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A calorimetric investigation of the influence of sucrose on the gelatinization of starch

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The gelatinization of starch in the presence of low levels of water and high levels of sucrose was studied. The gelatinization temperature was found to increase in the presence of sucrose, whereas the gelatinization enthalpy was unaffected. The gelatinization temperature range was not as broad in the presence of sucrose as without sucrose. Furthermore, the shape of the gelatinization endotherm was changed by the addition of sucrose. The double endotherm obtained in limited-water/starch systems was changed into a single endotherm, similar to the endotherm obtained in excess-water/starch systems although at a higher temperature. To obtain this change in the shape of endotherm more sucrose was needed for a waxymaize starch than for maize starch or potato starch. The effect of sucrose, thus, seemed to be both to restrict the gelatinization and to make the gelatinization occur more easily. The first effect (temperature) was related to the discussion in the literature on the glass transition of starch. The second effect (shape of the endotherm) may be due to a lower local viscosity in the presence of sucrose, resulting in a shorter time interval necessary for the transitions to occur.

INTRODUCTION

The influence of sugars on the gelatinization of starch has been investigated by different techniques, for example light microscopy (Lelievre, 1973; Bean & Yamazaki, 1978), rheological measurements (D'Appolonia, 1972; Cheer & Lelievre, 1983), differential scanning calorimetry (DSC) (Wootton & Bamunuarachchi, 1980; Evans & Haisman, 1982; Chungcharoen & Lund, 1987), and electron spin resonance (ESR) (Johnson *et al.*, 1990). The different techniques show that the gelatinization temperature increases, and that the swelling of starch granules decreases in the presence of sugars. Furthermore, different sugars exert this effect to different extents, when compared on a molar basis. Sucrose is commonly reported to have a greater effect than other disaccharides (Savage & Osman, 1978).

At water-to-starch ratios in the range 10:1–2:1 the effect on the DSC endotherm of adding sucrose is an increase of the gelatinization temperature. Most workers report an increase in the onset (T_o), peak maximum (T_m) and conclusion (T_c) temperatures (Evans & Haisman, 1982; Kim *et al.*, 1986; Chungcharoen & Lund, 1987; Buck & Walker, 1988) whereas Wootton and Bamunuarachchi (1980) noticed an effect only on T_m. The enthalpy of gelatinization (ΔH) has been reported to be unaffected by the addition of sugars (Evans & Haisman, 1982), but increased as well as decreased values have also been reported (Wootton & Bamunuarachchi, 1980; Kim *et al.*, 1986; Chungcharoen & Lund, 1987; Buck & Walker, 1988). In these experiments the water levels have been fairly high, as indicated above, whereas the sugar levels have not been very high. For example, Chungcharoen and Lund (1987) used a sucrose-to-starch ratio of 0·4:1 and Buck & Walker (1988) used a sucrose-to-starch ratio of 1:1.

Systems of lower water levels and higher sucrose levels (e.g. systems corresponding to cookie doughs) have also been investigated by DSC (Spies & Hoseney, 1982; Ghiasi *et al.*, 1983; Abboud & Hoseney, 1984). Also in these systems an increase in gelatinization temperature range was observed together with an increase in ΔH. In some of these investigations a change in the shape of the DSC endotherm was reported. The typical double endotherm, observed at low water content (Donovan, 1979), was changed by the addition of sugar into a single endotherm. This endotherm was shifted to higher temperatures, as described.

One explanation for the influence of sugars on the

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behaviour of starch has been that sugar 'binds' water, and the amount of water available for starch will, consequently, be lower (see e.g. Hoseney *et al.*, 1977). However, the results obtained by DSC have not supported such an explanation, as pointed out by, e.g. Spies & Hoseney (1982). If the water-to-starch ratio is decreased, T_0 remains the same, as does T_m (Donovan, 1979; Eliasson, 1980). At water-to-starch ratios below 2:1 a shoulder at the high-temperature side of the endotherm emerges, and T_c increases. At very low water levels an endotherm at a temperature above the typical gelatinization temperature range might be observed (Burt & Russell, 1983). If sucrose (or any other sugar) is added, T_o, T_m and T_c increase, which should not be the case if the only function sucrose had was to decrease the amount of water available to the starch. The observation that the double endotherm might change into a single endotherm under certain conditions suggests that more water is available to the starch (Ghiasi *et al.*, 1983).

The aim of the present investigation was to study starch gelatinization at lower water contents and higher sugar levels than has been done previously. The technique used was DSC, and the changes in the DSC endotherm from the double endotherm into the narrow single endotherm were examined in some detail.

