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Mechanical properties of wheatflake components

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The mechanical behaviour of breakfast wheat flake materials of different composition reconstituted as bar-shaped test pieces, to reduce the geometry and structure effects and allow better comparison of the matrix properties, is reported. The ground flakes comprised a control formulation and others in which one or more components had been subtracted. 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. The results on the bending modulus, E, at 20°C fell into two groups, depending on whether sucrose (wheat:sucrose = 5.9–6.1:1) was present. Sucrose lowered the modulus but by progressively less with decreasing water content below 22% (wet weight basis, w.w.b), the difference becoming negligible at water contents of 7–10% (w.w.b). However, the energy to break samples at 7% water content (w.w.b) was greater when sucrose was subtracted from the control formulation sample.

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 (Levine & Slade, 1990; Slade & Levine, 1993). 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.

Recently, mechanical properties and the glass transition have been studied, particularly in wheat starch and amylopectin (Zeleznak & Hoseney, 1987; Ollett *et al.*, 1991; Attenburrow *et al.*, 1992; Kalichevsky *et al.*, 1992a) and gluten (Hoseney *et al.*, 1986; Attenburrow *et al.*, 1990., 1992; Kalichevsky *et al.*, 1992b; Levine & Slade, 1993) as a function of water content. Comparison of the mixture of both components (Kalichevsky & Blanshard, 1992), as well as the effect of sugars, emulsifiers and lipid addition to gluten or starch, has been investigated (Ollett *et al.*, 1991; Kalichevsky *et al.*, 1992b, c; Kalichevsky & Blanshard, 1993). In these studies the specimens of simple geometry were obtained by hot pressing, or extrusion in the case of Ollett *et al.* (1991). Flattened wheatflakes were studied using a probe penetration technique in recent work (Georget *et al.*, 1995) which 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 and examples where one or more of the components had been subtracted. 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 were 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.

MATERIALS AND METHODS

Sample preparation

Wheatflakes were processed following the procedure described by Fast and Caldwell (1990), that is, wheat grains were first pressure cooked followed by granulating, flaking and toasting stages. The initial composition of the raw material mix for wheatflakes was as follows: flaked wheat, malt, sodium chloride

Table 1. Different formulations before processing (%)

Sample	Wheat	Sucrose	NaCl	Malt	Water
1	76	13	2	2	7
2	77	13	—	2	8
3	77	13	2	—	8
4	87	—	2	2	9
5	79	13			8
6	89	—	—	3	8
7	89		2	—	9
8	91	—	—	—	9

(NaCl), sucrose and water. By removing different ingredients from the original formulation, eight samples were produced. Table 1 gives the different formulations of the samples.

Samples were ground using a laboratory grinder (Type A10 IKA Labotecknik, Staufen, Germany). The moisture content of the powder was determined with a Mettler MP16 moisture balance (Mettler Instruments Ltd, High Wycombe, Bucks, UK). The initial water content was typically 2–3% (wet weight basis, w.w.b). Sufficient water was mixed with 12 g of powder to give a 20% water content (w.w.b) prior to moulding. The procedure was similar to that outlined by Kalichevsky *et al.* (1992a) and Livings (1994) except that using liquid nitrogen to add water to the sample as ice was not considered necessary as the water and the ground material gave a suitably homogeneous mixture.

A press was designed in this laboratory consisting mainly of a square mould ring of side 65 mm between two male compaction dies which were temperature controlled by four cartridge heaters and an inner cooling system. The mixture of powder and water obtained previously 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 up 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 cooling, the sample was removed. Approximately 10 g of material gave a 65 mm square sheet, 1.5–2 mm thick. Strips 24 mm long and 8 mm wide were cut off and the sides sanded to ensure that they were smooth and parallel. They were then conditioned for 2–3 weeks over saturated salt solutions to give a water content range of 7–33% (w.w.b). The higher water contents were achieved by leaving samples over water, albeit for approximately 12 h. The water content of the strips was determined by drying in a fan oven at 130°C to constant weight (Gallenkamp, Hotbox oven with fan, size 1).

