# A comparative study of the effect of sugars on the thermal and mechanical properties of concentrated waxy maize, wheat, potato and pea starch gels

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A comparative study was undertaken to examine the effect of sugars on the thermal and mechanical properties of ageing waxy maize, wheat, potato and pea starch gels. The addition of sugars, at a ratio of $1:0.5:1.5$ (w/w) for starch–sugar–water mixtures, inhibited chain reorganization in starch gels, as followed by differential scanning calorimetry and dynamic rheometry in the order, ribose > sucrose > maltotriose > water alone, glucose > fructose. Kinetic experiments on the evolution of storage modulus $(G')$ at 8°C indicated a progressive transition from a sigmoid curve (waxy maize) to a hyperbolic $G'$ – time relationship (potato and pea starches), consistent with an increasing proportion of amylose in the composite gels. The effects of sugars on the development of the retrogradation endotherm $(\Delta H)$ and gel rigidity $(G')$ were less pronounced for potato and pea starches than for waxy maize or wheat starches, presumably because of their higher amylose content, which dominates the gel network properties.

## INTRODUCTION

In the food industry there is a growing interest in formulating products with starches from a wide variety of botanical sources in order to meet specific functional requirements. Following thermal processing of starch-based products, undesirable textural changes occur upon storage, e.g. increases in crumb firmness of baked items. Chain ordering and aggregation are the molecular events which underlie the changes in structure and physical properties of starch materials, all of them collectively described by the term retrogradation. Retrogradation of starch has been considered to play a major role in the staling of baked products such as bread (Kulp & Ponte, 1981).

There have been some studies on retrogradation kinetics of different starches. Orford *et al.* (1987) followed the retrogradation of concentrated potato, pea, maize and wheat starch gels (10–40%, w/w), using rheological techniques. The initial rate of stiffness development followed the order pea > maize > wheat > potato

and was related to the amount of amylose solubilized during gelatinization. The long-term increase in modulus values was linked to the recrystallization of amylopectin and followed the order pea > potato > maize > wheat. Similarly, Russell (1987) studied the retrogradation of maize, potato, wheat and amylomaize starch gels (43%, w/w) by differential scanning calorimetry (DSC). Differences in the rate of retrogradation between these starches were explained in the context of different polymer microdomains being established upon gelation, i.e. amylopectin, amylose and amylose–lipid complexes. The rate and extent of retrogradation of a variety of starch gels were also examined by Roulet *et al.* (1990), using both rheological and calorimetric techniques. Potato and pea starches were found to be more prone to retrogradation than waxy and modified waxy-type starches.

There have been no reports of the effect of sugars on retrogradation of starches from different botanical sources. A comparative study was thus undertaken to examine the effect of sugars on the thermal and

mechanical properties of concentrated waxy maize, wheat, potato and pea starch gels. The sugars chosen in this study were fructose and glucose due to their ability to promote chain reorganization in ageing starch gels, maltotriose and ribose for their strong antiretrogradation behavior (Biliaderis & Prokopowich, 1994) and sucrose, a commonly used sugar in the baking industry. The time-dependent changes in structure of the starch–sugar composite gels were followed by both small strain dynamic rheometry and DSC. Understanding the component interactions in the starch–sugar–water system is important for improving the texture and shelf-life of high sugar content products such as cakes and cookies.

## MATERIALS AND METHODS

### Materials

Commercial samples of waxy maize (amioca), wheat, potato and pea starches were obtained from National Starch and Chemical Corp. (Bridgewater, NJ, USA), Ogilvie Mills (Midland, ON, Canada), Sigma Chemical Co. (St. Louis, MO, USA) and Protein Technologies International (St. Louis, Mo), respectively. The starches were vacuum-dried (60°C) and kept in a desiccator until used. All sugars were of analytical grade. Fructose and glucose were purchased from Mallinckrodt (Paris, KY, USA), sucrose from Fisher Scientific (Montreal, PQ, Canada), and ribose and maltotriose from Sigma. All other reagents were of analytical grade. Distilled water was used in all experiments. Starch was assayed by a dual-enzyme method using an $\alpha$-amylase (Tenase, Miles Laboratories, Elkhart, IN, USA) and glucoamylase (Diazyme L-200, Miles Laboratories) enzymic system as described by Banks *et al.* (1970). Glucose was assayed by the glucose oxidase–peroxidase–4-aminoantipyrine (dye) (Sigma) enzymic system (Biliaderis & Grant, 1979). Amylose contents were determined by potentiometric titration (Schoch, 1964), while the crude fat content of starch samples (3–4 g, dry wt) was obtained by Soxhlet extraction (16 h) with 85% methanol.