MATERIALS AND METHODS

Materials

Potato starch, waxymaize starch, maize starch and high-amylose maize starch (Hylon VII) were all commercial samples (Lyckeby National, Sweden). Amylopectin was purchased from Sigma and sucrose (analytical grade) from Mallinckrodt (St Louis, USA). Deionized distilled water was used.

Methods

Starch (200 mg) was weighed into a test tube and sugar solution and/or water was added to give the precalculated water-to-starch ratio (3:1 or 1:1) and sugar-to-starch ratio. Sugar solutions of the highest concentration possible, and not crystalline sugar, were used in order to obtain DSC thermograms without peaks caused by dissolution of the sugar. In the case of sucrose, it was possible to study sugar levels up to 1·7 g sucrose/g starch. Sugar solutions were weighed into the test tube, whereas water, when required, was added with a pipette. The samples were mixed thoroughly with the aid of a spatula, and then added to pre-weighed DSC sample pans (coated DuPont pans) which were immediately sealed.

The DSC measurements were carried out in a Perkin-Elmer DSC-2 with a heating rate of 10°C/min. An empty pan was used as a reference. The analysis was started at 22°C and continued to well above the gelatinization peak. After cooling, the pans were punctured and the dry matter content was determined by drying at 105°C for 16 h. The starch content was calculated from the dry matter content and the mixing ratio. The gelatinization enthalpy was expressed in J/g starch. The results given are the mean of three runs.

RESULTS

Potato starch and sucrose

When increasing levels of sucrose were added to potato starch at a water-to-starch ratio of 3:1, T_o, T_m and T_c all increased, whereas ΔH remained unchanged. T_o, T_m and T_c as a function of the sucrose-to-starch ratio are shown in Fig. 1. ΔH was 17·5 ± 0·9 J/g starch without added sucrose and 18·2 ± 1·2 J/g starch at the sucrose-to-starch ratio 1·7:1. The shape of the endotherms did not change with the increase in sucrose level (endotherms not shown). These results are in full agreement with the results reported by Evans and Haisman (1982). In their investigation, T_0 increased from about 57°C (330 K) for potato starch at a water-to-starch ratio of 10:1 to about 70°C at a sucrose-to-starch ratio of 3:1. In the present investigation (Fig. 1) T_0 increased from 58·3°C at a water-to-starch ratio of 3:1 to 72·1°C at a sucrose-to-starch ratio of 1·7:1. The effect was even more pronounced at the water-to-starch ratio 1:1 (Fig. 1). The delaying effect of sucrose is, thus, greater at lower water-to-starch ratios. This was also observed by Chungcharoen and Lund (1987) when sucrose was added to rice starches. In the present investigation the

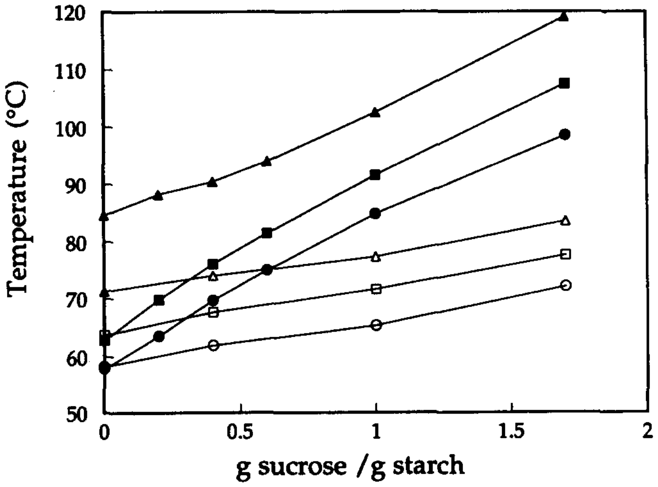

Fig. 1. The influence of sucrose on the gelatinization temperature interval of potato starch. ●, ○ T_0; ■, □ T_m; ▲, △ T_c. Filled symbols, water-to-starch ratio 1:1; open symbols, water-to-starch ratio 3:1.

water-to-starch ratio was always 3:1 (or 1:1), whereas in other investigations (e.g. Evans & Haisman, 1982) the medium-to-starch ratio was kept constant. These different approaches might explain the different results obtained concerning ΔH; if the sugar addition also means a decrease in water addition, ΔH might very well decrease (see below).