For the Charpy test, the same procedure was used, although 20 g of material was required to give plaques 3 mm thick. Strips 13.3 mm wide and 65 mm long were cut off and the sides again smoothed with sandpaper. The test pieces were notched using a low-speed diamond-impregnated wafering saw (Buehler Isomet, IL, USA) of sufficiently large radius (127 mm) to minimize notch curvature. This was fitted with a sample holder which could be indexed towards the blade by means of a micrometer in steps of 0.5 mm. Notches of widths 0.4 mm and various depths could then be made. The samples were then conditioned for 3 weeks over saturated salt solution to give a water content of 7% (w.w.b).

Instrumentation

DMTA measurements

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

Charpy test

The impact properties were obtained using a Zwick 5102 testing machine with a 0.5 J hammer. Two samples were tested at each notch depth and four unnotched samples. The energy to break was corrected for the pendulum air resistance by subtracting the free swing energy loss. The Charpy test has been widely adopted for fracture mechanics measurements on both metals and polymers (Bucknall, 1978).

RESULTS AND DISCUSSION

DMTA

Effect of water content

DMTA scans were performed on all samples at different water contents. Figure 1 shows the typical variation of the bending modulus, E, for the wheat–sucrose samples (5) 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.* (1992b) and Kalichevsky and Blanshard (1992) observed no effect of water content on the glassy modulus of gluten or gluten–amylopectin mixtures, respectively. However, Kalichevsky *et al.* (1993a) showed that the effect of increasing water content was to reduce the sub-glass transition stiffness in amylopectin. As with their data, the results of Fig. 1 indicate convergence of the glassy moduli at a temperature below the range studied.

With increasing water content, the T_g shifted towards lower temperature as observed previously for gluten and amylopectin and their mixtures (Kalichevsky *et al.*, 1992a, b; Kalichevsky & Blanshard, 1992). This

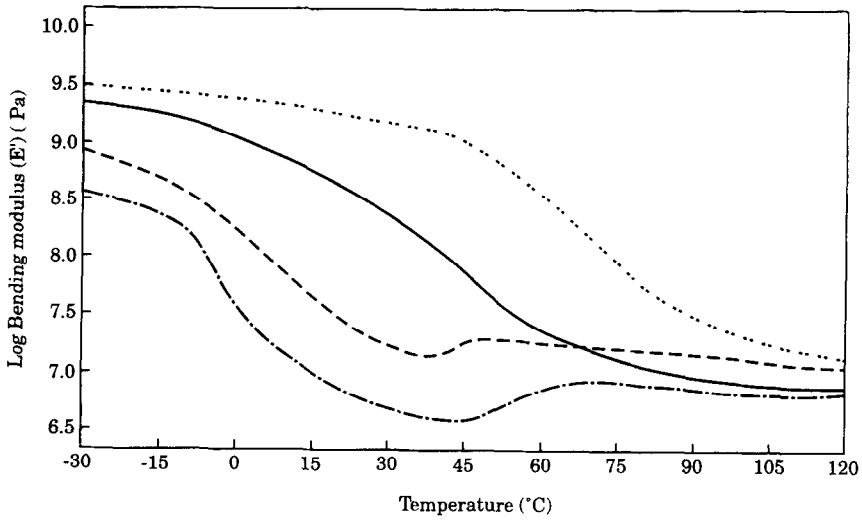

Fig. 1. DMTA log E for the wheat–sucrose sample (5) for different water contents as a function of temperature. (- - - -) 9%; (—) 14%; (– –) 23%; and (– -) 29%.

confirms the expected role of water having a plasticizing effect on the fabricated wheatflake samples. A shoulder occurred after the transition (Fig. 1), particularly at high water contents where the sample became stiffer as shown by a slight increase of the modulus. A similar response was reported by Kalichevsky *et al.* (1993a) for amylopectin who discussed its origin in terms of water loss during the temperature scan and an increase in crystallinity in samples of 24% (w.w.b.) water. A similar explanation would appear to apply to the two highest water contents of this study.

