

Effect of Sucrose on Starch Conversion and Glass Transition of Nonexpanded Maize and Wheat Extrudates

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ABSTRACT

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Nonexpanded “half products” were prepared by twin-screw extrusion of maize and wheat of fine and coarse particle size in three levels of sucrose, 0, 10, and 20% db. The degree of starch conversion in the extrudates was determined using X-ray diffraction, differential scanning calorimetry, and rapid viscosity analysis. Starch conversion was greater in the fine material compared with the coarse material and greater for wheat compared with maize. Sugar addition decreased starch conversion in all cases, but the effect was greater for maize compared with wheat and for the coarse material compared with the fine material. The thermal mechanical properties were studied by dynamic mechanical thermal

analysis to determine the effect of sugar on the glass transition temperature (T_g) in the four different materials. As expected, the mechanically determined T_g was reduced by sugar addition. Water plasticized wheat semolina less than the other three materials. It was suggested that this was because the extruded semolina was entirely amorphous, whereas X-ray analysis showed some crystallinity in the other three materials. Die swell was much less for maize grits possibly because elasticity decreased with decreasing starch conversion. The implications for the role of both water and sugar on the behavior of directly expanded extrudates are discussed.

Extrusion cooking has been used for large-scale production of cereal-based products from materials such as maize and wheat. Many of these products contain added sugars to enhance flavor and control texture.

Sugar effect on the extrusion of cereal source materials has been studied by many investigators (Moore et al 1990; Sopade and Le Grys 1991; Hsieh et al 1993; Ryu et al 1993; Jin et al 1994; Barret et al 1995; Jin et al 1995; Fan et al 1996a,b). It is generally observed that an increase of sucrose concentration increases the product density and reduces the sectional expansion of the extrudates, although Hsieh et al (1990) found that sugar addition caused an increase in expansion of rice flour at sugar concentration up to 8%. More recently, we have shown (Carvalho and Mitchell 2000) that, under comparable experimental conditions, sugar has much less influence on wheat flour expansion during extrusion compared with maize grits. Possible explanations suggested for the difference in the behavior of the two materials were a lower degree of plasticization of wheat by sugar compared with maize, the smaller particle size of wheat flour compared with maize grits, and the role of gluten in the wheat system.

The effect of sugar as a starch plasticizer has been studied by Kalichevsky et al (1993), who determined the depression of glass transition temperature (T_g) of amylopectin films by calorimetric and mechanical methods. Fan et al (1996a,b) investigated the effect of sugar inclusion on the extrusion of maize grits. The observed reduction in sectional expansion and specific mechanical energy (SME) was considered to be a consequence of the decrease in T_g on replacement of starch by sugar.

A reduction in T_g reduces viscosity of the starch melt enhancing shrinkage, post expansion, and reducing bubble wall strength. The purpose of this work was to compare the effect of sucrose on non-expanded ribbons prepared from maize grits, maize flour, wheat flour, and wheat semolina. In this way, the effect of cereal type and particle size could be distinguished. Nonexpanded ribbons were prepared to enable the glass transition temperature to be determined by dynamic mechanical thermal analysis (DMTA), which is the preferred method for obtaining information on T_g because this technique is 10–100 times more sensitive when compared with DSC (Menard 1999). Starch conversion was measured by a range of techniques to determine whether the large decrease in starch conversion on sugar inclusion reported for maize grits (Fan et al 1996b) would

be observed with the other three materials, and to find out if there is any relationship between the degree of starch conversion and the glass transition. A further objective of this work was to determine whether the die swell of the extruded ribbons correlated with starch conversion. It has been suggested (Mitchell and Areas 1991), that the elasticity of the starch melt, which determines die swell, increases with increasing starch conversion.

MATERIALS AND METHODS

Materials

Maize grits (MG) (8–9.5% protein, maximum 1% lipid) and maize flour (MF) (6.5% protein, maximum 2% lipid) were donated by Maizecor Foods Limited (Hull, UK); soft wheat flour (WF) (8.5–9% protein) was supplied by Bakery Choice (Worksop, UK); coarse semolina (CS) of durum wheat (11–13.5% protein) was donated by Allied Mills (Suffolk, UK); and icing sugar (sucrose) was donated by British Sugar (UK). The chemical composition of these materials was obtained from the manufacturers' product descriptions.

Particle-Size Determination

The particle-size distribution of the raw materials was measured (Mastersizer S, Malvern Instruments, Malvern, UK), using propanol-2 as a dispersant, and is shown in Fig. 1. The particle-size distribution was expressed as a percentage of the total volume, assuming spherical particles.

Sample Preparation

Starch materials were mixed in a planetary mixer (Peerless & Ericsson, Birmingham, UK) for 10 min, with one of three levels of sugar (0, 10, and 20% db).

