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THE EFFECT OF SUGARS ON THE MECHANICAL PROPERTIES OF PROCESSED CEREALS

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Abstract

Breakfast wheat-flake materials of different composition have been reconstituted as bar-shaped test pieces to reduce geometry and structure effects and allow better comparison of the matrix mechanical properties. The ground flakes comprised a control formulation and others in which components had been subtracted or substituted. The aim was to compare the mechanical properties of pressed specimens of multiple-component systems with those published for simpler one- and two-component materials. Sucrose or fructose, present in the ratio sugar:wheat 1:5.9–6.1, lowered the modulus of wheat-flake material, but by progressively lesser extent with decreasing water content below 22% (wet-weight basis, w.w.b), the difference becoming negligible at water contents of 7 to 10% (w.w.b). However, the energy to break wheat-flake samples and their fracture toughness were reduced more by fructose than sucrose addition to a control formulation sample at these water contents. The energy to break and fracture toughness increased markedly with increasing water content for all formulations.

Keywords: breakfast cereal, mechanical properties, sugars

Introduction

Breakfast cereals are complex foods, and in order to understand their textural characteristics, it is important to study their mechanical properties as they vary with composition and structure. Breakfast cereals are composed of biopolymers, principally starch and gluten. The mechanical properties of these polymers are determined, to a large extent, by their glass transitions [1, 2]. The combination of these polymers and the addition of other constituents in the process, such as water and sugar, alters the glass transition and the final properties of the flakes.

Mechanical properties in relation to the glass transition have been reviewed by Levine and Slade [3]. Ollett *et al.* [4], Attenburrow *et al.* [5] and Kalichevsky *et al.* [6] have studied stiffness and strength for bars of wheat starch

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or amylopectin as a function of water content. Attenburrow *et al.* [5, 7] and Kalichevsky *et al.* [8] have similarly studied gluten. The comparison of the mixture of both components [9], as well as the effect of sugars, polyols, emulsifiers and lipids addition to gluten or starch, has been investigated [4, 8, 10–13]. In these studies, specimens of simple geometry were obtained by hot-pressing or extrusion. Studies of the stiffness and toughness of pressed ground wheat-flakes with various components subtracted have recently been carried out [14]. Flattened wheat-flakes were loaded centrally using a small diameter probe [15]; results showed a decrease of the Young's modulus with increasing water content.

This paper reports the mechanical behaviour of different breakfast cereal flake materials which were milled and then moulded as bars and conditioned to different water contents. The flakes comprised a control formulation, without the normal added sucrose, and other samples where maltose, sucrose or fructose had been added. Some flakes were fabricated from wheat alone or with the addition of sucrose. A hot-press technique was used to reconstitute the ground flakes as bar-shaped specimens, to remove the geometry and structure effects and allow comparison of the matrix properties. Dynamic mechanical thermal analysis, together with some impact-failure tests, was used to compare the response of multiple-component systems with that published for simpler one- and two-component materials which were also in the form of hot-pressed bars. The impact data were compared with published studies on compacted particulates and polymers.

Experimental

Sample preparation

Wheat-flakes were processed according to the procedure described by Fast *et al.* [16], that is, wheat grains were first pressure-cooked, followed by granulating, flaking and toasting stages. The initial composition of the raw-material mix for wheat-flakes was as follows: flaked wheat, malt, sodium chloride, sucrose and water. Other flakes were produced by removing the sucrose or replacing it by fructose or maltose. Some flakes were made from wheat alone or wheat and sucrose. Table 1 gives the different formulations of the samples.

Samples were ground using a laboratory grinder (Type A10 IKA Labotechnik, Staufen, Germany). The moisture content of the powder was determined with a Mettler MPl6 moisture balance (Mettler Instruments Ltd, High Wycombe, Bucks, UK). The initial water content was typically 2–3% (w.w.b). Sufficient water was mixed with 12 g of powder to give a water content of 20% (w.w.b) prior to moulding. The procedure was similar to that outlined by Kalichevsky *et al.* [6] and Livings [17], except that using liquid nitrogen to add ice to the ground material was not necessary to produce a suitably homogeneous mixture.