The rubbery modulus was approximately independent of water content, whereas Kalichevsky and Blanshard (1992) for a gluten–amylopectin mixture, Kalichevsky *et al.* (1992b) for gluten and Kalichevsky *et al.* (1993a) for amylopectin observed a decrease with increasing water content. They attributed this trend to a decrease in cross-linking on addition of water. The largest fall in modulus, therefore, occurred at the highest water content. In this study the greatest decrease of modulus (by approximately 2.5 orders of magnitude) was for the lower water samples. Given the complexity of the present samples, it is perhaps surprising that at low water content the drop in modulus at T_g was so great. The increase in crystallinity at higher water contents mentioned above could nonetheless be expected to reduce the fall in modulus relative to the drier samples.

A maximum peak in $\tan\delta$ occurs at the T_g which shifted towards lower temperature with increasing water content (Fig. 2). For the temperature range of the study, the $\tan\delta$ peak intensity and width, respectively, slightly decreased and became somewhat broader with increasing water. Kalichevsky and Blanshard (1992) and Kalichevsky *et al.* (1993a) found a more marked but opposite trend for the $\tan\delta$ peak height and width with

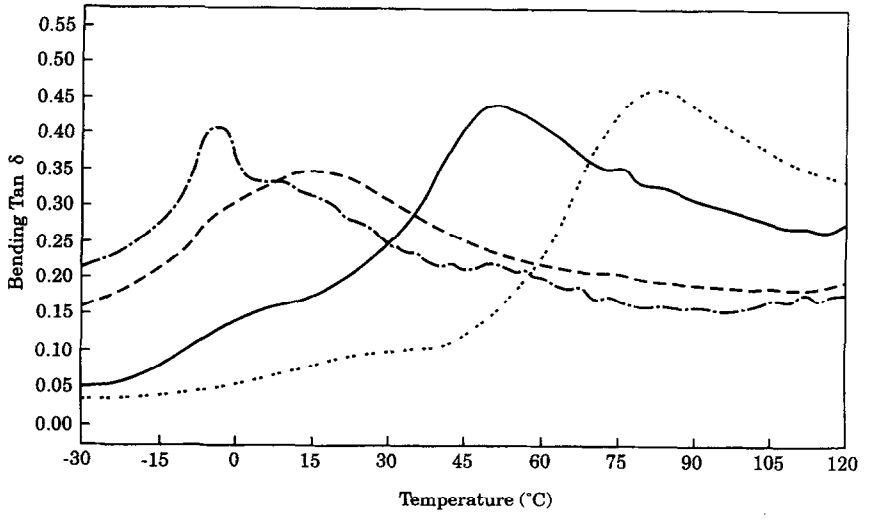

Fig. 2. DMTA $\tan\delta$ for the wheat–sucrose sample (5) for different water contents as a function of temperature. Symbols as in Fig. 1.

increasing water content in amylopectin–gluten (1:1) mixtures and amylopectin, respectively. Although plasticizers have been reported to broaden the loss peak for synthetic polymers, Ward, (1983) and Kalichevsky *et al.* (1993a) cited evidence from the literature for biopolymers and ionomers to support their observations. MacKnight *et al.* (1978) also mentioned that the breadth of the T_g peak indicates the heterogeneity of the material, which might apply to the present materials. This was supported in the data of Kalichevsky *et al.* (1993a) for different proteins where multiple components, cross-linking and order were cited as reducing the size of the transition. At the higher water contents this is consistent with the development of crystallinity broadening the transition, as cited by Kalichevsky *et al.* (1993b) for amylopectin–glucose mixtures.