Extrusion was performed using a Cleextral BC-21 (Cleextral, Firminy, France) co-rotating, intermeshing twin-screw, useful length 400 mm, barrel diameter 16:1, screw speed at 300 rpm, using a flat die with 1 mm width and a length of 30 mm. Screw configuration and heater zone set point temperatures are shown in Table I. The extruder was equipped with a precalibrated K-Tron T20 twin-screw volumetric feeder and a DKM-Cleextral TD/2 water pump, which were used to control the solid feed at 5 kg/hr and water input of 1.4 L/hr, giving a water content of $\approx 28\%$ wb in the final extruded ribbons. The moisture contents were determined gravimetrically by vacuum-drying at 70°C for 24 hr. The extruded ribbons were packed in aluminum film under vacuum and immersed in liquid nitrogen within 30 min of collection and stored in freezer at -80°C .

Additional water contents were obtained by storing a fraction of each of the samples in sealed containers over saturated salt solutions for 10 days.

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Sectional Expansion Index and Specific Mechanical Energy

Although there was no obvious expansion at the low temperatures, differences in extrudate dimensions were apparent. To measure these, the extrudates were cut into pieces, and their dimensions, height and width, were measured using calipers. The sectional expansion index (SEI) was calculated following the methodology described by Alvarez-Martinez et al (1988). The sectional expansion was the cross-sectional area of the product (assumed to be rectangular) divided by the cross-sectional area of the die. The specific mechanical energy (SME) was calculated as:

$$\text{SME (Whr/kg)} = \frac{[\text{screw torque (Nm)} \times \text{screw speed (rpm)} \times 2 \times \pi \times 2]}{\text{mass flow rate (kg/hr)}} \quad (1)$$

Rapid Visco Analysis

A Rapid Visco Analyser (RVA, Newport Scientific, Warriewood, Australia) was used to measure the apparent viscosity of samples as a function of temperature.

The samples were prepared from stored frozen ribbons (-80°C), which were subsequently dried in a fan oven at 60°C for 24 hr and then milled using a small coffee grinder (Braun). Measurements were made on powder passing through a $250\text{-}\mu\text{m}$ sieve. Sample (3 g, adjusted to 14% wb) was added to 25 g of distilled water. The time-temperature profile included initially holding the sample with the paddles rotating at 160 rpm, at 25°C for 5 min, to investigate the cold-swelling starch peak (Whalen et al 1997). Sample was heated to 95°C at a constant rate of $14^{\circ}\text{C}/\text{min}$, held at that temperature for 4 min, and then cooled to 25°C in 5 min at the same rate.

X-ray Diffraction

The samples for X-ray analysis were prepared. The ribbons were taken from the freezer at -80°C , cut into a circular shape to fit into the X-ray holder, placed between two metal plates, and heated at 50°C in a fan oven for 24 hr to obtain a flat shape. The final water content was $5 \pm 0.5\%$ (wb). The D5005 X-ray diffractometer

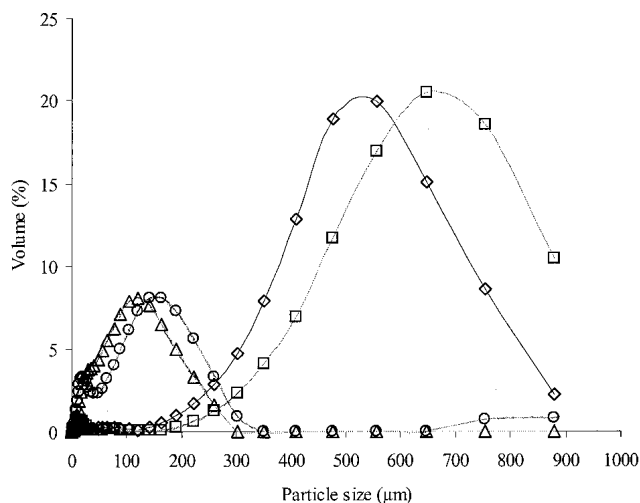


Fig. 1. Particle-size distribution of maize grits (\square), maize flour (\circ), soft wheat flour (Δ), and coarse semolina (\diamond) used for extrusion.

(Bruker AXS, Congleton, UK) used a Kristalloflex 760 X-ray generator running at 40 kV and 40 mA, which supplied $\text{CuK}\alpha$ radiation of wavelength 0.154 nm. Data were collected over the angular range of $4\text{--}38^{\circ}$ (2θ), at angular intervals of 0.05° (2θ). Duplicate scans made for each sample gave essentially identical spectra.

Differential Scanning Calorimetry (DSC)

A DSC-7 (Perkin-Elmer, Beaconsfield, UK) calibrated with indium was used to analyze $\approx 3\text{--}5$ mg of sample previously dried at 60°C for 24 hr and ground using a mortar and pestle. Samples were weighed into an aluminum pan; 1 part sample was added to 3 parts distilled water. The pans were scanned at a heating rate of $10^{\circ}\text{C}/\text{min}$ from 0 to 120°C after overnight storage for equilibration. An empty pan was used as a reference.