The changes in T_0, T_m and T_c with increasing sucrose levels at the water-to-starch ratio 1:1 are also shown in Fig. 1. It is evident from this figure that the addition of sucrose caused not only a delay in the gelatinization but also a more narrow temperature range. This is also seen in Fig. 2 where the corresponding DSC thermograms are shown. Those thermograms confirm the findings reported by, e.g. Spies & Hoseney (1982). When the sucrose concentration increased, the shoulder on the high-temperature side of the endotherm disappeared. The sucrose addition, thus, had the same effect as increasing the water content. With 0·4 g sucrose/g starch the double endotherm had changed into a single endotherm without any sign of a shoulder. It can be seen from Fig. 2 that at the low sucrose levels (below about 0·6 g sucrose/g starch) T_c is not as much affected as T_0 and T_m. ΔH was 16·5 ± 0·5 J/g starch for the sample without added sucrose and at the sucrose-to-starch ratio 1·7:1 ΔH was 15·3 ± 1·0 J/g starch.

The influence of the water content was also investigated, both with (0·4 g sucrose/g starch) and without added sucrose. The gelatinization temperatures are compared in Fig. 3 and the corresponding ΔH values in Fig. 4. The results in Fig. 3 show that T_0 and T_m do

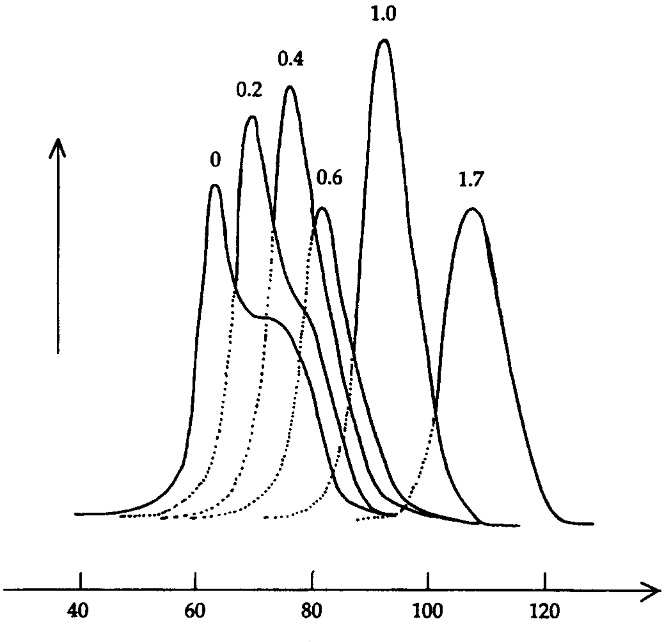

Fig. 2. The DSC thermograms of potato starch at different levels of sucrose (numbers above peaks indicate sucrose-to-starch ratios). The water-to-starch ratio was 1:1. The arrow indicates endothermic heat flow.