Table 1 Different formulations before processing (weight %)

Sample	Wheat	Fructose	Maltose	Sucrose	NaCl	Malt	Water
c+s	76	0	0	13	2	2	7
c	87	0	0	0	2	2	9
c+m	76	0	13	0	2	2	7
c+f	76	13	0	0	2	2	7
w+s	79	0	0	13	0	0	8
w	91	0	0	0	0	0	9

A press was designed in this laboratory, as described elsewhere [14]. The previously prepared mixture of powder and water was loaded between the two dies and the ring. A pressure of 35 kN was applied to the upper die with the use of a hydraulic pump. The whole device was heated to 100°C, and the sample was then left for 15 min in the rig, before cold water was circulated in the inner cooling system. After 10–15 min of cooling, the sample was removed. Approximately 10 g of material produced a 65 mm-square sheet, 1.5–2 mm thick. Strips 24 mm long and 8 mm wide were cut off, and the sides were sanded to ensure they were smooth and parallel. Strips were then conditioned for 2 to 3 weeks over saturated salt solutions to give a water content range 7 to 33% (w.w.b). The higher water contents were achieved by leaving samples over water, albeit only for about 12 h.

For the impact test, the same procedure was used, although 20 g of material were required to give plaques 3 mm thick. Strips 13 mm wide and 65 mm long were cut off, and the sides were again smoothed with sandpaper. The test pieces were notched to various depths and then conditioned as described above.

The water content of the strips was determined by drying to constant weight in a fan oven (Gallenkamp, Hotbox oven with fan, size 1).

Instrumentation

DMTA measurements

A Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA) was used in the single cantilever bending mode at a frequency of 1 Hz and strain of $\sqrt{2}$ (corresponding to a nominal peak-to-peak displacement of 23 μm). The heating rate was 2°C min^{-1}. The glass transition (T_g) was defined as the maximum of the peak in tanδ.

Charpy test

The impact properties were obtained using a Zwick 5102 testing machine with 0.5, 1 or 2 J hammers. Two samples were tested at each notch depth, and

two to three unnotched samples were also tested. The energy to break was corrected for the pendulum air resistance by subtracting the free-swing energy loss. This Charpy test has been widely adopted for fracture-mechanics measurements on both metals and polymers [18].

Results and discussion

DMTA

Effect of water content

DMTA scans were performed on all samples at different water contents. Fig. 1a shows the typical variation of the bending modulus, E', for the wheat samples which were in the 9–29% water content (w.w.b.) range at the start of the experiment. Similar behaviour was also observed in the other samples of different composition. At low temperature, the glassy modulus decreased with increasing water content. Kalichevsky *et al.* [8] and Kalichevsky and Blanshard [9] observed no effect of water content on the glassy modulus of gluten or gluten/amylopectin mixtures, respectively. However Kalichevsky *et al.* [19] showed that the effect of increasing water content was to reduce the sub-T_g stiffness in amylopectin.

With increasing water content, the fall in modulus at T_g occurred at lower temperatures, as observed previously for amylopectin [6], gluten [8] and their mixtures [9]. This confirmed the expected role of water as a plasticiser of the fabricated wheat-flake samples. A shoulder occurred after the transition (Fig. 1a), particularly at high water contents, where the sample became stiffer, as indicated by a slight increase of the modulus. A similar response for amylopectin was reported by Kalichevsky *et al.* [19], who discussed its origin in terms of water loss during the temperature scan and an increase in crystallinity in their samples containing 24% (w.w.b.) water. A similar explanation would appear to apply to the highest-water-content samples of this study.

The rubbery modulus was almost independent of water content at the lower water contents, whereas Kalichevsky and Blanshard [9] for a gluten/amylopectin mixture, Kalichevsky *et al.* [8] for gluten, and Kalichevsky *et al.* [19] for amylopectin observed a decrease with increasing water content. These workers attributed this trend to a decrease in crosslinking on addition of water. Therefore, in their studies, the largest fall in modulus occurred at the highest water content. In this study, the greatest decrease of modulus was observed for the lower-water-content samples.