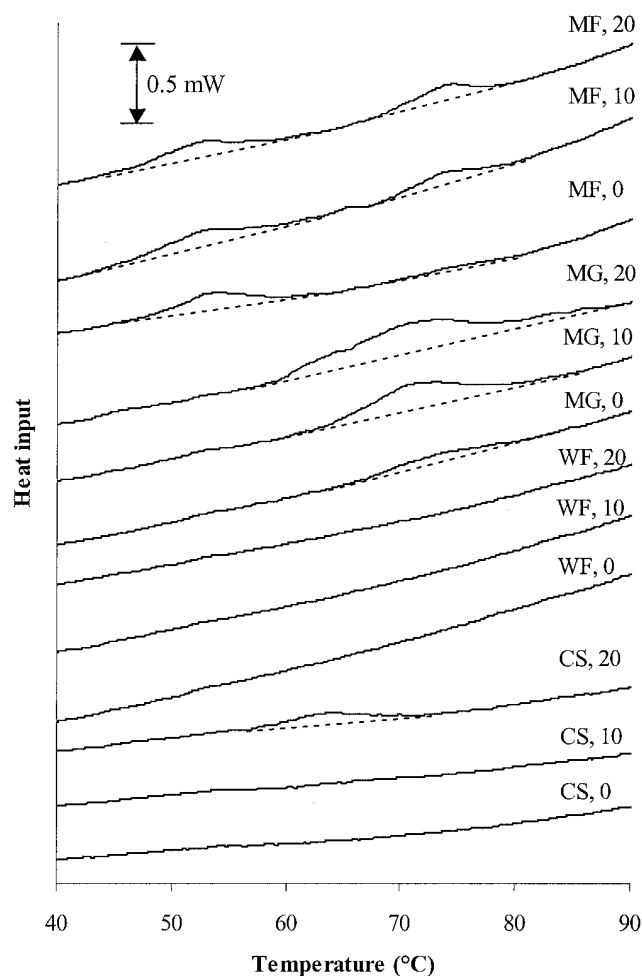


Fig. 2. Differential scanning calorimetry (DSC) thermograms for non-expanded extrudates of maize grits (MG), maize flour (MF), soft wheat flour (WF), and coarse semolina (CS). Sucrose levels in the extrudates: 0, 10, and 20% of cereal component, db.

TABLE I
Screw Configuration in Different Sections of the Extruder^a

Screw Section	1	2	3	4	5	6	7 ^b	8
Length, mm	10	50	50	50	50	50	25	25
Pitch, mm	33	25	25	16.66	16.66	16.66	16.66	16.66
Heating zones	1	2		3			4	
Temp. set point ($^{\circ}\text{C}$)	40	90		90			60	

^a From hopper to die.

^b Reverse pitch with three 3×4 mm slots.

Dynamic Mechanical Thermal Analysis (DMTA)

Extrudate pieces ≈ 2 cm length and 1 cm width equilibrated over saturated salt solutions at various relative humidity levels were measured in single cantilever geometry using a dynamic mechanical thermal analyzer (Mark III, Rheometrics, UK), at frequencies of 1, 5, and 10 Hz, strain $2\times$ (corresponding to a nominal peak to peak displacement of 32 μm) and temperature range of -100 to 150°C . The standard heating rate was $2^\circ\text{C}/\text{min}$. The samples with water content $<30\%$ db were covered with silicone oil to alleviate the problem of water loss at high temperatures.

The glass transition (T_g) can be studied by observing the change in storage modulus (E') and the loss tangent, which is the ratio of loss modulus to storage modulus ($\tan \delta = E''/E'$), as a function of temperature. For this work, T_g value was taken from the temperature at the $\tan \delta$ peak.

RESULTS AND DISCUSSION

WF and MF had similar particle-size distributions and were much finer than CS and MG, which had particle-size distributions centered at ≈ 550 and $650 \mu\text{m}$, respectively (Fig. 1). Measured SME values are reported in Table II. A clear decrease in SME from 168 to 104 Whr/kg was found for MG with increasing sugar content. These results are consistent with the findings of Sopade and Le Grys (1991), Fan et al (1996a), and Carvalho and Mitchell (2000), who found a reduction in the SME with sugar content for directly expanded systems. CS showed a slight decrease in SME from 151 to 126 Whr/kg (Table II), but no clear dependence on sugar content was found for wheat flour. This is also consistent with previously reported work (Carvalho and Mitchell 2000). The final extrudate temperature at the die was not measured. As no bubbling was observed (the product was a transparent ribbon in all cases), it can be assumed that the temperature exit at the die was $<100^\circ\text{C}$.

Starch Conversion

It is well established that starch conversion occurs during extrusion and this depends on water content and mechanical and thermal energy applied. The primary interest of this study was the effect of cereal type, sugar level and particle size.

Figure 2 displays the DSC endotherms for the extrudates. These endotherms can be compared with the endotherms for the native materials in Fig. 3. An endothermic peak characteristic of the gelatinization of native starch was seen in all the MG extrudates, although the size of this peak decreased with decreasing sugar content. Similar behavior was reported by Hsieh et al (1990) and Fan et al (1996b).

