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A DSC STUDY OF THE EFFECTS OF SUGARS ON THERMAL PROPERTIES OF RICE STARCH GELS BEFORE AND AFTER AGING

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Abstract

Thermal characterization of gelatinized binary rice starch-water and ternary starch-sugar-water gels before and after aging was carried out using differential scanning calorimetry. The glass transition temperature of the maximally freeze-concentrated solution (T_g') in both fresh and aged gels was observed to decrease progressively with increasing sugar concentration. Aging of the gels generally shifted T_g' to higher temperatures, but had little or no effect on the ice melting peak temperature (T_m). The presence of various sugars could either accelerate or retard starch (amylopectin) recrystallization, depending on the type and concentration of sugar, as well as on starch/water ratio. A hypothesis based on the dual antiplasticizing-plasticizing effects of sugars was postulated to explain the observed effects. Of the sugars studied, xylose and fructose appeared to display exceptional retardative and accelerative effects, respectively, on retrogradation.

Keywords: aging, amylopectin, DSC, gels, glass transition, recrystallization, retrogradation, rice starch, sugars

Introduction

Native granular starches are partially crystalline in nature. Freshly gelatinized starch, on the other hand, may be considered to be in the completely amorphous state. Upon cooling, a crystalline structure is reformed. In concentrated gelatinized non-waxy starches, the crystallization process is dominated by amylose in the early gelation stage and by amylopectin over long-term storage [1, 2], the latter being thermoreversible at ≥100°C [1, 3, 4] and primarily responsible for the staling (or increase in firmness) of starchy products.

The development of crystallinity in starch gels during storage, also generally referred to as starch (amylopectin) retrogradation, is influenced by many factors including the presence of sugars which are important and common ingredients in most starch-based products. However, despite extensive research over the years, the effects of sugars on starch retrogradation remain very much a subject of controversy. Several workers [5–9] have reported that sugars retard the re-

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crystallization of gelatinized starch, whilst others [10–13] have provided evidence to the contrary. Slade and Levine [5] have suggested that sugars inhibit retrogradation by raising the effective network glass transition temperature (T_g) of the starch gels (relative to T_g of the corresponding network plasticized by water alone). Thus, according to WLF kinetics [14], the rate or extent of starch recrystallization at ambient storage temperatures (T) diminishes because of the lower $\Delta T(=T-T_g)$. However, those authors have not been able to explain why, under similar conditions, certain sugars such as fructose and mannose were observed to accelerate rather than retard retrogradation.

It is worthwhile noting that the contradictory conclusions regarding the effects of sugars on starch recrystallization have been drawn from studies carried out at different starch:water ratios and over limited ranges of sugar concentrations. There has as yet been no study conducted over a broad enough range of sugar concentration at different water contents. This has been done in the present investigation, in an attempt to resolve the conflicting results in the literature concerning the effects of sugars on starch retrogradation. Differential scanning calorimetry (DSC) was employed to compare the thermal behaviour of binary rice starch–water and ternary rice starch–sugar–water gels, before and after aging, over a broad temperature range from –100 to +100°C.

Experimental

Materials

Non-waxy rice starch, with an amylose content of 22.5% (determined using the method of Williams *et al.* [15]), was obtained from Sigma Chemical Co. The sugars investigated were analytical grade *L*-arabinose (Fluka), *D*-xylose (Sigma), *D*-fructose (Riedel deHaen), sucrose (Sigma), and maltose (BDH). These were used without further purification. Sugar concentration is expressed as g sugar/100 g dry starch, unless otherwise stated. Freshly distilled deionized water was used in all experiments.

Differential scanning calorimetric (DSC) studies

Rice starch and water were mixed by hand in the ratio of 3:4 and 1:1. The concentration of sucrose was varied from 0–160% by weight of dry starch in the 3:4 system, and from 0–100% in the 1:1 system. The concentration of all the other sugars investigated ranged from 0–100% in the 3:4 system.