A peak maximum in tanδ occurred at T_g, and T_g shifted towards lower temperature with increasing water content (Fig. 1b). For the temperature range of study, the tanδ peak became more intense and somewhat narrower with increas-

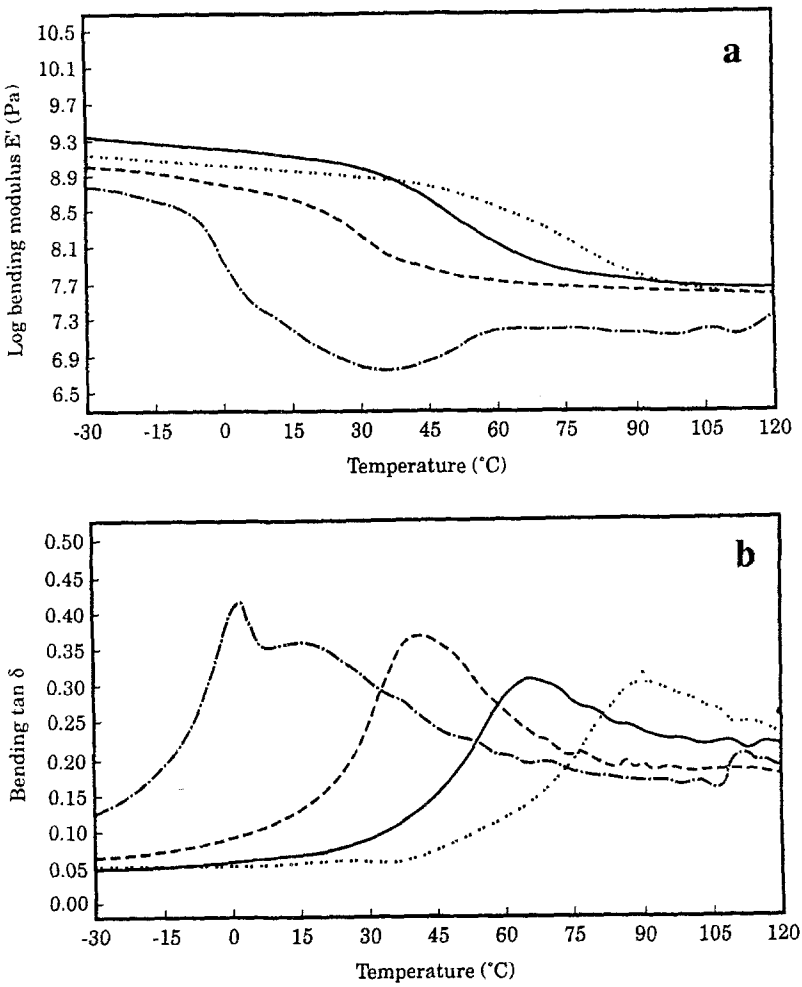

Fig. 1 DMTA a) LogE' and b) tanδ as a function of temperature for the wheat samples (w) of different water contents (- -) 10%, (—) 14%, (– –) 18%, (— -) 31%

ing water content. Kalichevsky and Blanshard [9] and Kalichevsky *et al.* [19] found a more marked but similar trend for the tanδ peak height and width with increasing water content in amylopectin/gluten (1:1) mixtures and amylopectin, respectively. Kalichevsky *et al.* [19] cited evidence from the literature for biopolymers and ionomers to support their observations. In wheat-sucrose mixtures, the peak was observed to broaden and become less intense with increasing water content [14].

At the highest water content, a sharp peak in tanδ superimposed the T_g peak and appeared around 0°C. Kalichevsky *et al.* [12] mentioned the possible con-

tribution of ice, for water contents above 27% in amylopectin. This appears to have contributed to the tanδ peaks at high water content, as shown in Fig. 1b. Data for T_g and E' were not extracted from DMTA scans in which there was this evidence of ice, because of the effect of ice formation on the water distribution.