In contrast, no residual endotherm was observed after the extrusion of WF (Fig. 2), whereas for MF this endotherm was found at all sugar levels but was considerably smaller than observed for MG. The small endotherm seen at $\approx 50^\circ\text{C}$ in the MF extrudates could reflect a degree of starch retrogradation in this sample that occurred before drying. This was not seen in the MG or the wheat samples. It is possible that this was because retrogradation would only involve converted starch, and there was less conversion in the MG compared with the MF. Ward et al (1994), reported that on storage, amylopectin isolated from maize developed more crystallinity than that from wheat, although Jacobson et al (1997), using a turbidometric analysis, found no difference between the retrogradation of unmodi-

fied maize and wheat starches. The X-ray diffractograms confirmed the lower degree of conversion in MG, showing substantial native A-pattern features at all sugar levels (Fig. 4), most obviously evidenced by the peaks at 15° and 23° (2θ). In contrast, WF and MF extrudates presented a V-type pattern characterized by the presence of a peak at 19° . This peak is more pronounced with decreasing sugar content. The V-pattern is due to the presence of amylose-lipid complexes (Mercier et al 1978). As sugar content decreases starch conversion increases and more amylose is available to complex with lipids. The E-pattern was not observed in any of the materials tested. This tends to appear in cereal extrudates produced under high temperature and lower water content conditions (Donald et al 1993; Fan et al 1996b). The X-ray pattern of CS was the most amorphous at all sugar levels.

The RVA responses for the systems are shown in Fig. 5. These results are less easy to interpret unequivocally than the X-ray and DSC results. For MG extrudates at the highest sugar level, the temperature where a rise in viscosity was observed was very similar to that for the unprocessed cereal (Fig. 6). This supports the view that, of the extrudates, this sample contained the highest level of native material. The slight difference between the profiles for native MF and MG may reflect the faster hydration rate of the former, due to the smaller particle size. At reduced sugar levels, the viscosity increase for the MG extrudates shifted to lower temperature, which we believe was due to the increasing importance of noncrystalline but intact granules that swelled at temperatures lower than the native material. These particles dominated the RVA response of all the MF extrudates. In contrast to the maize extrudates, significant cold-water viscosity was found for the wheat samples at the lower sugar levels. This was due to extensively damaged particles or high molecular weight polysaccharide liberated from the granule structure (Whalen 1999) and was evidence for greater starch conversion in the wheat samples compared with maize. The very low viscosities found for the WF, both for the hot-water swelling peak and the cold-water peak, support the view that this was the most highly con-

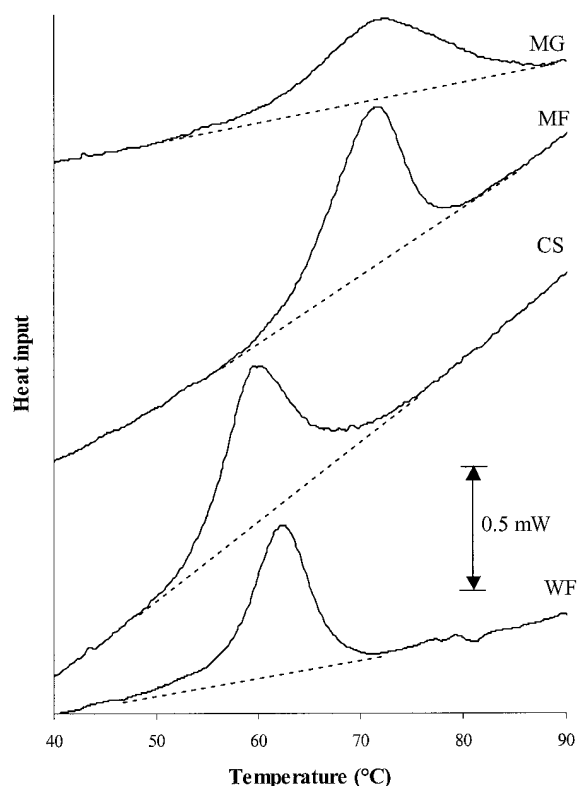


Fig. 3. Differential scanning calorimetry (DSC) thermograms for non-extruded maize grits (MG), maize flour (MF), soft wheat flour (WF), and coarse semolina (CS).

TABLE II
Specific Mechanical Energy (SME) of Nonexpanded Extrudates
at Different Sucrose Levels

Cereal Type	SME (Whr/kg) at 3 Sucrose Levels (% db)		
	0	10	20
Maize grits (MG)	168.2	135.9	104.6
Maize flour (MF)	127.2	151.6	135.9
Coarse semolina (CS)	151.6	151.1	126.2
Soft wheat flour (WF)	149.6	152.6	151.6

verted material. These low viscosities suggest disruption of granule integrity and polysaccharide degradation.

In summary, the results from all three techniques suggest that starch conversion decreases with increasing particle size and sugar content and was greater for wheat compared with maize. The increase in starch conversion with decreasing particle size has been observed (Yeh and Hwang 1992; Carvalho and Desrumaux et al 1998; Ascheri 1999). This could be explained by slower hydration of starch in the particle center for the larger particles, an effect that may be greater in the presence of high levels of sugar because of preferential partition of water into the sugar phase before starch conversion.