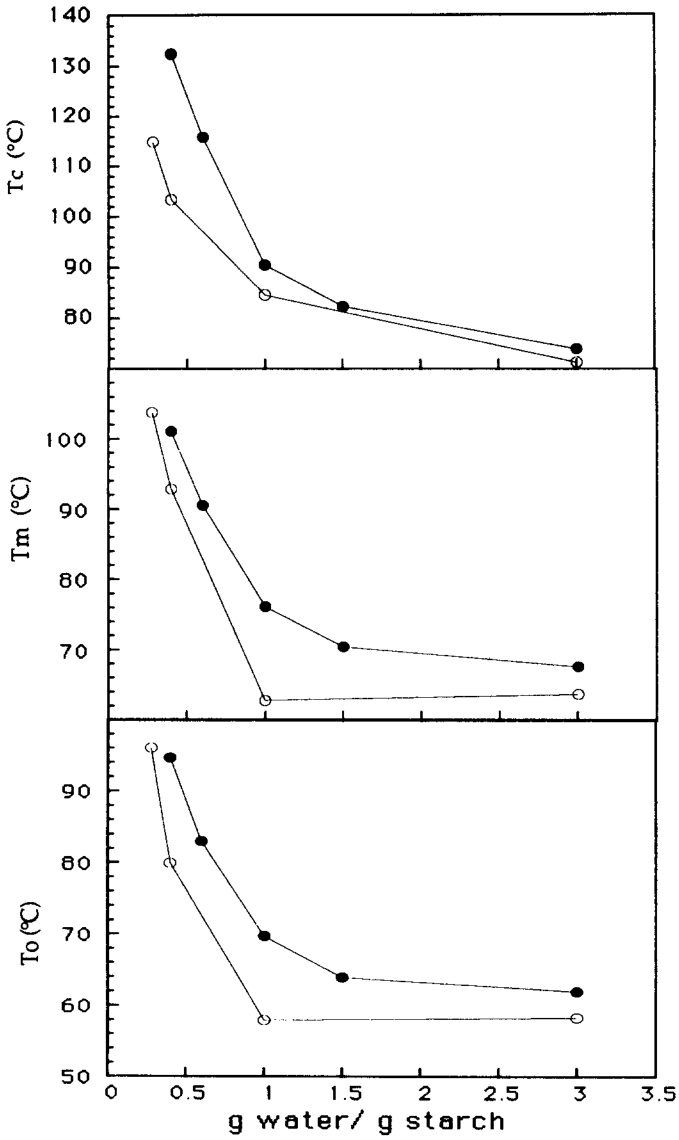

Fig. 3. The influence of water content on the gelatinization temperature interval of potato starch. ○ No sucrose added; ● 0·4 g sucrose/g starch.

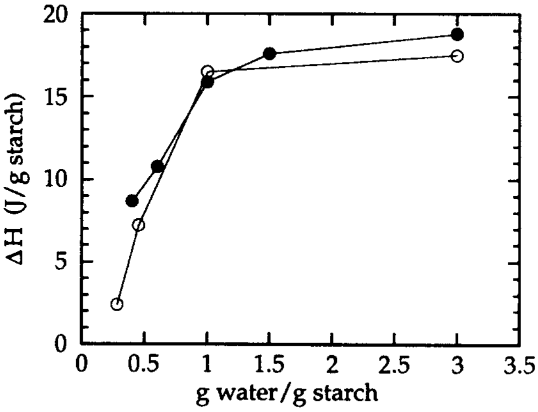

Fig. 4. The influence of water content on the gelatinization enthalpy of potato starch. ○ No sucrose added; ● 0·4 g sucrose/g starch.

not depend on the water content above a water-to-starch ratio of 1:1. However, when sucrose is added, T_o and T_m both depend on the water content at all water-to-starch ratios. T_o and T_m were higher in the presence of sucrose at all water-to-starch ratios. T_c, on the other hand, was similar for samples with and without sucrose at high levels of water, but when the water-to-starch ratio decreased to below 1:1, T_c was higher in the presence of sucrose.

ΔH decreased with decreasing water content below 1 g water/g starch (Fig. 4), as expected (Donovan, 1979). If the standard deviation (±5%) is taken into account, there seems to be no difference in ΔH for samples with and without sucrose at a given water content.

Maize starch and sucrose

The reason for using potato starch for the main part of this work was to avoid complicated thermograms caused by the transition of the amylose-lipid-complex. Once the influence of sucrose on the gelatinization process was established in the case of potato starch, it was thought to be of interest to look at other starches. Maize starch was chosen because of the possibility to study starches differing in amylose content. The influence of sucrose on the gelatinization of waxymaize starch, 'normal' maize starch and high-amylose maize starch was studied at a water-to-starch ratio of 1:1. The DSC thermograms are shown in Fig. 5, and the corresponding gelatinization parameters in Table 1. At the sugar-to-starch ratio 1:1 the result obtained for the normal maize starch was very similar to the result obtained for potato starch. The double DSC endotherm was transformed into a single endotherm (Fig. 5), T_o, T_m and T_c increased, ΔH also increased (Table 1). In the case of waxymaize starch (with almost 100% amylopectin) the endotherm still showed a shoulder at the sucrose-to-starch ratio 1:1, and even with 1·5 g sucrose /g starch there were signs of a shoulder (Fig. 6).