### Preparation of starch gels

The waxy maize starch gels were prepared by heating starch/sugar slurries in hermetically sealed stainless steel tubes (30 mm i.d. × 65 mm height). Degassed sugar solutions were added to starch (2 g) to obtain a ratio of 1:0·5:1·5 (w/w) starch–sugar–water mixture. The tubes were immersed in a boiling-water bath (98°C) for 15 min and subsequently cooled in a water bath at 25°C for 15 min. Immediately after cooling, the gels were transferred to the lower precooled (8°C) plate of the parallel plate geometry (30 mm diameter) of the rheometer. The upper plate was then lowered on to the gel to a gap of 1·0 mm, and the excess of material was trimmed from the periphery with a blade. Light mineral oil (Mallinckrodt) was added to a level just cover-

ing the upper plate and held by a layer of masking tape surrounding the base of the apparatus as described by Biliaderis & Zawistowski (1990). Using this method, evaporation of the sample was prevented during kinetic rheological testing. All samples were allowed to relax for 10 min before the rheological measurements commenced.

Starch gels containing amylose (wheat, potato and pea starches), were prepared by heating starch/sugar slurries in a hermetically sealed container (disk dimensions 80 mm i.x. × 1 mm thickness; Biliaderis & Tonogai, 1991). Using this apparatus, 1 mm thick gels were cast without the loss or addition of water and mechanical damage of the gel network. Degassed sugar solutions were added to the starch (3 g) to obtain a ratio of 1:0·5:1·5 (w/w) starch–sugar–water mixture and stirred for 5 min to ensure that a homogeneous slurry was formed. The slurry was then transferred to the stainless steel container and heated. Due to the broad range in physical and chemical properties of the starches used, different gel-curing procedures were required to gelatinize totally the starch/sugar slurries. For wheat starch/sugar mixtures, the disk was first immersed in a boiling-water bath (15 min) and subsequently quenched–cooled in a water bath at 25°C. Pea starch/sugar slurries required heating in an oil bath at 120°C for 15 min. Potato starch/sugar slurries were initially allowed to swell (water bath at 60°C for 15 min) in the stainless steel container, transferred to an oil bath at 105°C (15 min) and subsequently cooled in a water bath at 25°C for 15 min. Gel disks with a diameter of 30 mm were then cut from the gel, placed on the precooled bottom plate of the parallel plate geometry, and the top plate was lowered on to the gel. Paraffin oil was used to prevent loss of moisture during storage, as described above.

### Dynamic rheological testing

The mechanical properties of starch gels were probed by small amplitude oscillatory rheological testing using a Bohlin VOR Rheometer (Bohlin Reologi, Edison, NJ, USA) operated with a parallel plate geometry (30 mm diameter) and a torque element of 93·2 g cm. The kinetic aspects of gel structure development were monitored at 0·2 Hz, 10% amplitude and 8°C; data were collected for 36 h at 15 min intervals. Further details of the experimental procedures for the rheological tests are described elsewhere (Biliaderis & Zawistowski, 1990; Biliaderis & Tonogai, 1991).

The dynamic rheological parameters used to characterize the gels were: storage modulus, $G'$, and tan $\delta$ or loss tangent (tan $\delta = G''/G'$, where $G''$ is the loss modulus).