Starch conversion in an extrusion process is due to a combination of mechanical and thermal energy (Zheng and Wang 1994). The mean values of the SME for the wheat and maize systems are not significantly different. The increased starch conversion for wheat could be explained by its greater susceptibility to thermal conversion. In excess water, the gelatinization temperature, as indicated by the position of the endotherm, is lower for wheat compared with maize (Fig. 3). Also, at the water contents relevant to this work ($\approx 30\%$ wb), the peak temperature of the DSC endotherm (T_p) is $\approx 30^\circ\text{C}$ higher for maize compared with wheat (Wang et al 1989). Since it has been proposed (Wang et al 1989) that the rate constant for conversion depends on T/T_p , where T is the temperature experienced by the starch at any point in the process, it is to be expected that the thermal conversion of maize is much lower than wheat.

Sugar may be expected to reduce starch conversion through two mechanisms: an increase in the melting temperature and a reduc-

tion in the mechanical energy component. It is generally recognized that the melting temperature of starch increases with sugar content (Slade and Levine 1987; Ahmad and Williams 1999), although we have argued that, at low water contents, this effect is not so large as generally found at high water contents (Farhat et al 1999). In these experiments, only for MG was there a strong SME decrease with increasing sugar content. Because SME may be related to the T_g through the melt viscosity (Fan et al 1996b), it was of interest to determine whether there was a significance difference between the four systems studied in plasticization by sugar.

The T_g values obtained from the DMTA $\tan \delta$ peak are shown in Fig. 7. As would be expected, the values were highly dependent on water content (Slade and Levine 1987; Kaletunç and Breaslaer 1993). There was also clear evidence for plasticization by sugar for all four systems as found by Kalichevsky et al (1993).

The predicted T_g , for a model system based on starch-sucrose-water, was based on the formula described by Ten Brinke et al (1983) for mixtures:

$$T_g = \sum W_i \Delta C_{pi} T_{gi} / \sum W_i \Delta C_{pi} \quad (2)$$

where W_i is the weight fraction, T_{gi} is the glass transition temperature, and ΔC_{pi} , (J/gK) the difference in specific heat capacity between the liquid and glassy states of component i . The values used for T_g were 229, -139 , and 38°C , and for ΔC_p were 0.41, 1.94 (Kalichevsky and Blanshard 1993), and 0.76 (Orford et al 1990) for amylopectin, water, and sucrose, respectively. We recognize that the starch in the flours used did not entirely consist