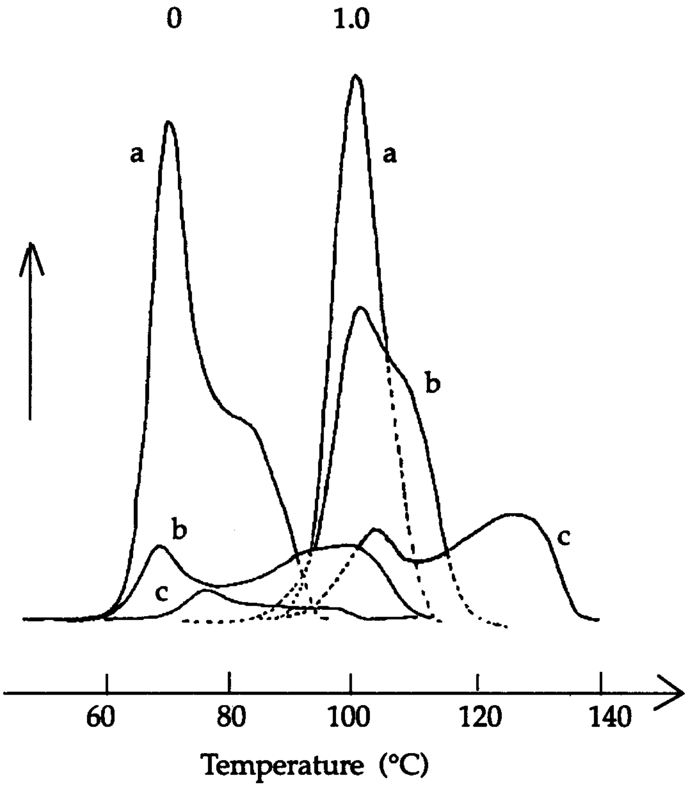

Fig. 5. The influence of sucrose on the DSC thermogram of maize starches differing in amylose content: (a) normal maize starch; (b) waxymaize starch; (c) amylomaize starch. The level of sucrose per gram starch is indicated. The water-to-starch ratio was 1:1. The arrow indicates endothermic heat flow.

T_o, T_m and T_c increased as expected, ΔH also increased (Table 1). This increase was considerable, from 6·88 J/g starch without sucrose to 20·1 J/g starch at the sucrose-to-starch ratio 1:1. A further increase in the sucrose-to-starch ratio to 1·5:1 did not affect ΔH, but there was a further increase in T_o, T_m and T_c. When these starches were gelatinized at a high water content (3 g water/g starch) ΔH was 13·2 ± 0·2 J/g starch for the normal

Table 1. Effect of sucrose on the gelatinization parameters of maize starches differing in amylose content

Sample	T_o (°C)	T_m (°C)	T_c (°C)	ΔT[a] (°C)	ΔH (J/g starch)
Waxymaize starch 1:1[b]	62·5 ± 1·3	69·2 ± 0·1	108·0 ± 2·0	45·5	6·88 ± 1·05
+ 1·0 g sucrose/g starch	93·1 ± 1·5	101·5 ± 0·5	118·3 ± 0·8	25·2	20·1 ± 0·8
+ 1·5 g sucrose/g starch	103·0 ± 0·6	111·6 ± 0·5	123·5 ± 0·6	20·5	20·2 ± 1·8
Waxymaize starch 3:1[b]	64·9 ± 0·2	71·7 ± 0·2	77·8 ± 0·4	12·9	16·8 ± 0·7
Maize starch 1:1[b]	63·9 ± 0·5	70·6 ± 0·4	93·8 ± 1·2	29·9	12·8 ± 0·3
+ 1·0 g sucrose/g starch	92·6 ± 0·5	100·2 ± 0·3	110·9 ± 0·5	18·3	14·5 ± 0·7
Maize starch 3:1[b]	65·5 ± 0·5	71·1 ± 0·6	76·4 ± 0·4	10·8	13·2 ± 0·2
High-amylose maize starch 1:1[b]	69·8 ± 1·1	76·5 ± 0·5	100·3 ± 0·1	30·5	2·76 ± 1·06
+ 1·0 g sucrose/g starch	92·0 ± 1·4	104·0 ± 0·5	135·8 ± 0·8	43·8	12·7 ± 2·1
High-amylose maize starch 3:1[b]	67·6 ± 0·1	74·6 ± 0·4	105·7 ± 0·1	38·1	8·18 ± 0·15

[a] $\Delta T = T_c - T_o$.
[b] 1:1, 3:1 = water-to-starch ratio.