### Differential scanning calorimetry

Calorimetric measurements of ageing starch/sugar gels were carried out using a DuPont thermal analyzer equipped with a 910 DSC high pressure cell. Starch samples (3·0–3·3 mg) were suspended in aqueous sugar

**Table 1. Composition and physical properties of starches**

| | Starch content (%)[a] | Amylose content (%)[b] | Lipids (%)[c] | DSC characteristics[d] | | | |
|---|---|---|---|---|---|---|---|
| | | | | Starch gelatinization | | Amylose–lipid complex | |
| | | | | $T_p$ (°C) | $\Delta H$ (J/g) | $T_p$ (°C) | $\Delta H$ (J/g) |
| Waxy maize | 98·5 ± 0·2 | <2·0 | 0·50 | 70·0 ± 0·1 | 14·1 ± 0·2 | | |
| Wheat | 98·9 ± 0·1 | 21·1 ± 0·4 | 0·68 | 59·2 ± 0·1 | 10·1 ± 0·3 | 105·0 ± 0·3 | 1·8 ± 0·1 |
| Potato | 98·1 ± 0·2 | 25·0 ± 0·6 | 0·01 | 57·5 ± 0·1 | 15·5 ± 0·3 | | |
| Pea | 96·4 ± 0·1 | 32·5 ± 0·6 | 0·01 | 60·4 ± 0·2 | 11·1 ± 0·1 | | |

[a]Means ± SD (n = 3).
[b]Based on starch content.
[c]SEM < 5%.
[d]DSC data on 40% (w/w) starch dispersions.

solutions to obtain a ratio 1·0:0·5:1·5 (w/w) starch–sugar–water mixtures and then hermetically sealed in DuPont DSC pans. The starch suspensions were first heated from 25 to 135°C (10°C/min) to gelatinize the granules under pressure 1400 kPa, with $N_2$) and thus eliminate the problem of pan failure due to moisture evaporation at temperatures above 120°C. The samples were then cooled to room temperature and stored for a designated period of time (9, 12, 18, 24, 48, 72, 96 or 114 h) at 6°C. Analysis of the retrogradation endotherm and gelatinization characteristics of granular starches was carried out using an ambient DSC cell. Aged starch/sugar gels or granular starch slurries (40%, w/w) were scanned from 20 to 135°C at 10°C/min. The DSC was calibrated using indium, and an empty pan was used as reference. All other conditions for the operation of the calorimeter were as described previously (Biliaderis *et al.*, 1985).

## RESULTS AND DISCUSSION

### Composition and physical properties of starches

The composition and properties of granular starches used in this study are given in Table 1. A broad range of physical and chemical properties was found among these starches. Starch content assays gave values greater than 96·4% in all cases. With respect to factors known to affect starch rheology, pea starch was observed to have the highest amylose content of 32·5%, followed by potato and wheat starch. The amylose content of waxy maize starch was found to be less than 2%. The lipid contents of waxy maize and wheat starches were 0·50 and 0·68%, respectively. Only traces of granular lipids were found in both pea and potato starch. All starches exhibited a relatively high gelatinization enthalpy, with potato starch having the highest enthalpy value (15·5 J/g) and wheat starch the lowest (10·1 J/g). The high gelatinization enthalpies imply that no major structural alteration occurred in the granules of these starches during isolation. Wheat, potato and pea starches were found to have similar gelatinization

temperatures ($T_p$ = 57–60°C), whereas waxy maize starch (40%, w/w) exhibited a much higher value ($T_p$ = 70°C). The thermal profile of aqueous dispersions of wheat starch exhibited an additional melting endotherm at $T_p$ = 105°C associated with the melting of amylose–lipid complexes.

### Dynamic rheological studies

Rheological methods are frequently employed to measure the gelation and retrogradation of starch and its polymeric constituents (Miles *et al.*, 1985a,b; Ring *et al.*, 1987; Clark *et al.*, 1989; Biliaderis & Zawistowski, 1990). It has been suggested that gelation of amylose (concentration <10%) involves rapid formation of double helical structures from an amorphous sol upon cooling, which act as junction zones among polymer chains (Goodfellow & Wilson, 1990). These coil-to-helix transitions are intermolecular processes which lead to the establishment of a three-dimensional hydrated gel network. Further lateral aggregation of double helices leads to formation of B-type crystalline structures. In contrast, gelation of amylopectin (concentration >10%) is a much slower process involving recrystallization (B-type crystals) of the outer branches (DP = 15) of this polymer (Ring *et al.*, 1987). For starches containing both amylose and amylopectin, a composite gel network forms, consisting of swollen amylopectin-enriched granules filling an interpenetrating amylose gel matrix (Miles *et al.*, 1985a). During long term storage, amylopectin recrystallizes, thus increasing the rigidity of the swollen granules and this in turn reinforces the continuous amylose phase. The latter process of structure development (i.e. recrystallization of amylopectin) is considered to contribute to the undesirable textural changes (staling) of starch-based foods (Kulp & Ponte, 1981).