Samples (ca. 10 mg, weighed to 0.01 mg) were filled into aluminium sample pans which were then hermetically sealed using a DuPont encapsulation press. All samples were equilibrated for at least 1 h before being heated at 10°C min^{-1} from 20 to 120°C in a DuPont 2910 differential scanning calorimeter, equipped with a standard DSC cell and a Thermal Analyst 2000 Controller, to achieve complete gelatinization. The overall gelatinization enthalpy (ΔH_G) was determined as described by Seow and Teo [16]. The thermograms of the completely amorphous gelatinized samples, before aging, were obtained by immediate quench-cooling to –100°C using a cooling can filled with liquid nitrogen, and then heating at 10°C min^{-1} to 100°C, with the DSC cell being constantly purged with nitrogen gas at a flow rate of approximately 150 ml min^{-1}. An empty aluminium reference pan was used to balance the heat capacity of the sample pan. Other gelatinized samples were cooled to 15°C, removed from the DSC cell, and stored at 15°C in a refrigerated incubator for two weeks. The thermal profiles of the aged samples were then determined, as described above, after quench-cooling to –100°C and heating to 100°C at 10°C min^{-1}. An immediate rescan of the aged samples after this treatment yielded thermal profiles which were practically identical to those of the corresponding freshly gelatinized samples.

Heat flow was calibrated using pure indium, while temperature was calibrated using pure indium, distilled deionized water and pure mercury. Analysis was carried out using the DuPont DSC Standard Data Analysis Program Software (Version 4.0 B). All measurements were performed in triplicate.

Results and discussion

Low-temperature transitions

Figure 1 shows representative low-temperature DSC curves of fresh and aged gelatinized 3:4 rice starch–water systems containing different levels of sucrose. Devitrification of ice was not observed in most cases, except at very high sugar concentrations (≥150%). The glass transition of the maximally freeze-concentrated solution and the endothermic transition associated with the melting of ice are clearly recognisable [17,18]. Their respective transition temperatures (T'_g and T_m) are designated in Fig. 1, with T'_g being derived from the peak of the derivative heat-flow curve (not shown). The phenomenon of multiple T'_g s reported by Slade and Levine [17, 19] was also observed in the present study, and only the major transition was measured as T'_g.

As expected [13, 17, 18], T'_g and T_m were observed to decrease with increasing sucrose concentration, as shown in Fig. 2, for both the 3:4 and 1:1 starch–water systems, fresh or aged. Qualitatively similar results were obtained for systems containing other sugars (Fig. 3).

The effectiveness of the various sugars in depressing T'_g appears to decrease with increasing sugar molecular mass, the disaccharides being much less effective than the monosaccharides. The various sugars obviously acted as plasticizers of starch, together with water, thereby depressing T'_g, as has been clearly explained by Slade and Levine [5,17]. As expected, the T'_g and T_m values