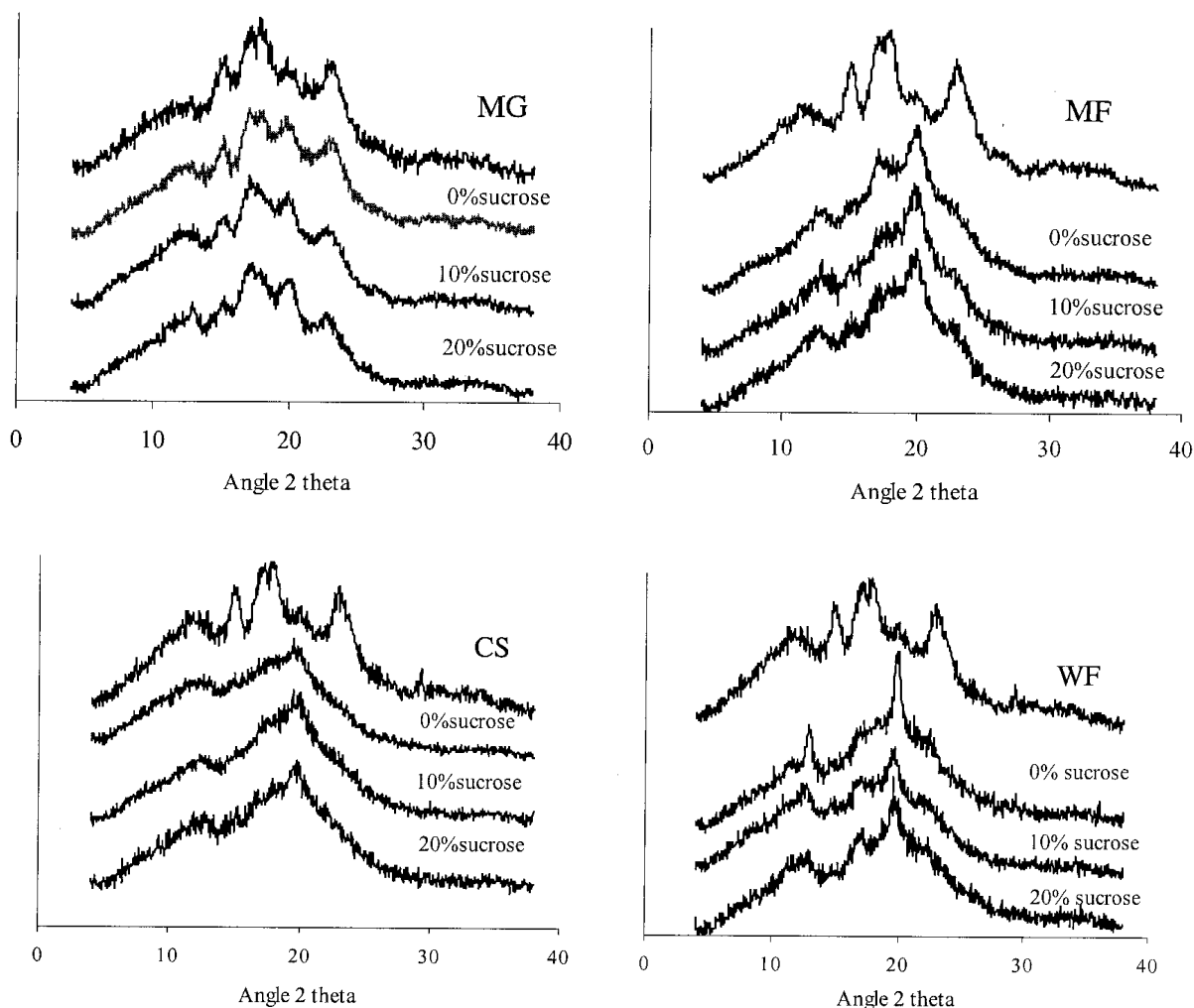


Fig. 4. X-ray diffractograms for nonexpanded extrudates of maize grits (MG), maize flour (MF), soft wheat flour (WF), and coarse semolina (CS) at different sucrose levels.

of amylopectin, nevertheless, the use of these models provides a convenient way of comparing the four systems. Overall, the shape of the curves and the magnitude of plasticization by sugar were consistent with the model predictions. There were, however, some departures. The most significant was the observations that, at all sugar levels, CS was less plasticized by water, compared with the other materials. This could perhaps be explained by the amorphous structure of the CS extrudates as indicated by X-ray profiles. Partially crystalline systems are more sensitive to water than are fully amorphous systems, as water is likely to partition preferentially into the amorphous regions (Jouppila and Roos 1997). If the results are considered as a whole, there is no evidence that difference in sugar plasticization can explain the apparent lack of an SME dependence on sugar content for wheat and maize flours. A possible explanation is that sugar mixes less efficiently with the larger particle size material and forms with water a separate low viscosity phase which persists until very close to the die end of the extruder, as previously suggested (Carvalho and Mitchell 2000). This phase becomes increasingly important as the sugar level increases.

Relationship Between Puffing and Starch Conversion

One of the objectives of this work was to try to understand why sugar had a smaller effect on the expansion of wheat flour compared with maize grits in a directly expanded system (Carvalho and Mitchell 2000). In an expanded system, two factors contribute to expansion

at the die, the growth and subsequent collapse of water bubbles and the die swell due to melt elasticity (Kokini et al 1991). In this work, extrusion occurred at $<100^{\circ}\text{C}$ and therefore the first mechanism was not present. There were significant differences ($P < 0.001$) in the die swell as shown by the SEI values reported in Fig. 8. These show some correlation with starch conversion, decreasing in the order $\text{WF} > \text{CS} > \text{MF} > \text{MG}$ and generally decrease slightly with increasing sugar content. This would be consistent with the increase in elasticity as the melt changed from a particulate colloidal structure to a polymeric type (Mitchell and Areas 1991). Elasticity results from the entanglement between starch polysaccharides released from granule structure as a result of the starch conversion process.

It is possible that the relatively small effect of sugar on wheat expansion compared with maize (Carvalho and Mitchell 2000) could be due to the higher degree of starch conversion in the former case. Changes in the state of highly converted starch had little effect on the elasticity component. It is well known that the effect of water content on expansion is different for different cereals (Whalen et al 1999). Maize grits shows a large increase in expansion with decreasing water content. We suggest that the reason for this is that, for maize, the degree of starch conversion is relatively low compared with other cereals and is particularly strongly dependent on the mechanical energy. Reducing the water increases the SME and increases starch conversion moving to higher degrees of conversion and greater elasticity. At the relatively low degrees of starch con-