Dynamic rheometry has proved a useful physical probe to monitor the kinetics of structure development in ageing starch gels. It allows continuous assessment of the dynamic moduli without breaking structural elements formed in the sample upon ageing. However, such measurements require that testing is carried out in
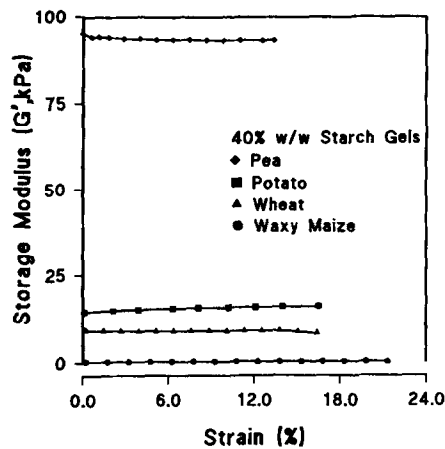
**Fig. 1.** Typical shear strain sweeps of 40% (w/w) waxy maize, wheat, potato and pea starch gels at 25°C. The values of the storage modulus ($G'$) were measured at 0·2 Hz as a function of increasing strain.

the linear viscoelastic region for the specimen (i.e. stress is proportional to strain). There are relatively few reports on dynamic rheological testing of starch networks, particularly for concentrated systems (i.e. >30% solids) (Biliaderis, 1992). In fact, there have been no rheological studies of the effect of sugars on starch gelation and retrogradation processes at high starch solids levels, conditions which resemble actual food formulations.

Before any kinetic measurements were made the starch gels were first tested over a range of shear strains to determine appropriate conditions for nondestructive testing. It was found that measurements performed at lower than 2% strain satisfy the requirements for linear viscoelasticity of all starch gel systems studied (Fig. 1).

The botanical source of starch significantly influences the mechanical properties of its aqueous pastes and gels (Orford et al., 1987; Roulet et al., 1990; Biliaderis, 1992). The initial phase of structure development in starch gels is dominated by the formation of a three-dimensional chain network involving amylose molecules (Miles et al., 1985b). The higher the amount of amylose solubilized during gelatinization, the greater is the rigidity of the gel (Orford et al., 1987; Roulet et al., 1990; Biliaderis & Juliano, 1993). A comparison of the

initial $G'$ (storage modulus) development in starch gels showed the following trend: pea > potato > wheat > waxy maize starch (Table 2); this ranking certainly follows the amylose content trend of these starches (Table 1). The relative high initial rigidity values of potato starch gels contradicted the work of Langton & Hermansson (1989) as well as of Svegmark & Hermansson (1991a,b). These authors reported that cereal starches form stronger gels than does potato starch due to a more efficient separation of amylose and amylopectin during gelatinization. However, in their investigations much lower starch concentrations were employed (5–10%, w/w) than in the present study. Even though there is an obvious relationship between initial rigidity and amylose content of the gel, other factors also have an impact on starch gel properties. For example, variation in the swelling power, number fraction of swollen granules (Wong & Lelievre, 1981) as well as differences in the amounts of granular lipids (Biliaderis & Tonogai, 1991), are known to affect the mechanical properties of starch gels. The extent to which the sugars affected the initial $G'$ value of the gels varied among wheat, potato and pea starches (Table 2).

In addition to $G'$, the initial and final (after 36 h of storage at 8°C) tan $\delta$ values of the gels are given in Tables 2 and 3, respectively. This parameter is sensitive to changes in $G'$ and $G''$ with respect to each other. Large decreases in tan $\delta$ were observed for waxy maize gels upon ageing. These trends are consistent with the view that gel network formation proceeds via crystallization of the outer short DP chains (Ring et al., 1987; Biliaderis & Zawistowski, 1990). The corresponding changes in tan $\delta$ for the non-waxy gels were much smaller, particularly for pea starch. For these materials, gel network structure is rapidly established by interchain amylose cross-linking, resulting in low tan $\delta$ values at the early stages of the gelation process. Upon storage, the slower crystallization events, involving amylose and amylopectin chains, seem to alter the viscoelastic properties of the amylose containing gels very little.