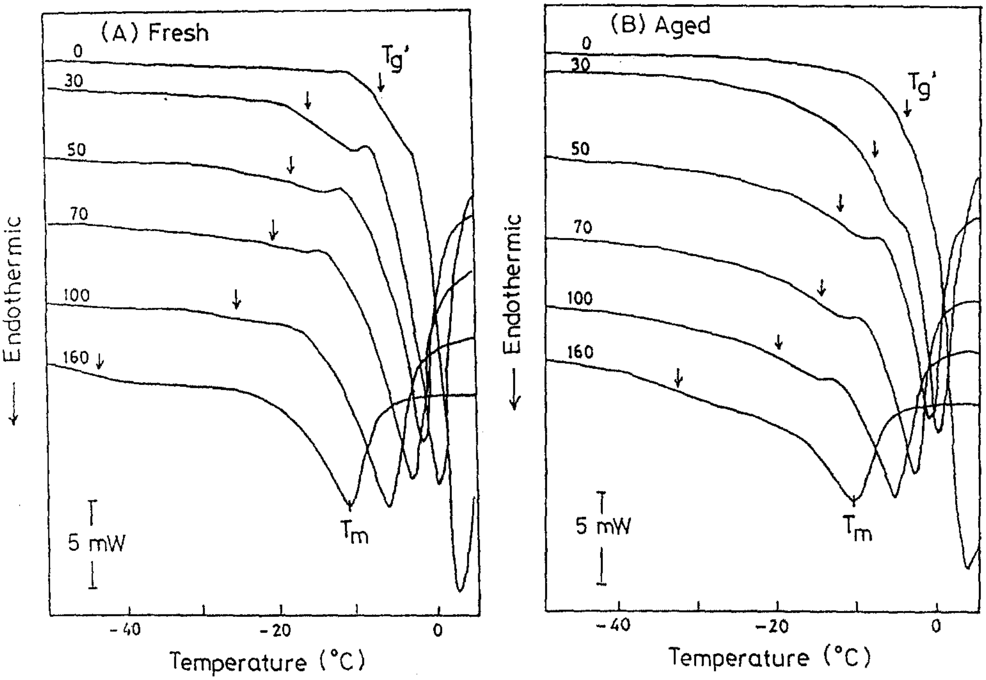

Fig. 1 Effect of sucrose concentration (% w/w dry starch) on the low-temperature DSC thermal profiles of (A) fresh and (B) aged (at 15°C for 2 weeks) rice starch gels at a starch/water ratio of 3:4

of the fresh gels were lower in the concentrated 1:1 system than in the more dilute 3:4 system, at any particular level of addition of sucrose based on the weight of dry starch (Fig. 2).

Over the range from 0–100%, T_g' decreased monotonically with increasing sugar concentration, since the average molecular mass of the starch-plasticizer mixture decreases, leading to an increase in free volume [17, 19]. The compositional dependence of T_g' in the fresh gels appeared to be curvilinear, whilst that in the aged samples was more or less rectilinear, with the exception of the system containing xylose. However, it is clear from Fig. 2A that when the addition of sucrose exceeded a critical concentration (100–120%), T_g' dropped very sharply before levelling off. The reason for the existence of such a 'cusp' in the T_g'-composition curves for sucrose systems is not immediately clear, although such a phenomenon is commonly encountered in synthetic polymer–diluent mixtures [20–23]. The two distinct T_g'/concentration dependencies may be due to the changeover from a relatively polymer-rich glass (with a higher T_g') to a plasticizer (sugar)-rich glass (with a T_g' of –43.5 to –46.8°C) in which the polymer no longer contributes to the free volume of the mixture [23].

