutions are shown in Figure 1 for various sucrose concentrations. The heating DSC curves were more symmetrical for lower sucrose concentrations (<20 w/w %) as observed in a starch-water system whose starch concentration was lower than 40% (Shiotsubo and Ta-

Table I. Carbohydrate Contents of Various Sweet Potatoes (Taira and Yasui, 1987)

variety	carbohydrate	starch	fructose	glucose	myo-inositol	sucrose	soluble sugar
Okinawa-20go	89.7	66.75	1.48	1.80	0.15	11.83	15.26
Koganesengan	91.3	72.61	0.42	0.50	0.16	10.68	11.75
Tamayutaka	90.6	71.83	2.88	3.96	0.21	4.33	11.38
Beniazuma	93.6	76.96	0.36	0.44	0.18	8.56	9.55
Benikomachi	92.2	75.83	1.65	1.94	0.17	5.69	9.45
Kanto-93go	91.2	76.86	1.24	1.55	0.12	5.26	8.17
Kanto-98go	94.0	78.53	1.43	1.87	0.16	5.48	8.94
IP-2-3-82-3	91.7	75.00	0.30	0.31	0.14	9.38	10.13

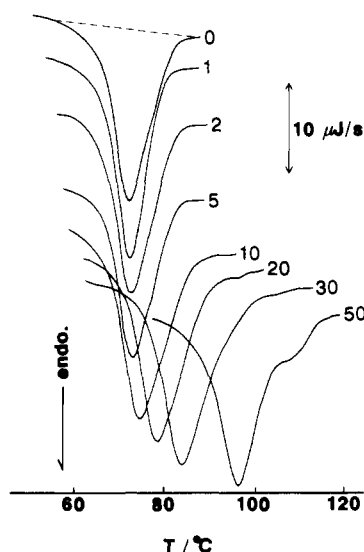


Figure 1. Heating DSC curves of 33 w/w % sweet potato starch in sucrose solution. Heating rate: 1 °C/min. Figures at the right of each curve represent sucrose concentration in w/w %.

kahashi, 1984; Biliaderis et al., 1986). Shiotsubo and Takahashi also reported from differential thermal analysis of 17 w/w % potato starch that T_p shifted to higher temperatures with increasing heating rate but it was independent of heating rate below 1 °C/min. According to these authors, if the endothermic curve was symmetrical and the heating rate was slow enough to provide information about equilibrium state, the gelatinization temperature determined from T_p was believed to have the meaning that half of the starch specimen has been gelatinized at the temperature T_p . Determination of the gelatinization temperature from DSC heating curves is often based on its onset temperature at which the heating DSC curve begins to deviate from the baseline (Wada et al., 1979; Nakazawa et al., 1984). We use mainly the peak temperature T_p in the present work because it can be determined much more precisely than the onset temperature, and T_p does not depend on concentration of starch in the concentration range lower than 40 w/w % (Shiotsubo and Takahashi, 1984). The T_p of sweet potato starch was reported as 76.9 °C by Wada et al. (1979) and as 72.5–74.3 °C by Kitada et al. (1988). These were higher than our value (72.4 °C), presumably since both of the other studies adopted a faster heating rate (5 °C/min) than ours (1 °C/min). In addition to this, in the work of Wada et al. (1979) the starch concentration seems much higher than 40%, although they did not determine the starch concentration precisely.

Figure 1 shows that the peak temperature together with the onset temperature (T_o) and the final temperature at which the endotherm returned to the baseline (T_f) shifted to higher temperatures with increasing sucrose concentration. Since the peak became broader and more asymmetric with increasing sucrose concentration, neither T_o nor T_f shifted parallel with the peak temperature T_p .

Wootton and Bamunuarachchi (1980), however, reported that T_o and T_f were not affected by the increase of sucrose concentration up to 45%. Another small peak or shoulder appeared at higher temperatures in a DSC curve for a starch–sucrose–water system with sucrose concentration higher than 20 w/w %. Peak broadening at higher temperatures and the appearance of small peaks might be induced by the lack of water for the gelatinization.