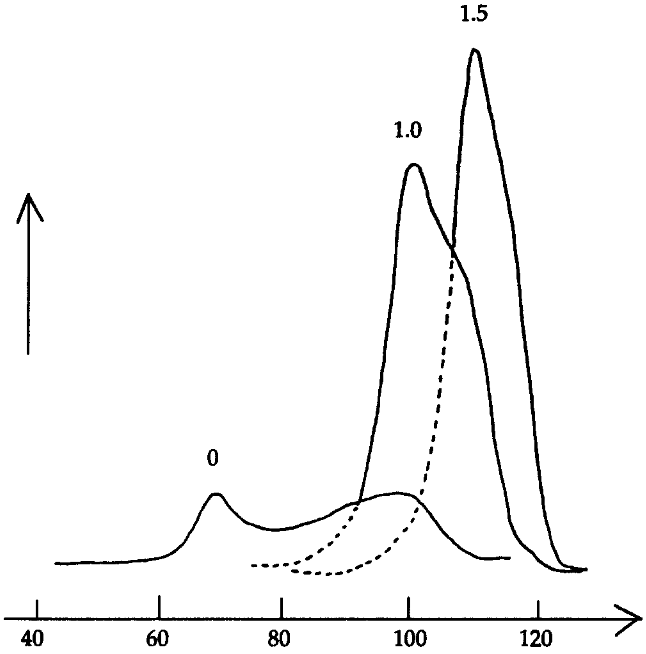

Fig. 6. The influence of sucrose on the DSC thermogram of waxymaize starch. The level of sucrose per gram starch is indicated. The water-to-starch ratio was 1:1. The arrow indicates endothermic heat flow.

maize starch and 16·8 ± 0·7 J/g starch for the waxymaize starch.

In the case of the high-amylose maize starch a better resolved second endotherm was obtained in the presence of sucrose (Fig. 5). T_o, T_m and T_c increased, but the gelatinization temperature range ($T_c - T_o$) did not decrease, as observed for the other starches. Instead, it increased from 31°C without sucrose to 44°C in the presence of sucrose. Also ΔH increased, from 2·76 J/g starch without sucrose to 12·7 J/g starch in the presence of sucrose. When the high-amylose starch was gelatinized at a water-to-starch ratio of 3:1 a ΔH value of 8·2 J/g starch was obtained. However, the DSC endotherm of the high-amylose maize starch is difficult to evaluate owing to the overlapping of the gelatinization transition and the transition caused by the amylose-lipid-complex (Eliasson *et al.*, 1988).

Table 2. Transition temperature (T_{cx}) and enthalpy (ΔH_{cx}) of the amylose-lipid complex in maize starch with and without sucrose

g sucrose/g starch	T_{cx}(°C)	ΔH_{cx} (J/g starch)
0·0	109·8 ± 0·6	1·90 ± 0·07
1·0	126·3 ± 1·4	0·61 ± 0·36

Water-to-starch ratio was 1:1.

The amylose-lipid-complex in the presence of sucrose

In the case of the normal maize starch the transition caused by the amylose-lipid complex is well separated from the gelatinization endotherm. It is, thus, possible to study the influence of sucrose on the amylose-lipid-complex. The transition temperature (T_{cx}) and enthalpy (ΔH_{cx}) are given in Table 2. T_{cx} was affected in the same way as the gelatinization temperature, i.e. it increased in the presence of sucrose. ΔH_{cx}, on the other hand, seemed to decrease in the presence of sucrose.

Amylopectin and sucrose

The effect of added sucrose on amylopectin was investigated. When amylopectin is heated in the DSC, the transition observed will not be a gelatinization endotherm, but rather melting of retrograded amylopectin. It was found that if amylopectin (potato, commercially available) was mixed with water and immediately heated in the DSC, no endotherm was observed. If the sample was stored for one day (either with or without a pre-heat-treatment in the DSC) an endotherm resulted. The influence on this endotherm of added sucrose is shown in Table 3 and Fig. 7.

The influence of sucrose on the transition of amylopectin at a sucrose-water-amylopectin ratio of 1:1:1 was in some way similar to the corresponding sucrose-water-starch system. There was an increase in transition temperature and an increase in ΔH, but the transition temperature range was not very much affected. It was 35·1°C without sucrose and 32·3°C in the presence of sucrose. In the case of waxymaize starch the corresponding values were 45·5 and 25·2°C, respectively.

Table 3. Effect of added sucrose on the DSC parameters of retrograded amylopectin

g sucrose/g starch	T_o (°C)	T_m (°C)	T_c (°C)	ΔH (J/g amylopectin)
0·0[a]	47·8 ± 0·9	63·0 ± 0·6	78·9 ± 0·2	7·0 ± 0·6
0·4[a]	47·9 ± 0·3	65·5 ± 1·0	93·7 ± 4·0	10·9 ± 1·2
0·0[b]	43·1 ± 1·1	57·2 ± 0·6	78·2 ± 2·8	4·8 ± 0·8
1·0[b]	61·4 ± 1·0	80·0 ± 2·4	93·7 ± 3·5	6·7 ± 1·3

Water-to-amylopectin ratio was 1:1.

[a] Amylopectin and water (and sucrose, if present) were mixed, heated in the DSC and stored for 4 days (room temperature) before analysis.

[b] Amylopectin and water were mixed and stored for one day. Sucrose was added immediately before DSC analysis.