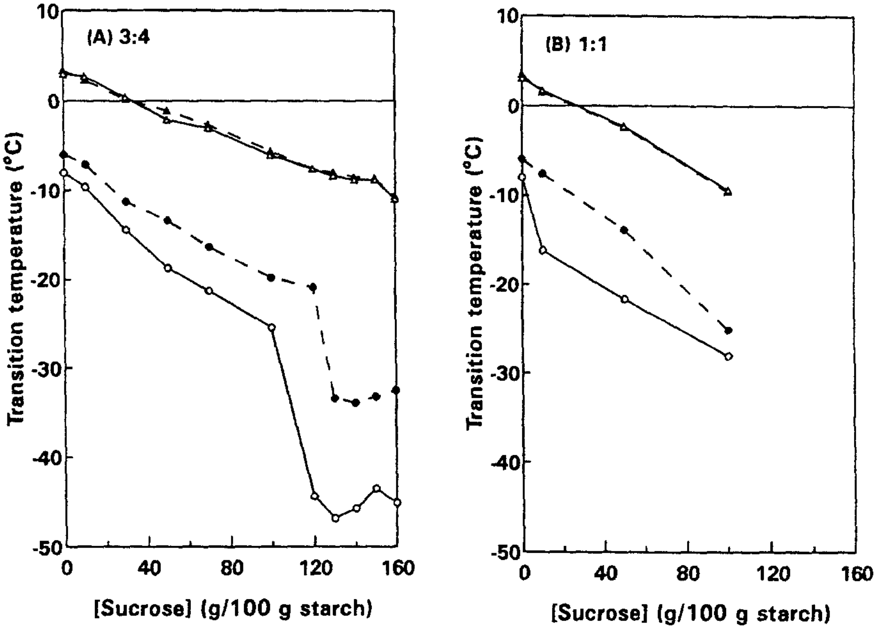

Fig. 2 Effect of sucrose concentration on T_g' and T_m of fresh and aged rice starch gels at a starch/water ratio of (A) 3:4 and (B) 1:1 [o, T_g'-fresh; ●, T_g'-aged; △, T_m-fresh; ▲, T_m-aged]

The effects of aging on T_g' and T_m are shown in Figs 2 and 3. While the ice peak temperature did not appear to be affected by amylopectin recrystallization, T_g' of the aged samples was higher than that of the corresponding fresh gels, in agreement with the findings of Huang *et al.* [18]. The general increase in T_g of a partially crystalline polymeric system with increasing % crystallinity may be ascribed largely to loss of segmental mobility as the density of microcrystalline crosslinks increases [24, 25]. Additionally, amylopectin is known to recrystallize into a B-type polymorph which requires incorporation of water molecules into the crystal lattice, thereby reducing the amount of plasticizing water in the system and resulting in an elevated T_g [5, 17].

Starch (amylopectin) recrystallization

Recrystallization of starch molecules occurs during storage of starch gels. Reheating of an aged starch gel in a differential scanning calorimeter produces an endothermic transition, over a relatively broad temperature range from 40–90°C, which is not present in the DSC scans of the freshly gelatinized samples. Such a transition is generally attributed to the melting of recrystallized amylopectin [5, 26]. Figure 4 shows the effects of increasing sucrose concentration on the DSC curves of rice starch–water (3:4) gels aged at 15°C for 2 weeks. The

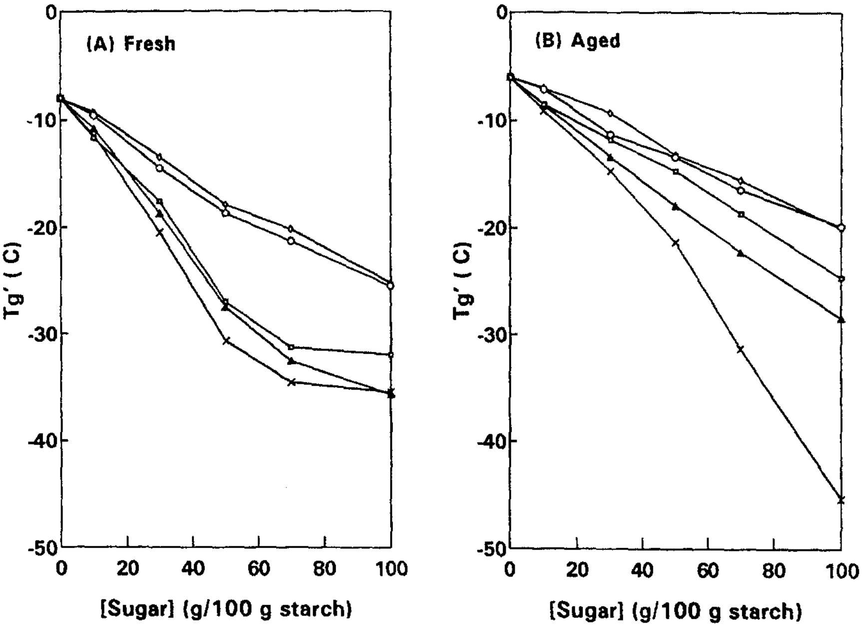

Fig. 3 Changes in T_g' of (A) fresh and (B) aged rice starch gels at a starch/water ratio of 3:4, as a function of the concentration of different sugars [×, xylose; ▲, arabinose; □, fructose; o, sucrose; ◊ maltose]

endothermic transition was skewed to higher temperatures and broadened considerably in the presence of sucrose, indicating increased stability as well as greater heterogeneity of the amylopectin crystallites formed. The other sugars studied generally produced the same effects as sucrose.