Effect of other constituents

In Fig. 2, the dependence of E' and tanδ on temperature, for wheat and wheat plus sucrose samples at 9–10% water content, is shown. The glassy

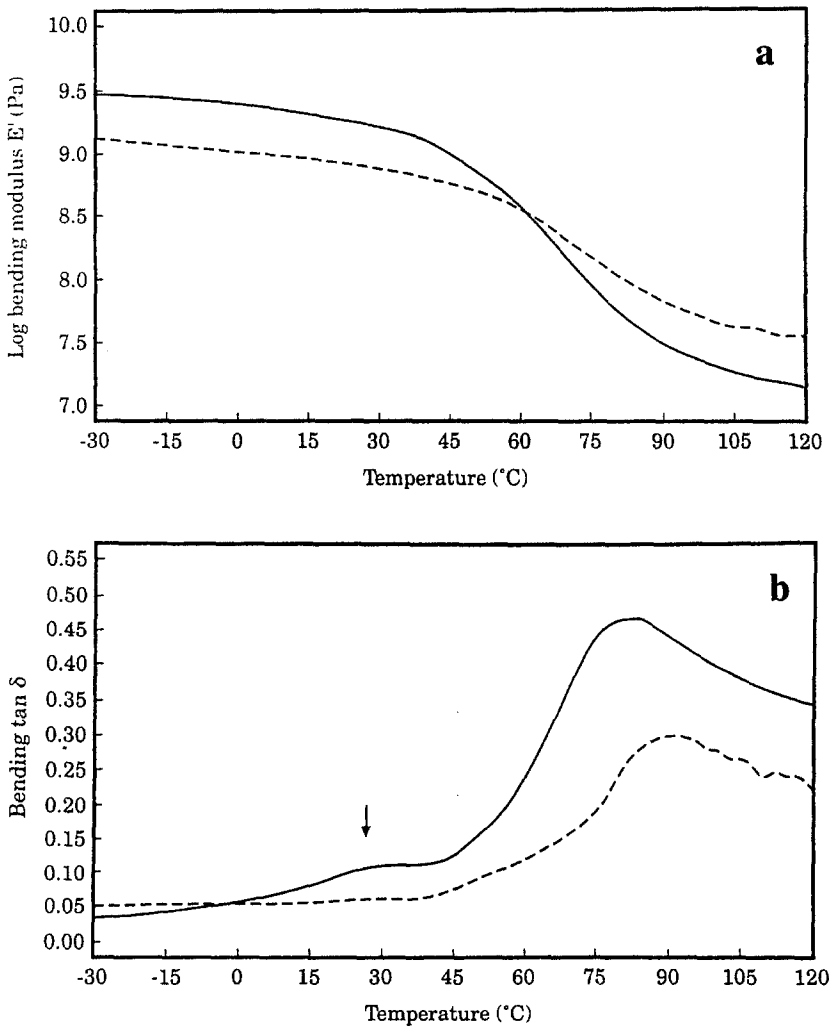

Fig. 2 DMTA a) LogE' and b) tanδ as a function of temperature for the wheat (w) (– –) and wheat and sucrose (w+s) (—) samples at 9–10% water content (w.w.b). Low temperature shoulder arrowed on (b)

modulus (low temperature limit E' values) increased and the rubbery modulus decreased upon the addition of sucrose (Fig. 2a). The plasticising effect of sucrose on fabricated wheat samples is seen in Fig. 2b, where the tanδ loss peak shifted towards lower temperature by approximately 8°C. Fig. 3 shows the dependence of E' and tanδ on temperature for the control wheat-flake mixture alone or with the addition of sucrose or fructose, also for samples at 9% water content. The tanδ peak positions were depressed by 13–15°C. In comparison with Fig. 2, similar features are seen in both E' and tanδ on the addition of su-