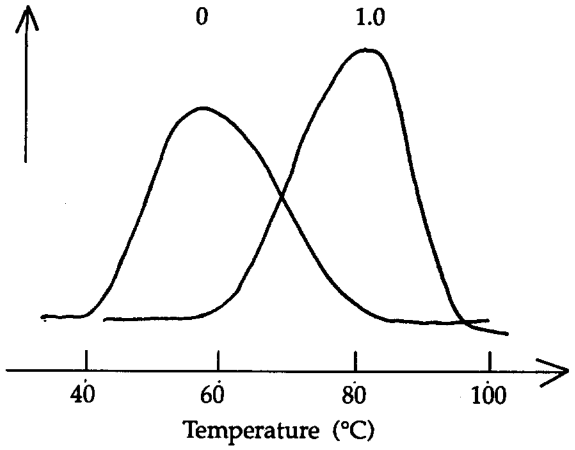

Fig. 7. The influence of sucrose on the DSC thermogram of amylopectin. The water-to-amylopectin ratio was 1:1 (a) Without added sucrose; (b) with 1 g sucrose/g starch. The arrow indicates endothermic heat flow.

DISCUSSION

Sucrose affects the DSC endotherm in different ways, depending on the starch–water level. In systems with excess water (i.e. a single, narrow endotherm in the starch–water system) sucrose causes an increase in T_o, T_m and T_c, whereas ΔT (= $T_c - T_o$) is more or less unaffected (Fig. 1). In limited-water systems (i.e. a double endotherm is obtained for the starch-water mixture) T_o, T_m and T_c increase when sucrose is added, but ΔT decreases. This means that the double endotherm is changed into the type of endotherm obtained in excess-water systems. ΔH seems not to be affected by sucrose. The amount of sucrose necessary to bring about the change from a double endotherm into a single endotherm depends on the starch. In the case of potato starch (at a water-to-starch ratio of 1:1) the single endotherm was obtained at the sucrose-to-starch ratio 0·4:1 (Fig. 2). Maize starch showed a single endotherm at a sucrose-to-starch ratio of 1:1 (other ratios were not investigated) whereas waxymaize starch showed a double endotherm at a sucrose-to-starch ratio of 1·5:1 (Fig. 6). The disappearance of the shoulder on the high-temperature side of the endotherm is thus related to the amount of amylopectin in the starch. As amylopectin builds up the crystalline domains in the starch granule (French, 1984), the effect of sucrose seems to be related to the degree of crystallinity of the starch granule. In the case of potato starch, ΔH did not depend on the amount of sucrose present (Fig. 4). Especially in waxymaize starch and high-amylose maize starch the addition of sucrose caused an increase in ΔH. The addition of sucrose could, thus, be said to correspond to a movement to the right in the diagram in Fig. 4.

As was discussed above, it has been argued that sucrose 'binds' water and thus makes less water available for starch. Results obtained by DSC at different water-to-starch ratios have shown that this explanation cannot be correct. Spies and Hoseney (1982) suggested that the delay in gelatinization was caused by the decreased water activity of the sugar solution compared with water, and by the molecular size of the sugar. They speculated that starch–sugar interactions played a role. Sugar is supposed to stabilize the starch granule structure (Kim *et al.*, 1986). Evans and Haisman (1982) explained the effect on the gelatinization temperature by a combination of water activity and volume fraction of water inside the granules. More recently, Slade and Levine (1988) used a polymeric approach to discuss the effects of sugars on starch gelatinization. They interpreted the role of water as being a plasticizer which depresses the glass transition temperature (T_g) of starch, and, thus, also the subsequent melting of crystallites. The effect of sugars was described as being anti-plastizicing, i.e. sugars diminish the depressing effect of water on T_g. This seems to explain satisfactorily the influence on T_o and T_m. The effect of sucrose on the amylose-lipid-complex (T_{cx}) could be interpreted in the same way.