The % recrystallization was calculated as $\Delta H_R/\Delta H_G \times 100$, where ΔH_R is the retrogradation enthalpy and ΔH_G is the overall gelatinization enthalpy. Figure 5 shows the changes in extent of amylopectin retrogradation, in 3:4 as well as 1:1 starch–water systems, as a function of sucrose concentration. In the former system, the extent of amylopectin recrystallization increased to a maximum value with increasing sucrose concentration, before decreasing with further addition of sucrose, until, at a level of 160% sucrose, retardation of retrogradation (as compared with the binary system) was clearly evident. In the more concentrated 1:1 system, however, the addition of sucrose retarded retrogradation, with % recrystallization decreasing progressively with increasing sucrose concentration. It should be noted that, for the binary starch–water systems, the retrogradation tendency was much greater in the 1:1 system than in the more dilute 3:4 gel.

A comparison of the retrogradation tendency of 3:4 systems containing different sugars is given in Fig. 6. Xylose and arabinose showed similar trends as sucrose, except that maximum recrystallization and inhibition of retrogradation

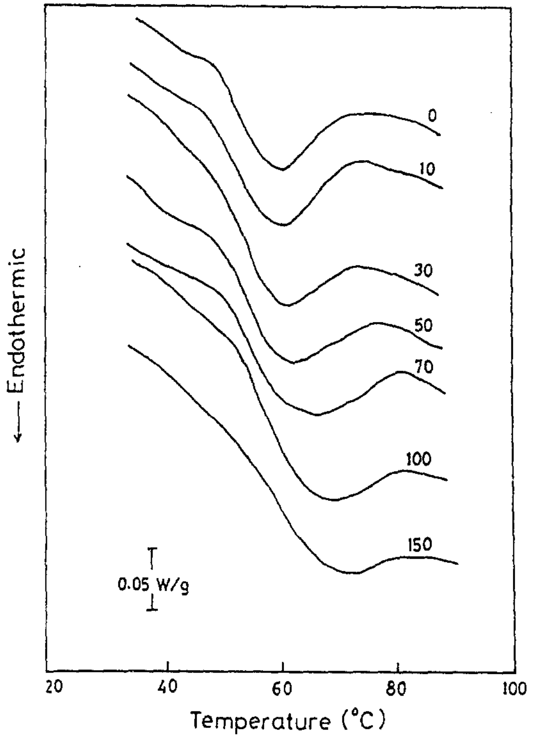

Fig. 4 Effect of sucrose concentration (% w/w dry starch) on the DSC endothermic transition associated with melting of retrograded starch in rice starch gels at a starch/water ratio of 3:4 after aging at 15°C for 2 weeks. All thermal curves are normalized to 1 g of dry starch

(as compared with the respective binary systems) occurred at lower sugar concentrations (based on weight of dry starch). Fructose and maltose, on the other hand, were found to increase retrogradation over the concentration range studied (0–100%), albeit only to a small extent in the latter case. It is likely, as in the case of sucrose, that retrogradation would reach a peak at some higher fructose or maltose concentration.

The results of the present study suggest that a given sugar may accelerate or delay starch (amylopectin) retrogradation, depending on its nature and concentration, as well as on the initial moisture content in the system. It now seems clear that the inconsistent effects of sugars on the retrogradation of specific types of starches reported by different researchers were due to differences in starch and sugar concentrations used in the various studies. It would be imprudent, therefore, to generalize the effects of sugars on starch retrogradation as being either accelerative or retardative, merely on the results of studies conducted over limited ranges of starch and/or sugar concentration.