As in a fringed-micelle model which has been used for partially crystalline polymers (Wunderlich, 1981), starch consists of somewhat crystalline regions and somewhat amorphous regions. Gelatinization of starch is considered to be a process in which the crystalline region is changed into an amorphous region, as observed by birefringence (Bean and Yamazaki, 1978; Bean et al., 1978; Spies and Hoseney, 1982) or X-ray diffraction (Miles et al., 1985; Roulet et al., 1988) measurements. Recently, the endothermic peaks in DSC curves for the gel–sol transition of thermoreversible gels were explained by using a zipper model (Nishinari et al., 1990). The disappearance of the crystalline region in starch–water systems may be assumed as the opening process of molecular zippers. Each molecular zipper consists of N parallel links that can be opened from both ends. The starch–water system can be assumed to consist of N single zippers. According to this treatment, the heat capacity C of such a system is given by

$$\frac{C}{k} = \mathcal{N} \left(\log \frac{G}{x} \right)^2 \left[\frac{2x}{(1-x)^2} + \frac{N(N+1)x^N[-x^{N+1} + (N+1)x - N]}{[1 - (N+1)x^N + Nx^{N+1}]^2} \right] \quad (1)$$

where k is the Boltzmann constant, G is the degree of rotational freedom of a link, and $x = G \exp(-E/\tau)$, where E represents the energy required to open the link and τ is the product of k and the absolute temperature. Assuming the order of magnitude for the energy E as $2300k$, which is the approximate value for hydrogen-bonding energy, and the number of links N as 100, we could fit the calculated curve using eq 1 to the experimental DSC heating curve (Figure 2). From this curve fitting, we obtained the rotational freedom of a link G for gelatinization curves for starch–water systems with various concentrations of sucrose. Results are shown in Table II. As is seen clearly from Table II, G decreased with increasing concentration of sucrose. Since hydrogen bonds may be newly created by the addition of sucrose, and the mobility of links will decrease, this is quite reasonable. Of course, the fitting of experimental curve cannot be carried out perfectly because starch is polydisperse and there must be the distribution of the number of links N and of the energy E . The calculated curve obtained by using only one set of N , E , and G values is too sharp for an experimental curve. However, as a first approximation, we could find values of G by assuming reasonable N , E , and N values, and as a result G was found to be a decreasing function of sugar concentration. Experimental DSC curves for gelatinization became broader with increasing sucrose

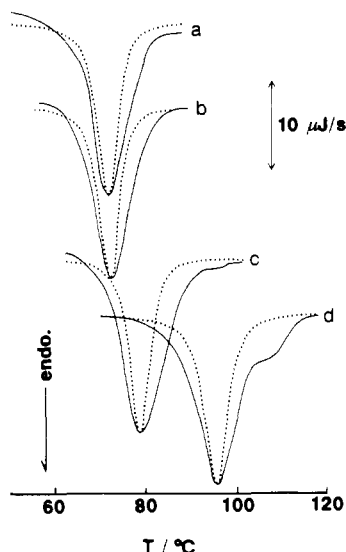


Figure 2. Examples for observed heating DSC curves (solid lines) and the best-fitted calculated curves (dotted lines) using eq 1. Starch content: 33 w/w %. Heating rate: 1 °C/min. (a) Sucrose 0 w/w %, $G = 760$, $N = 10\ 800$; (b) sucrose 2 w/w %, $G = 740$, $N = 10\ 800$; (c) sucrose 20 w/w %, $G = 685$, $N = 11\ 200$; (d) sucrose 50 w/w %, $G = 490$, $N = 12\ 000$.

Table II. Relationships between the Degree of Rotational Freedom G and Sucrose Concentration Calculated by Equation 1 with $E = 2300k$ and $N = 100^a$

sucrose concn, wt %	G	sucrose concn, wt %	G
0	760	10	725
1	744	20	685
2	740	30	620
5	735	50	490

^a N was chosen so that the calculated curves fit best with observed heating DSC curves.

concentration. This may be interpreted as follows: the distribution of the energy required to open the link E and the rotational freedom of a link G will become broader as a result of newly created hydrogen bonds by the addition of sucrose.

Figure 1 shows that the gelatinization temperature shifted to higher temperatures with increasing sucrose concentration. A similar tendency was observed in the presence of glucose or fructose as shown in Figure 3. T_p shifted to higher temperatures in the following order: sucrose > glucose > fructose. The order is the same as reported by Slade and Levine (1987) for the system that contains starch, sugar, and water in the same amount. The amount of water immobilized by sugars was in the following order: sucrose > glucose > fructose. Sugar concentrations in the edible part of sweet potato are nearly 10–20% of starch (Taira and Yasui, 1987), that is, several percent of sugars to 33% starch. Even such a small amount of sugars can increase the gelatinization temperature. There are two possible reasons for the increase in T_p by the addition of sugar. (1) Hydration of sugar molecules decreases the effective water, which is equivalent to the effect that starch concentration becomes higher. (2) Interaction of sugar molecules with molecular chains in starch stabilizes the crystalline region of starch. The experimental findings, that T_p and the gelatinization enthalpy (ΔH_1) of the first run DSC heating do not depend on starch concentration in water-rich condition, suggest that the first factor is less important at least when sugar concentration is low. The dynamic hydration numbers, which is the number of water molecules in the hydration cosphere, of sucrose, glucose, and fructose are 25.2, 18.6,