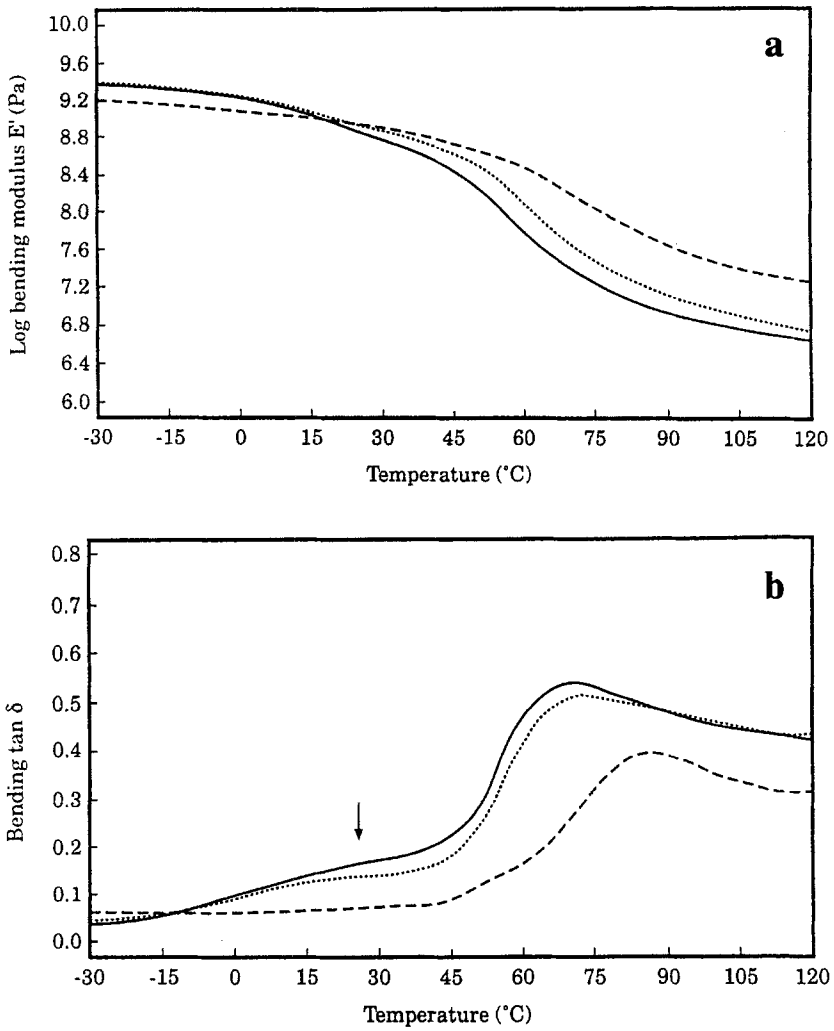

Fig. 3 DMTA a) LogE' and b) tanδ as a function of temperature for the control (c) (– –), added sucrose (c+s) (—), and added fructose (c+f) (- - -) samples at 9% water content (w.w.b). Low temperature shoulder arrowed on (b)

crose or fructose. The studies of gluten-fructose (2:1) mixtures by Kalichevsky *et al.* [8] yielded similar observations, and they explained this phenomenon in terms of: a) reinforcement of the gluten matrix by the sugar glass at low temperatures and b) the sugar behaving as a viscous liquid which reduces the rubbery modulus of gluten at high temperatures. Amylopectin-fructose (1:2) and amylopectin-sucrose addition (10:1) mixtures were studied by Kalichevsky *et al.* [12, 19], and similar results were obtained. Figures 2b and 3b show that the tanδ peak height was higher in the presence of the sugar, as also observed by Kalichevsky *et al.* [19] for fructose addition at up to 40% fructose to amylopectin.

In the low-water-content (9–10% w.w.b.) systems of Figs. 1b–3b, a low temperature shoulder below the principal T_g occurred between 15 and 30°C, which was more prominent in the sugar-containing samples. This type of feature has also been observed by Kalichevsky *et al.* [6] and Appelqvist *et al.* [20] for amylopectin. It is also relevant that two glass transition temperatures were observed for the gluten–sugar [8] and amylopectin–sugar [12] systems studied by Kalichevsky *et al.* The second transition in the present study was, however, never as well-defined as that in the high ratio sugar-amylopectin samples of Kalichevsky *et al.* [12, 19].