When the effect on the shape of the gelatinization endotherm is regarded, the effect of sucrose seems not to be anti-plastizicing effect, rather the addition of sucrose seems to make the gelatinization occur more easily. The reasons for the existence of a double endotherm at certain water levels have been discussed by several authors (Donovan, 1979; Biliaderis *et al.*, 1986; Slade & Levine, 1988). The reason for the double endotherm has been attributed to the destabilization of crystalline domains when the amorphous parts are hydrated, an effect that will be different at low and high water contents (Donovan, 1979). The double endotherm has also been explained by recrystallization processes occurring during the DSC scan (Biliaderis *et al.*, 1986). It has also been discussed that the DSC endotherm is composed of a change in heat capacity caused by the glass transition in the amorphous region followed by the melting of crystallites (amylopectin branches) (Slade & Levine, 1988). One aspect of the gelatinization of starch at high water content is its high cooperativity (Shiotsubo & Takahashi, 1986). The gelatinization temperature range for the whole starch granule population is 10–15°C (Fig. 1), whereas one single granule gelatinizes over a very narrow temperature range (less than 1°C according to Evans & Haisman, 1982). Shiotsubo and Takahashi (1986) estimated the size of the cooperative unit to be 290 D-glucosyl residues. If the chain length in the amylopectin is taken as 20 as an average, this corresponds to 14·5 chains or 7–8 double helices. The number of double helices in one amylopectin cluster of the A-type has been estimated at 37 (Eliasson *et al.*, 1987), i.e. the cooperativity of the gelatinization process involves just a part of a crystalline domain.

This cooperativity is lost when the water content is lowered, but it is regained when enough sucrose is present (Fig. 2). However, the cooperativity is not regained in the presence of sucrose for recrystallized amylopectin (Fig. 7). It is therefore suggested that in order to achieve the high cooperativity two conditions have to be fulfilled. Firstly, the native structure of the starch granule has to be present. Secondly, the viscosity of the medium surrounding the crystalline domain has to be low.

The importance of the native starch granule structure is shown in that the melting of the recrystallized amylopectin was not cooperative during the same conditions as was native starch. Furthermore, it is known that enzymatically hydrolysed starch granules do not show the cooperative gelatinization behaviour (Donovan & Mapes, 1980; Komiya & Nara, 1986). As Donovan (1979) suggested, this effect could be caused by the fact that the amorphous starch (amylose and/or amylopectin), when hydrated, destabilizes the crystallites. Such a destabilization could result in a very quick melting process, like the opening of a zipper, when enough water is present. In the recrystallized amylopectin the amorphous starch has already been hydrated and the destabilizing effect is not obtained.

The gelatinization process will result in increased viscosity, and eventually slow down the process. At high water content the increase in viscosity (i.e. the macroscopic viscosity) occurs after the gelatinization endotherm has been passed. However, when the water content is lowered, the viscosity, or gel strength is highest somewhere in the middle of the temperature range corresponding to the gelatinization process (Eliasson & Bohlin, 1982). An increased viscosity will decrease the mobility of the molecules present, and the processes occurring will slow down. The mobility of water and other molecules in a starch–water system (measured by nuclear magnetic resonance or ESR) depends on the water content, and is lower in samples of high starch content (Jaska, 1971; Nolan *et al.*, 1986; Biliaderis & Vaughan, 1987). As a consequence the gelatinization process will occur over a broader time interval when the starch concentration increases, which is the same as a broader temperature interval during the DSC scan. When starch is heated in sucrose solutions, the viscosity decreases with increasing sucrose at high sugar concentrations (Cheer & Lelievre, 1983). The viscosity (η) of some of the starch–sucrose–water mixtures used in the present investigation was measured at room temperature at a fixed shear rate (36·9/s). The water-to-starch ratio was 1:1, and the following results were obtained. At the sucrose–starch ratio 0·4:1, η was 1·45 Pas, at the sucrose–starch ratio 0·6:1, 0·65 Pas and at the sucrose–starch ratio 1:1, 0·46 Pas. Ghiasi *et al.* (1983) showed that a very viscous starch–water mixture (even something that looks like a dry powder) can be changed into a liquid of low viscosity by the addition of sucrose. The result was related to the volume of solvent present: the volume of a sucrose-water solution of the ratio 1:1 is greater than the same amount of water (Ghiasi *et al.*, 1983). When the effect of sucrose on the DSC endotherm is considered, it is evident that the effect is not simply due to the starch-medium volume. The ratio between starch and sucrose-solution will be the same for maize starch and waxymaize starch (Fig. 5); however, there is a single endotherm in the case of maize starch and a double endotherm in the case of waxymaize starch. Instead, there might be a larger proportion of crystalline material to melt in the waxymaize starch, and a longer period of time or higher temperature is required.

The macroscopic viscosity is not the same as the local viscosity surrounding the crystallites inside the starch granule, and to confirm the influence of the local viscosity on the DSC endotherm this viscosity should be measured. Some support for the explanation given above was obtained in a recent paper by Johnson *et al.* (1990). They used ESR to investigate the mobility of a hydrophilic probe in a starch–sugar–water system. At high sucrose concentrations the mobility was not decreased even after heating to 95°C, whereas in a corresponding starch–water system the mobility decreased at temperatures as low as 55°C.

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