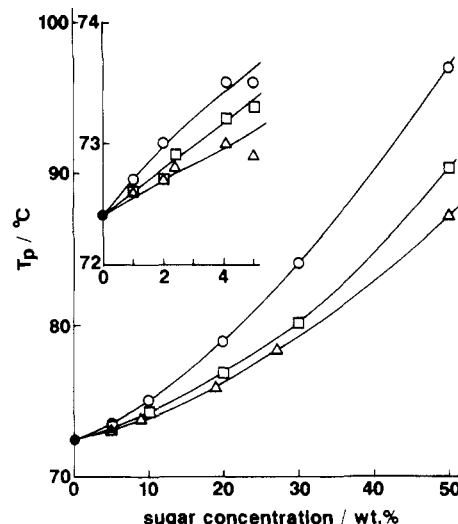


Figure 3. Peak temperature T_p as a function of sugar concentration. Starch content: 33 w/w %. Solvent: O, sucrose; □, glucose; Δ, fructose. (Inset) Magnification at low sugar concentration range.

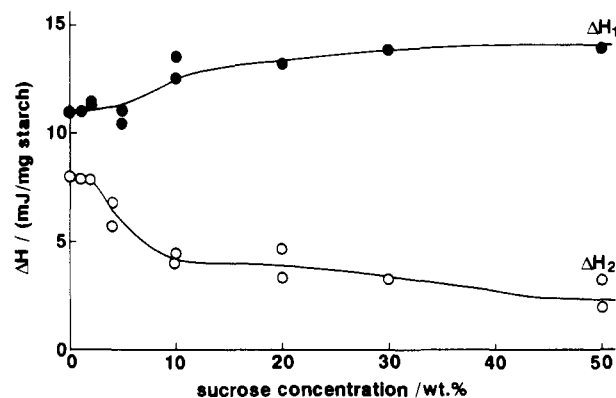


Figure 4. Relationships between heat of gelatinization per milligram of starch and sucrose concentration for 33 w/w % sweet potato starch. ●, First run; ○, second run after 14 days of storage at 5 °C.

and 16.5, respectively (Uedaira et al., 1989). The water which forms the cosphere of sugar becomes 1.65, 1.86, and 1.33 g/g of sugar. As was mentioned above, T_p was found to be almost independent on starch concentration below 40 w/w %. The quantity of water involved in the cosphere of sugars cannot increase the effective concentration of starch higher than 40 w/w %. Therefore, hydrated water by the sugar of low concentration is not enough to increase gelatinization temperature by the immobilization of water molecules.

The gelatinization enthalpy (ΔH_1) of the first run DSC heating increased with increasing sugar concentration up to 10% as illustrated with solid circles in Figure 4. Our findings are different from those of Wootton and Bamunuarachchi (1980) and Chungcharoen and Lund (1987), who found that sucrose decreased gelatinization energy. When sugar concentration is low, the system contains sufficient free water for gelatinization. The increase of T_p and ΔH_1 suggests that the crystalline region of starch is stabilized by sugar at low sugar concentrations. When sugar concentration becomes higher than a level at which available water begins to lack in the system, i.e., the effective starch concentration exceeds 40 w/w %, the gelatinization energy ΔH_1 ceased to increase. The endothermic peak temperature of the system with insufficient water shifted to higher temperatures, and the peak became broader with decreasing water content. At a certain water

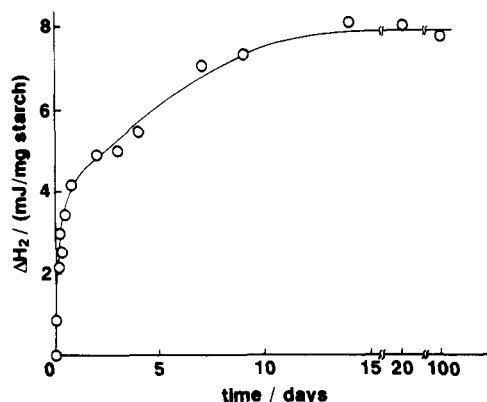


Figure 5. Time dependence of regelatinization energy for 33 w/w % sweet potato starch. DSC pan was stored at 5 °C after the first run.