The overall kinetics of the gelation process for the 40% (w/w) waxy maize starch gels (at 8°C) generally followed a sigmoid $G'$-time curve in which the storage modulus reached plateau values in the first 24 h of storage

**Table 2. The effect of sugars on the initial values of storage modulus ($G'$,kPa) and tan $\delta$ of 40% (w/w) starch gels\***

| | Parameter | Control | Additive | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | | Fructose | Glucose | Sucrose | Maltotriose | Ribose |
| Waxy maize | $G'$ | $0.6 \pm 0.2^{ab}$ | $1.1 \pm 0.2^{c}$ | $1.2 \pm 0.2^{c}$ | $1.1 \pm 0.3^{c}$ | $0.8 \pm 0.1^{b}$ | $0.4 \pm 0.1^{a}$ |
| | tan $\delta$ | 0.75 | 0.62 | 0.68 | 0.66 | 0.72 | 0.76 |
| Wheat | $G'$ | $11.9 \pm 2.3^{b}$ | $10.8 \pm 2.6^{b}$ | $12.3 \pm 0.4^{b}$ | $16.7 \pm 1.0^{c}$ | $13.3 \pm 0.4^{bc}$ | $6.3 \pm 0.7^{a}$ |
| | tan $\delta$ | 0.13 | 0.12 | 0.08 | 0.07 | 0.07 | 0.13 |
| Potato | $G'$ | $20.7 \pm 0.3^{a}$ | $69.7 \pm 17.0^{b}$ | $65.1 \pm 9.1^{b}$ | $21.9 \pm 5.5^{a}$ | $21.5 \pm 1.1^{a}$ | $17.5 \pm 5.3^{a}$ |
| | tan $\delta$ | 0.13 | 0.03 | 0.03 | 0.11 | 0.12 | 0.12 |
| Pea | $G'$ | $131.3 \pm 28.5^{bc}$ | $152.0 \pm 4.2^{c}$ | $132.0 \pm 2.1^{bc}$ | $117.5 \pm 3.5^{bc}$ | $113.0 \pm 2.8^{b}$ | $72.6 \pm 10.9^{a}$ |
| | tan $\delta$ | 0.03 | 0.02 | 0.03 | 0.04 | 0.09 | 0.04 |

\*Composite gels consisted of starch–sugar–water mixtures of 1·0:0·5:1·5 (w/w).
Means ± SD ($n = 3$); values within each group followed by the same letter (in row; additive effect) are not significantly different ($P < 0.05$).
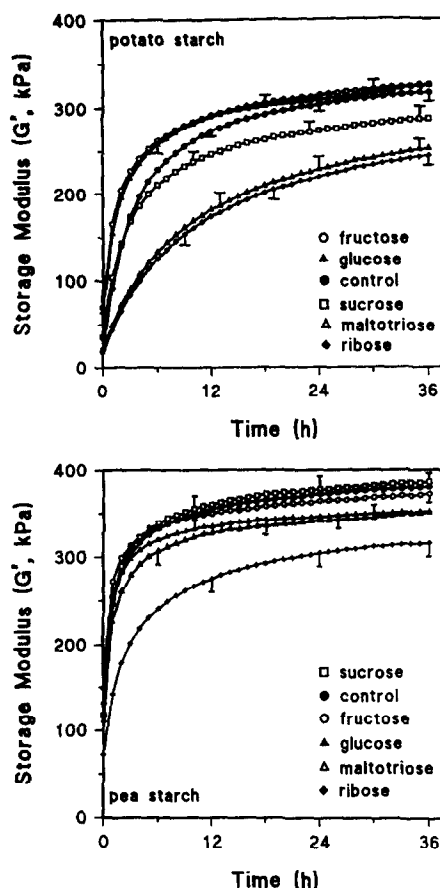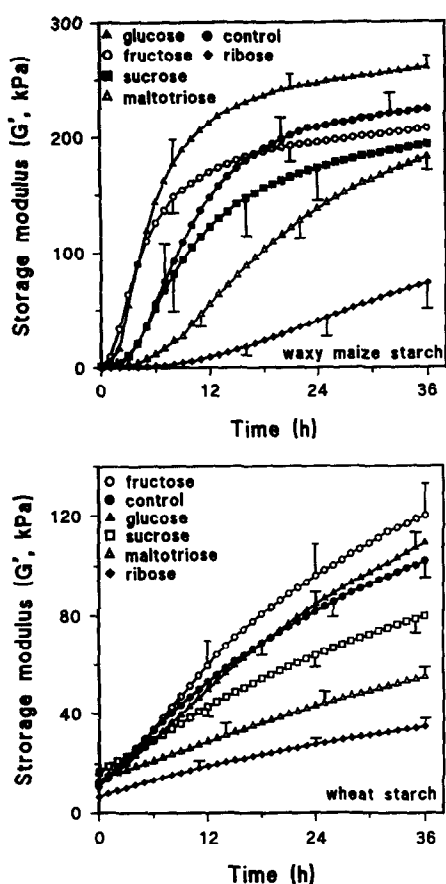
**Fig. 2.** Effect of added sugars on the storage modulus (*G'*) of ageing waxy maize and wheat starch gels stored at 8°C. Dynamic rheological measurements were made at 0·2 Hz and strain <2%. Sugars were incorporated at a ratio of 1:0·5:1·5 (w/w) in starch–sugar–water mixtures.