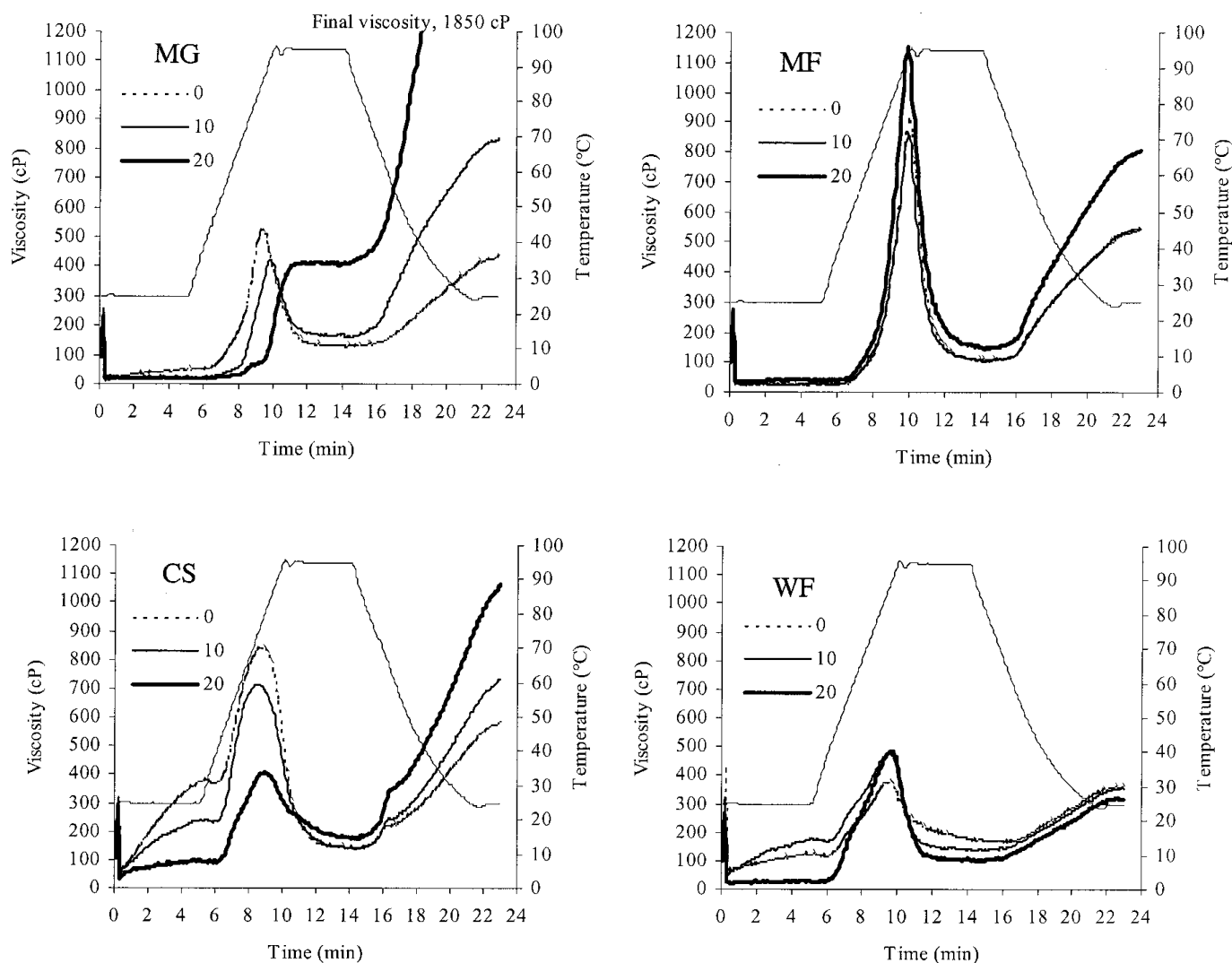


Fig. 5. Effect of sucrose on the paste viscosity of nonexpanded extrudates of maize grits (MG), maize flour (MF), soft wheat flour (WF), and coarse semolina (CS). Sucrose levels in the extrudates: 0, 10, and 20% of cereal component, db.

version suggested for extruded maize grits, this has a large effect on the die swell component as shown in Fig. 8. Another factor which may contribute to an increase in expansion of a puffed product with increasing starch conversion could be the greater stability of the bubble wall due to more entanglements between polymers in more highly converted starch. The simple hypothesis is that at

low degrees of conversion, increasing starch conversion increases expansion, whereas at higher degrees of conversion, the influence of starch conversion on expansion is not important. Further work is being done to confirm the relationship between melt elasticity and starch conversion by directly measuring elasticity in a twin barrel capillary rheometer.

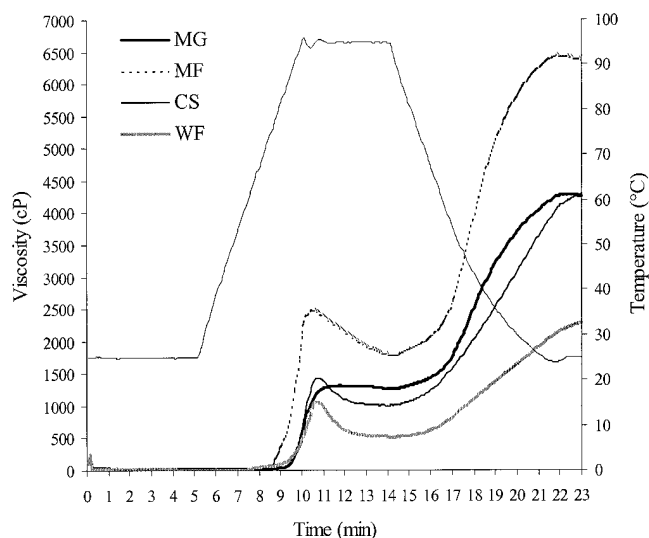


Fig. 6. Paste viscosity of nonextruded maize grits (MG), maize flour (MF), soft wheat flour (WF), and coarse semolina (CS).