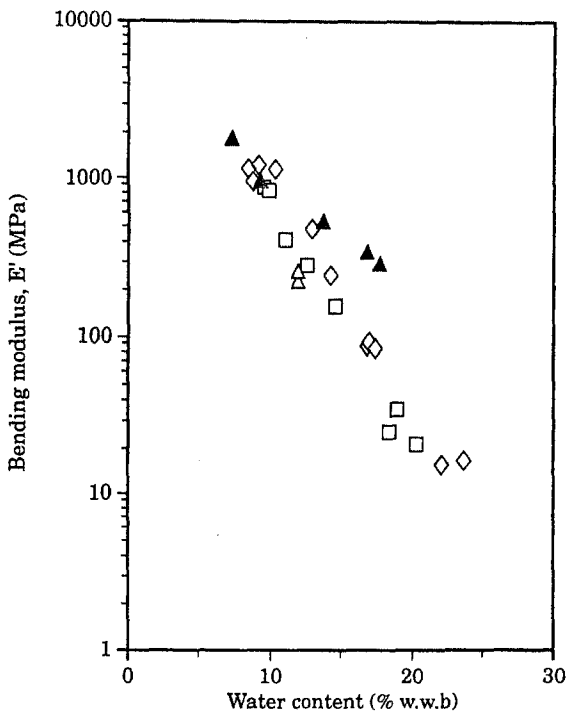

Fig. 4 DMTA E' at 20°C as a function of water content for different compositions (Table 1): (▲) control (c); (□) control +sucrose (c+s); (◊) control +fructose (c+f); (Δ) control +maltose (c+m)

Figure 4 shows the variation of the bending modulus with water content, determined at room temperature (20°C), for different samples based on the control (c). The bending modulus, E', was lower in the presence of a sugar than for sugar-free samples, the difference becoming negligible at the lower water contents of 7 to 10% (w.w.b). This confirmed the effect of maltose, sucrose and fructose as plasticisers in wheat-flakes-fabricated samples and is in general agreement with the changes in the room-temperature Young's modulus measured by a three-point-bend test on gluten–fructose [8], amylopectin–fructose [12], and starch–glucose [4] mixtures.

In Fig. 5, T_g is plotted against water content. For the different compositions, T_g fell from 100°C to 15°C with water content increasing from 7 to 22% (w.w.b). Consideration of Figs 4 and 5 shows that maltose, sucrose or fructose appeared to depress T_g of the control independent of water content, but the modulus was affected more at higher water contents. Kalichevsky *et al.* [8], in their studies of similar ratio sugar addition to gluten (1:10), commented that T_g was not greatly influenced as a function of water content in comparison with the mechanical properties. Sucrose addition to amylopectin [12] and gluten [8], at 1:10 ratios, lowered T_g by 0–10°C and 5°C, respectively. Fructose addition to amylopectin [12] and gluten [8], at 1:10 ratio, lowered T_g by 12–38°C and 7°C,

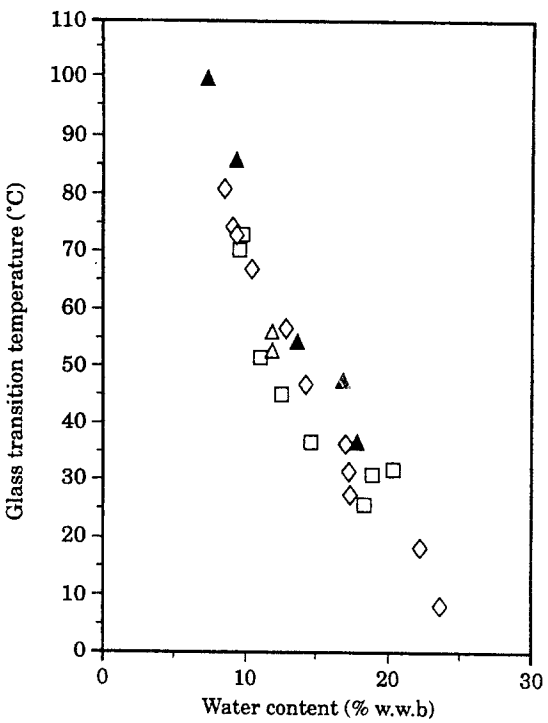

Fig. 5 T_g as a function of water content for different compositions. Symbols as in Fig. 4

respectively. The data of Figs 2b, 3b and 5 indicate T_g was lowered by 10–15°C which is consistent with these values.