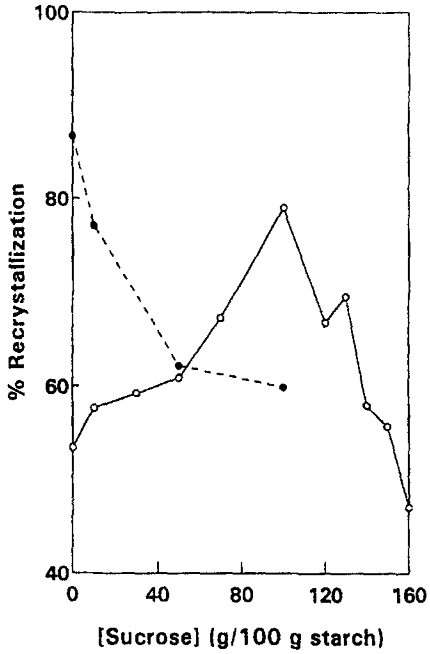

Fig. 5 Effect of sucrose concentration on % starch recrystallization in rice starch gels at a starch/water ratio of 3:4 (o) and 1:1 (•) after aging at 15°C for 2 weeks

In the 3:4 system, xylose appears to have exceptional inhibitory effects on starch retrogradation at moderate-to-high concentrations, while fructose appears capable of promoting retrogradation even at relatively high concentrations. These unusual features of xylose and fructose, amongst the monosaccharides, have been previously reported [5, 17]. Most sugars will display anti-staling properties when incorporated into starch-based baked goods, because of the relatively low moisture contents of the products.

Mechanism(s) of action of sugars

The effects of sugars on the thermal properties of ternary starch–water–sugar gels and on starch recrystallization during storage are extremely complex. Current theories cannot be considered adequate, because they account only for either the accelerative [13] or retardative [5, 17], but not both, effects of sugars on amylopectin recrystallization. A universal theory should also take into account the variation in effects exhibited by different sugars.

It is interesting to note that water in a binary starch–water gel appears to exert the same influences on starch retrogradation as does sugar in a relatively dilute ternary starch–sugar–water system. A maximum rate or extent of amylopectin recrystallization has generally been observed at around 50% moisture (or a starch/water ratio of 1:1) in binary systems [5, 27, 28]. Longton and LeGrys [27] had speculated that, depending on the initial moisture content of the system and its position on either the ascending or descending branch of the % retrogradation versus moisture content bell-shaped curve, addition of sugars (and other hydrophilic materials), which compete with the starch molecules for water in the system, might affect the effective moisture content in such a way as to cause either an acceleration or a retardation of retrogradation, although no hard evidence was presented to support such a supposition. A similar hypothesis based on changes in "available water" was proposed by Gudmundsson *et al.* [29] to explain the effects of water-soluble arabinoxylan on starch retrogradation. The results of the present study are in accord with such a hypothesis. However, a mechanism based on a reduction in "water availability" on addition of sugars cannot fully explain why a particular optimum moisture content for maximum retrogradation should exist. An alternative hypothesis, based on polymer science principles [5, 17, 19] and plasticizer action, is described below.

It is suggested that the increase in % retrogradation over the range of moisture content from 30–50% in binary systems could be due to an antiplasticization effect [30], as water molecules interact with starch molecules via hydrogen