**Fig. 3.** Effect of added sugars on the storage modulus (*G'*) of ageing potato and pea starch gels stored at 8°C. Dynamic rheological measurements were made at 0·2 Hz and strain <2%. Sugars were incorporated at a ratio of 1:0·5:1·5 (w/w) in starch–sugar–water mixtures.

(Fig.2). Addition of sugars dramatically affected the kinetics of structure formation. Glucose greatly promoted rigidity development throughout the entire storage period, whereas fructose initially (first 12 h) enhanced the kinetics, compared to the control, and later retarded the process. Sucrose, maltotriose and especially ribose were found to retard significantly the *G'* development.

The kinetic profiles of *G'* in Figs 2 and 3 showed a progressive shift from a sigmoid curve (waxy maize) to

a hyperbolic *G'*–time relationship (potato and pea starches). These two types of curves are typical of amylopectin and amylose gelation, respectively (Biliaderis & Zawistowski, 1990). The storage modulus profiles of Figs 2 and 3 suggest that the linear starch fraction, present in greater amounts in potato and pea starches, dominates the gel network properties of these materials.

For wheat starch gels, the initial phase of *G'* development (associated mostly with amylose gelation) was not significantly influenced by the addition of fructose,

**Table 3. The effect of sugars on the storage modulus (*G'*, kPa) and tan δ of 40% (w/w) starch gels after 36 h storage at 8°C[*]**

| | Parameter | Control | Additive | | | | |
|---|---|---|---|---|---|---|---|
| | | | Fructose | Glucose | Sucrose | Maltotriose | Ribose |
| Waxy Maize | *G'* | 238·0 ± 4·2[c] | 205·5 ± 13·4[b] | 260·7 ± 9·7[c] | 194·0 ± 21·2[b] | 182·7 ± 11·1[b] | 73·4 ± 22·2[a] |
| | Tan δ | 0·12 | 0·13 | 0·19 | 0·13 | 0·13 | 0·13 |
| Wheat | *G'* | 101·9 ± 6·7[d] | 120·0 ± 12·7[c] | 109·0 ± 1·4[c] | 79·8 ± 5·7[c] | 54·8 ± 0·4[b] | 34·7 ± 3·3[a] |
| | Tan δ | 0·03 | 0·02 | 0·01 | 0·04 | 0·04 | 0·04 |
| Potato | *G'* | 318·0 ± 4·2[c] | 327·0 ± 9·9[c] | 325·5 ± 3·5[c] | 261·5 ± 0·7[ab] | 276·0 ± 24·0[b] | 254·0 ± 11·3[a] |
| | Tan δ | 0·10 | 0·09 | 0·06 | 0·07 | 0·03 | 0·06 |
| Pea | *G'* | 380·3 ± 6·5[c] | 376·5 ± 9·2[c] | 351·5 ± 17·7[b] | 386·0 ± 1·4[c] | 352·5 ± 3·5[b] | 315·0 ± 22·6[a] |
| | Tan δ | 0·02 | 0·03 | 0·02 | 0·03 | 0·02 | 0·04 |