Charpy test

The energy to break unnotched bars, W^*, was consistently higher for the sample (c) without sucrose (0.047 J), compared to those with sucrose (c+s) (0.034 J) or fructose (c+f) (0.027 J), at water contents of 7–9% (w.w.b.). Despite the absence of an imposed flaw, the standard error was small enough (0.001), so that the values may be concluded to be different. The value of W^* increased markedly with increasing water content (Fig. 6), out of proportion to the sugar–related differences. An estimate of the critical energy release rate, G_c, was made, based on the energy to break, W^*, for notched samples of different notch sizes, as described by Plati and Williams [21]:

$$W^* = G_c B D \Phi$$

where B is the sample width, D is the sample depth, and Φ is a calibration factor which depends on the ratios a/D and 2L/D, where a is the crack depth and 2L is the span. Values of Φ were calculated by Plati and Williams for this geometry and were used in the calculations reported here. Data from Charpy tests conform to this relationship (Fig. 7). An estimate of the fracture toughness, G_c,

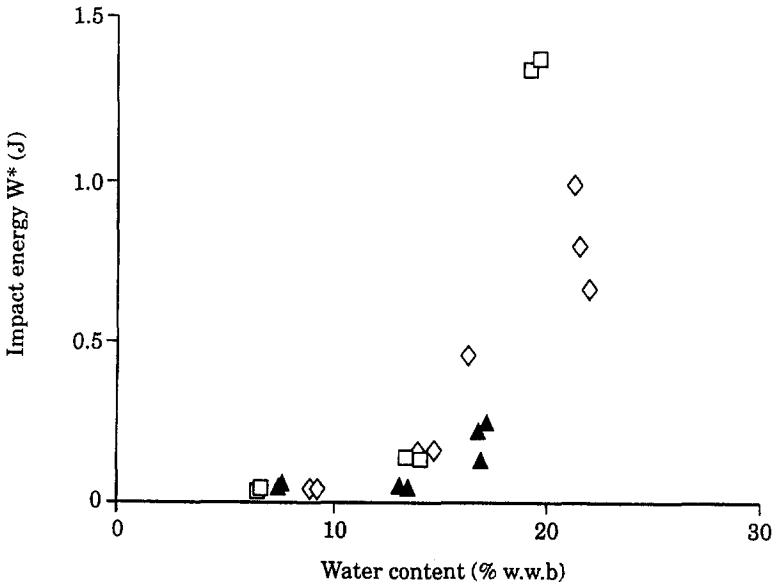

Fig. 6 Charpy test data for energy to break unnotched samples, W^*, as a function of water content (% w.w.b.) for different compositions (Table 1): (▲) control (c); (□) control+sucrose (c+s); (◊) control+fructose (c+f) (Δ)

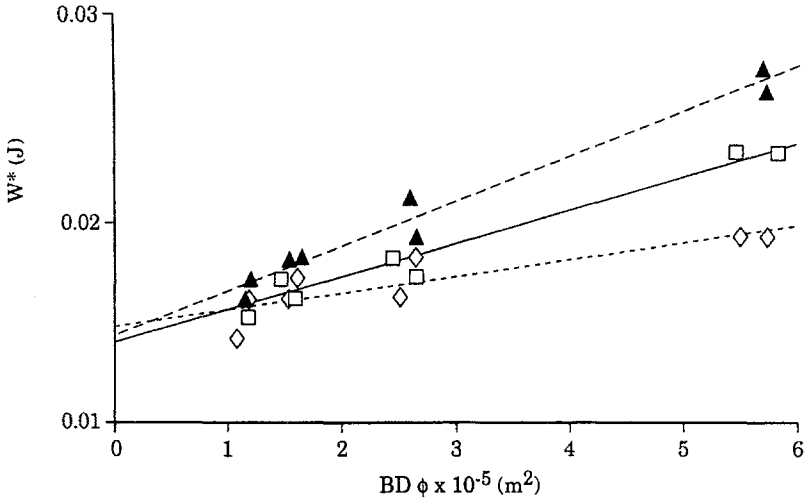

Fig. 7 The energy to break notched samples, W^*, as a function of $BD\Phi$ for different compositions at a water content of 7–9% (w.w.b.). Symbols as in Fig. 6