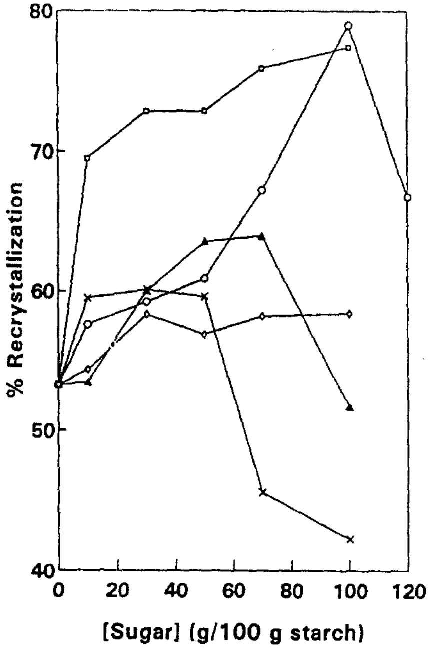

Fig. 6 Starch recrystallization (%) as a function of sugar concentration in rice starch gels at a starch/water ratio of 3:4 containing different types of sugars [×, xylose; ▲, arabinose; □, fructose; o, sucrose; ◊, maltose]

bonding and various other forces. Such interactions induce nucleation as well as growth of starch crystallites. This increase in crystallinity is followed by a decrease at higher moisture levels, when the increasing amount of water present exerts its "normal" mechanical plasticizing effects by swelling the amorphous regions and producing a progressively softer gel. It should be noted that the term, "antiplasticization", is here used in the synthetic polymer science context to mean an increase in rigidity and crystallinity of the gel network at low plasticizer contents, even though there is a decrease in molecular or segmental T_g [30]. It should not be confused with the same term used by Slade and Levine [17] to indicate an enhancement of T_g.

Similarly, the small polyhydroxy sugar molecules, which also act as plasticizers and are non-entangling in nature [17, 19], may be said to be able to interact with starch molecules in the starch gels, in much the same way as water does. Such interactions have, in fact, been observed using electron spin resonance [31] and nuclear magnetic resonance [32, 33]. At low sugar concentrations in relatively high-moisture systems (e.g. at a starch–water ratio of ≤3:4), where the amorphous regions in the binary systems would have been already highly plasticized by water, it is suggested that such interactions similarly lead to an antiplasticizing effect which stimulates formation of network junction zones. The increase in number of crosslinking points produces a more extensive and stable gel network, when compared with the binary starch–water gel. Thus, although the molecular or segmental T_g decreases on addition of sugars, as a result of free volume increase through kinetic plasticization, a gel with higher modulus would likely be obtained at low sugar concentrations, as compared with the binary system, because of the restriction on mobility of the outer branches of amylopectin, imposed by the relatively tightly held sugar molecules. Such an increase in modulus or rigidity in the presence of relatively low amounts of sugars has, in fact, been observed in several starch gels [10, 11]. However, the absence of an increased modulus in non-waxy starch gels, on addition of small amounts of sugars, does not necessarily contradict such a hypothesis, since the contribution from amylose-sugar interactions to the rigidity of such gels, not manifested in DSC scans, has to be taken into account. In this respect, it is noteworthy that Biliaderis and Zawistowski [34] have observed that the addition of low molecular weight starch hydrolysis products reduced the storage modulus of wheat starch gels in certain cases, but raised the rigidity of waxy maize starch gels, the latter being consonant with recrystallization kinetics as determined by DSC.

An increase in sugar concentration beyond a certain critical or threshold level, which varies with the type of sugar and the moisture content of the system, probably induces greater swelling of the amorphous regions, with the gel becoming softer and more flexible through the "normal" plasticizing action of both diluents (i.e. water and sugar). Analogous to the case of water [19], a distinction can probably also be made between the kinetic effect of T_g depression by sugars acting as plasticizers and their independent mechanical effect on the modulus of the system at any particular temperature. Starch recrystallization cannot apparently be related to T_g' of the gels under such circumstances.

In a more concentrated starch gel (e.g. the 1:1 starch–water system), where a high degree of antiplasticization already exists, sugars would exert their normal plasticizing effects by swelling the amorphous regions of the gel and keeping the crystallizable outer branches of amylopectin apart, thereby maintaining a softer texture for a longer period of time.

The variable effects of different sugars on starch retrogradation probably hinge on their differential ability to interact (principally by hydrogen-bonding) with starch as well as water molecules, in ways yet to be fully understood.

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