*Means ± SD (*n* = 3); values within each group followed by the same letter (in row; additive effect) are not significantly different (*P* < 0·05).

glucose and maltotriose, whereas ribose decreased the kinetics in all stages. For potato starch gels, fructose and glucose were found to accelerate the early gelation–retrogradation events, while ribose and maltotriose had an inhibitory effect. With the exception of ribose, all other sugars influenced the kinetics of $G'$ development in pea starch gels very little. The storage modulus–time profiles also indicated that the $G'$ of potato and pea starch gels reached pseudoplateau values in shorter times than those of waxy maize and wheat starches. In addition to amylose content, the higher rigidity values obtained for aged potato and pea starch gels could reflect the lack of granular lipids from these starches, which are known to retard retrogradation (Orford et al., 1987; Biliaderis & Tonogai, 1991).

Overall, the viscoelastic properties of ageing starch gels are greatly influenced by the addition of sugars. The extent to which these solutes affect the initial phase of $G'$ development (associated mostly with amylose gelation) varies among wheat, potato and pea starch gels. It is not clear if the influence of sugars on the initial structure development was caused by a direct effect on the interchain associations or indirectly by affecting the amount of amylose which was leached out of the granules during gelatinization. The later phase of $G'$ development (mainly due to amylopectin recrystallization) was also affected by the sugars. The waxy maize

and wheat starch gels were more sensitive to long-term changes in rigidity by the sugars than those of potato and pea starches, presumably because of their lower amylose content. The results of this study also indicated that the higher the amylopectin/amylose ratio the wider the range of $G'$ values for the composite starch–sugar gel networks.

## Differential scanning calorimetry studies

The DSC has been used extensively to monitor retrogradation of starch materials as reviewed by Biliaderis (1990). During storage of starch gels the development of the 'retrogradation' endotherm $(T_p = 45–60°C)$ has been considered to reflect reordering of the outer short chains (DP = 15) of amylopectin (Ring et al., 1987). The influence of sugars on the development of retrogradation endotherm for waxy maize starch gels (40%, w/w) is shown in Fig. 4. The addition of sugars, at a ratio of $1:0.5:1.5$ (w/w) for starch–sugar–water mixtures, inhibited chain reordering (40%, w/w; 6°C) in the order, ribose > sucrose > maltotriose > water alone, glucose > fructose. Similar effects on the time-dependent changes in $\Delta H$ were also observed for the 40% (w/w) wheat starch gels (Fig. 4) and concur with the DSC findings of Slade & Levine (1987) for the effect of sugars (wheat starch–sugar–water $(1:1:1,$
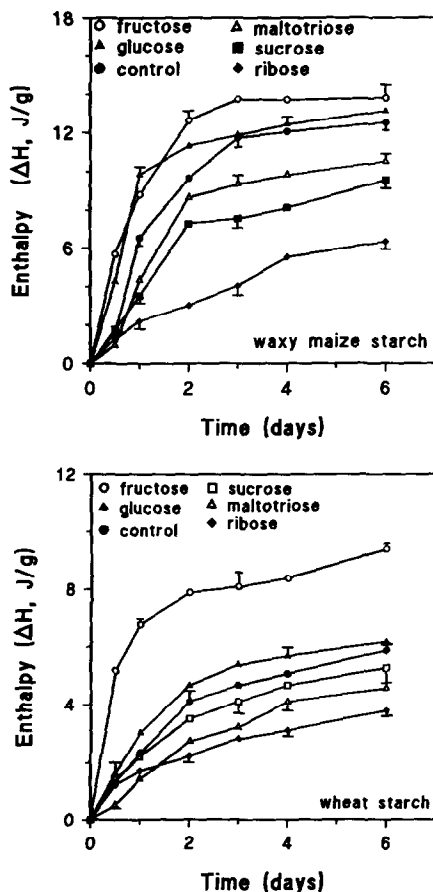