level, the second small peak or a shoulder appeared at a higher temperature than the main endothermic peak temperature. These phenomena were observed when sucrose concentration exceeded 20 w/w % (Figure 1). Since the hydration number of sucrose is reported as about 6.5 (moles of water/mole of sugar) (Bociek and Franks, 1979), the hydrated water corresponds to about 7 w/w % in 20 w/w % sucrose solution. Then, nonhydrated water is nearly 73 (=80 - 7) w/w % in 20 w/w % sucrose solution and is about 29 mg (=40 mg × 0.73) in each DSC pan used in our experiment. The ratio of starch to nonhydrated water is 20:29, which is nearly the same starch concentration (40 w/w %) below which T_p and ΔH_1 are independent of starch concentration in a starch-water system. Therefore, the shift of peak temperature to higher temperatures at lower sucrose concentration than about 20 w/w % is mainly attributed to stabilization of the starch crystalline region by sugar. The increase of viscosity, yield stress, and rigidity observed in starch-sugar systems (Bean and Osman, 1959; Cheer and Lelievre, 1983) might be caused by the same mechanism of stabilization. In the system which contains sugar of higher concentration, sugar does not seem to stabilize so much the crystalline region of starch because the ΔH_1 did not increase with increasing sucrose concentration beyond 20 w/w % as shown in Figure 4 (solid circles). The lack of effective water owing to hydration of sugar molecules becomes the dominant factor to increase gelatinization temperature beyond the sucrose concentration 20%.

The heat required for regelatinization (ΔH_2) of 33 w/w % sweet potato starch as a function of storage time is shown in Figure 5. The degree of retrogradation which was estimated by the area of the endothermic peak at the second run tended toward the saturated value after 14 days of storage at 5 °C for 33 w/w % starch. Saturated regelatinization energy of the starch was about 73% of gelatinization energy (ΔH_1) which was required for the first run DSC heating. Since amylose did not show any heat flow in heating DSC measurement, the endothermic peak was attributed to the gelatinization of amylopectin. According to Miles et al. (1985), the retrogradation process of starch consists of two crystallization stages. In the first stage, the fast development of gel structure and crystallinity in starch gels was found to be dominated by amylose gelation. In the first stage, the shear modulus and the X-ray peak intensity for amylose and starch gels did not decrease by heating. Therefore, this stage cannot be detected by DSC measurement. In the second stage, the crystallinity in starch gels continues to develop slowly, mainly in amylopectin. This was related to the endothermic peak in the second run DSC heating and to the slow

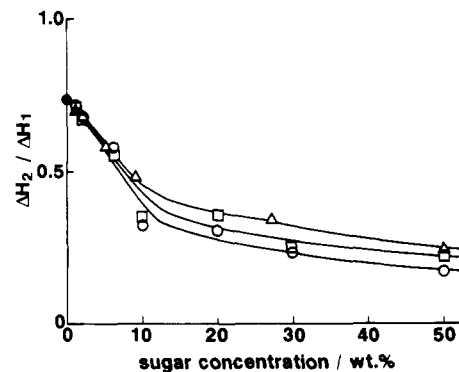


Figure 6. Retrogradation ratio ($\Delta H_2/\Delta H_1$) for 33 w/w % sweet potato starch as a function of sugar concentration. O, Sucrose; □, glucose; Δ, fructose.

development of the shear modulus. This change was thermally reversible: The X-ray peak intensity and the shear modulus fell, by heating, to the value just after the first stage. Since the DSC pan was sealed, amylopectin could not be decomposed. The smaller value of the saturated regelatinization energy than of the gelatinization energy suggests that some amylopectin granules crystallize thermoirreversibly.

In contrast with ΔH_1 , the heat required for regelatinization (ΔH_2) after storage for 14 days at 5 °C decreased with increasing sugar concentration (Figure 4). The retrogradation ratio was estimated by $\Delta H_2/\Delta H_1$ and plotted against sugar concentration in Figure 6. The retrogradation ratio decreased with increasing concentration of sugars. At low concentrations of sugars, the retrogradation ratio was not so different for three sugars. The retrogradation ratio decreased in the order sucrose > glucose > fructose at higher sugar concentrations. Slade and Levine (1987) reported that the extent of recrystallization of a 1:1:1 starch-sugar-water mixture after 8 days of storage at 25 °C increased in the order fructose > water alone > glucose > sucrose. Our results showed that fructose also prevents retrogradation, although it was not so effective as glucose and sucrose. The mechanism of retrogradation inhibition is considered as follows: Sugar molecules interact with starch molecular chains to stabilize the amorphous and entangled matrix of gelatinized starch (Spies and Hosney, 1982; Slade and Levine, 1987). Sucrose is more effective than glucose and fructose in the T_p increase. Low concentration of water-soluble sugars made the retrogradation of starch slower, so that the softness of cooked sweet potato may be durable.

ACKNOWLEDGMENT

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Registry No. Sucrose, 57-50-1; glucose, 50-99-7; fructose, 57-48-7; starch, 9005-25-8.