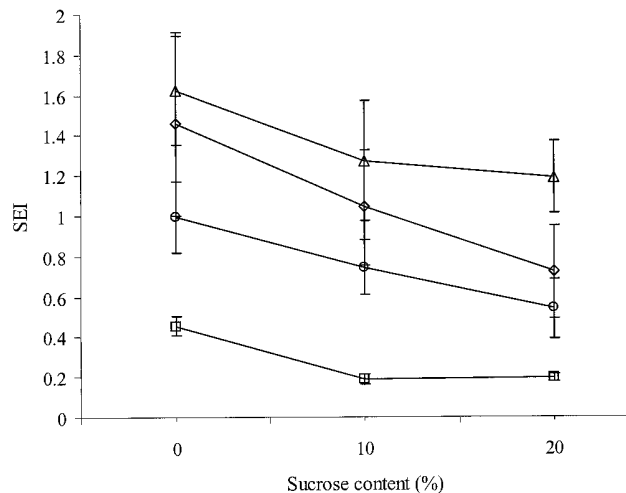


Fig. 8. Effect of sucrose on the sectional expansion index (SEI) of non-expanded extrudates of maize grits (\square), maize flour (\circ), soft wheat flour (Δ), and coarse semolina (\diamond). Error bars = standard deviation from 12 measurements.

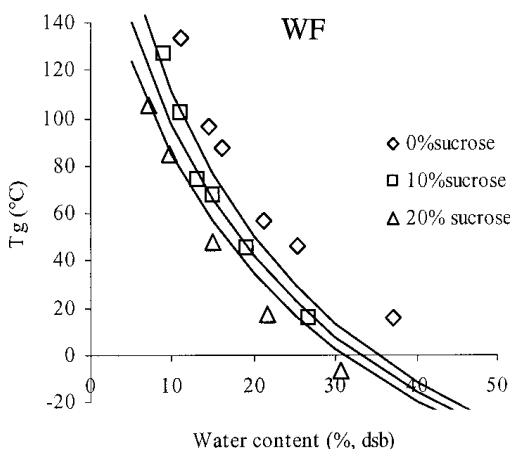
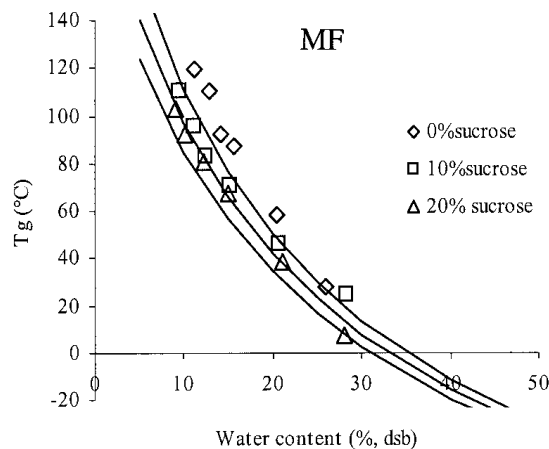
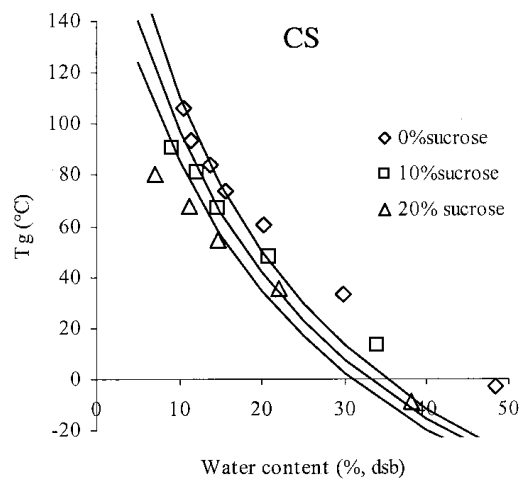
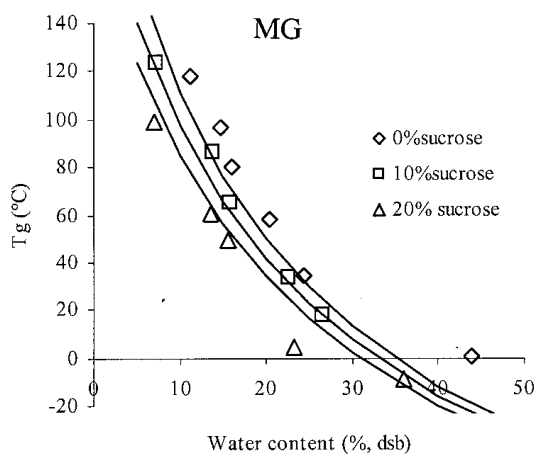


Fig. 7. Plot of DMTA $\tan \delta$ peak of experimental results for maize grits (MG), maize flour (MF), soft wheat flour (WF), and coarse semolina (CS). Curves represent theoretical T_g derived from the Ten Brinke (1983) equation for sugar levels of 0, 10, and 20% (predicted T_g decreased with increasing sucrose content).

CONCLUSIONS

The degree of starch conversion in nonpuffed ribbons prepared from wheat and maize was greater for wheat compared with maize and decreased with increased content of added sucrose and with increasing particle size of the cereal component. Plasticization by sugar and water was observed in all cases. However, the extent of water plasticization was lower for coarse wheat compared with the other three systems. It is suggested that this was because of the more amorphous character of the coarse wheat extrudates. It is suggested that the smaller effect of sugar on the expansion of wheat flour compared with maize grits was due to the greater degree of starch conversion in the latter system at all the sugar levels. Die swell was much lower for maize grits compared with the other systems, probably because of the lower elasticity in the less converted starch.

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