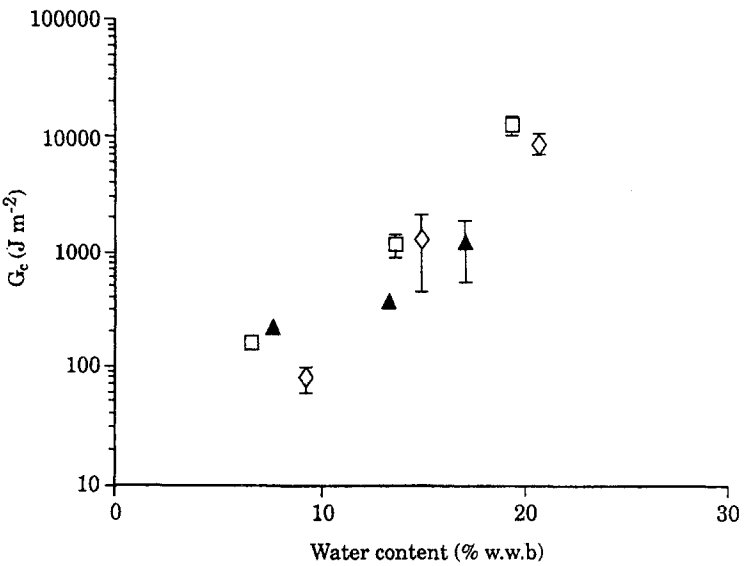

Fig. 8 Critical strain energy release rate, G_c, for the different compositions as a function of water content (% w.w.b.), showing standard errors. Symbols as in Fig. 6

indicates that this was highest for the sucrose-free samples and lowest for the fructose-containing samples at a water content of 7–9 % (Fig. 8). The effect of increasing water content was to increase the fracture toughness by up to two orders of magnitude. It should be emphasised that these values of G_c are not ab-

solute, since they depend on particle size, as shown elsewhere [22] and for other compacted materials by Adams *et al.* [23]. Mullier *et al.* [24] found G_c values of 1 to 45 J m^{-2} for glass and sand-filled polyvinyl pyrolidone. Phillips and Harris [25] reported G_c values of 100 to 300 J m^{-2} for glass-filled polyester, and Powell [26] gave G_c values from 400 to 5000 J m^{-2} for polyester and polystyrene. Plati and Williams [21] gave values of the order 10^4 J m^{-2} for tough polymers. Recent data on the impact properties of starch–synthetic polymer composites showed an increase in the impact energy with increasing water content [27]. In the context of sample breakage, Kalichevsky *et al.* [8, 12] reported that the addition of fructose (at a 1:2 level) to gluten or amylopectin reduced the water content below which their samples were brittle in three-point-bend tests. Kalichevsky and Blanshard [11] also reported that the maximum force to break or yield was much greater for amylopectin alone than in the presence of sugars. Further work is needed to clarify the compositional effects on fracture.

Conclusion

The stiffness of hot-pressed test pieces of ground wheat flakes of various compositions has been compared with that reported in the literature for gluten and amylopectin and their mixtures with each other and with sugars. The general features of the gluten and amylopectin systems were exhibited by wheat and by the more complex samples, although water content affected the rubbery modulus less than previously reported. The tanδ peak was smaller and broader at high water content, compared to that observed for amylopectin and amylopectin/gluten (1:1) mixtures. The fall in the bending modulus at the glass transition was greatest at lower water content, contrary to previous results for the simpler systems. The breadth of the principal tanδ peak for the wheat-flake materials may reflect the heterogeneity of the mixture. A low temperature shoulder on the main tanδ peak was better-defined in the sugar-containing flakes. The omission of sucrose or fructose (added to wheat in the ratio 1:5.9–6.1) from any of the wheat mixtures affected the temperature-dependent bending modulus. At 20°C, the addition of maltose, sucrose or fructose increasingly reduced the stiffness, as the water content was increased from 7% (w.w.b). Charpy impact tests showed that the energy to break and the toughness were decreased more by the addition of fructose than of sucrose to the wheat mixture at a water content of 7–9% (w.w.b.), but that in all cases, these parameters increased strongly with water content increasing to 20% (w.w.b.).

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