Fig. 4. Effect of added sugars on the retrogradation endotherm $(\Delta H)$ of ageing waxy maize and wheat starch gels stored at 6°C. Sugars were incorporated at a ratio of $1:0.5:1.5$ (w/w) in starch–sugar–water mixtures.
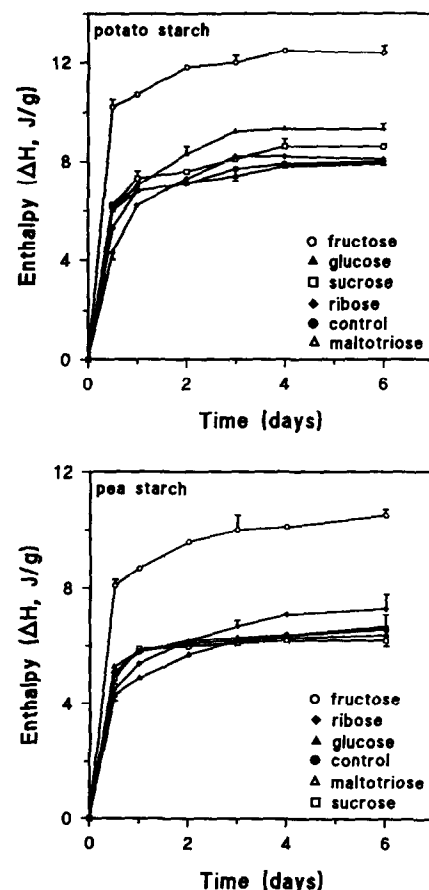


Fig. 5. Effect of added sugars on the retrogradation endotherm $(\Delta H)$ of ageing potato and pea starch gels stored at 6°C. Sugars were incorporated at a ratio of $1:0.5:1.5$ (w/w) in starch–sugar–water mixtures.

w/w)) on retrogradation of wheat starch. The effects of sugars on the retrogradation endotherm were less pronounced for potato and pea starch gels (Fig. 5) with the exception of fructose. This solute strongly accelerated the process. Glucose slightly promoted the retrogradation of potato starch (Fig. 5), while sucrose, maltotriose and ribose did not significantly affect the kinetics of $\Delta H$ development for either potato or pea starch gels.

Overall, the modification of starch gel structure by the sugars followed similar trends to the rheological data. Thus, fructose strongly promoted the formation of ordered structures, while maltotriose and ribose retarded the kinetics of $\Delta H$ development. These effects were reduced with increasing amylose content of the composite gels. A comparison between the DSC and rheological data for pea and potato starch gels also revealed some differences in the sensitivity between the two techniques to monitor gel structure development. For example, while the DSC data indicated greater differences between the control and fructose-containing gels, the corresponding rheological responses were smaller (Figs 3 and 5). Similar observations can be made for the control and ribose-containing gels when comparing the DSC and rheological data (Figs 3 and 5). These findings may reflect the different timescales over which DSC and rheological measurements are made as well as differences in the sensitivities of the two techniques when responding to various elements of structure which develop in the ageing network.

## CONCLUSIONS

A comparative study was undertaken to examine the effect of sugars on the thermal and mechanical properties of concentrated gels prepared from granular starches with a broad range of physical and chemical characteristics. Waxy maize and wheat starch gels were found to be more sensitive to the addition of sugars in the development of structural 'order', as proved by both dynamic rheometry and DSC, than those of potato and pea starches. The higher the amylopectin/amylose ratio in the gels the wider the range of $G'$ and $\Delta H$ responses for the composite gels. The retrogradation data also indicated that the responses of the starch–sugar gels were solute-specific; e.g. fructose accelerated the events, while maltotriose and ribose had an opposite effect. On the basis of DSC data for a large number of polyhydroxy compounds incorporated in waxy maize starch gels we have recently submitted that chain reordering in composite gels is related to the compatibility of the solute with the water structure (Biliaderis & Prokopowich, 1994). Small carbohydrate molecules which fit well in the hydrogen bonded structure of water have a stabilizing effect on the polymer chains, thus retarding chain reordering. The reverse is true for incompatible solutes that greatly disturb the water structure.

A comparison between the rheological and DSC data revealed some differences in sensitivity between the two techniques for monitoring gel structure formation. DSC is a physical probe of structure at a molecular level, namely, formation of double helical structures among the amylopectin chains. On the other hand, dynamic rheometry monitors the development of physical cross-links either in the form of simple chain entanglements or crystallites of amylopectin.

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