At the highest water content, a sharp peak in $\tan\delta$ superimposed the T_g peak and appeared around 0°C. Blond (1994) attributed the latter to the melting of ice in a study of fructose solutions. Kalichevsky *et al.* (1993b) also mentioned the possible contribution of ice above water contents of 27% in amylopectin. This would appear to contribute to the $\tan\delta$ peaks at high water content as shown in Fig. 2. Data for T_g and E were not extracted from DMTA scans where this evidence for ice existed, due to its effect on the water distribution.

A low temperature transition below the principal T_g occurred as shown in Fig. 2. This type of feature has also been observed by Kalichevsky *et al.* (1992a) and Appelqvist *et al.* (1993) for amylopectin. It is also relevant that two glass transition temperatures were observed for the gluten–sugar and amylopectin–sugar systems studied by Kalichevsky *et al.* (1992b, 1993b).

In Fig. 3, the T_g is plotted against water content for a wheat sample (8) and one having the control formulation (1). DMTA results obtained from Kalichevsky *et al.* (1992b) and Kalichevsky *et al.* (1992a), respectively, for gluten and amylopectin were added as a comparison. In the available water content range, the T_g for the control formulation-fabricated samples was closer to that of gluten, while that for wheat alone was closer to amylopectin. Two high temperature DMTA peaks were reported by Kalichevsky and Blanshard (1992) for amylopectin–gluten mixtures. The results here using a higher pressing temperature resulted in a single peak, consistent with the studies of Davies and Nicholls cited in Kalichevsky and Blanshard (1992).

Effect of other constituents

In Fig. 4a, the logarithm of the bending modulus E is plotted for the control formulation-fabricated samples (1) and without sucrose (4). At low temperature, the glassy modulus was increased and the rubbery modulus decreased due to the effect of sucrose. Kalichevsky *et al.* (1992b) also observed this in gluten–fructose (2:1)

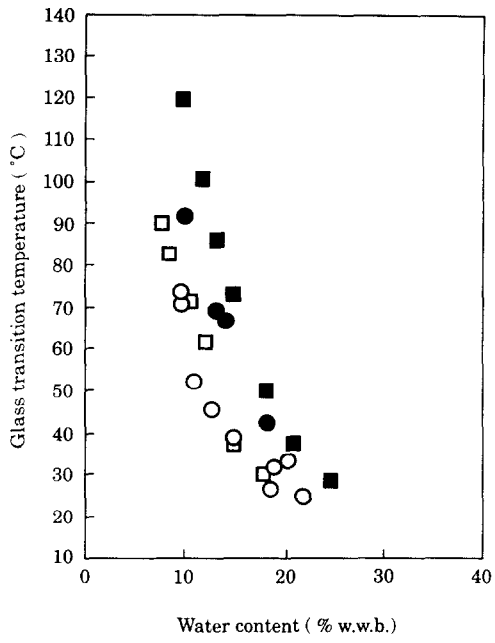

Fig. 3. T_g of (■), amylopectin (Kalichevsky *et al.*, 1992*a*); (□), gluten (Kalichevsky *et al.*, 1992*b*); (●), wheat (8); and (○), control formulation (1) as a function of water content.

mixtures and explained this effect by the reinforcement of the gluten matrix by the sugar glass at low temperature. At a high temperature, sucrose is thought to behave like a viscous liquid which reduces the gluten rubbery modulus.

The plasticizing effect of sucrose on fabricated samples is observed in Fig. 4b where the $\tan\delta$ loss peak shifted towards lower temperature for a 9% (w.w.b) moisture content. This was also found for gluten by Kalichevsky *et al.* (1992b) and for amylopectin by Kalichevsky *et al.* (1993b) who studied fructose addition at a 1:2 ratio and sucrose addition at a 1:10 ratio. The $\tan\delta$ peak height was higher in the presence of sucrose which was also observed by Kalichevsky *et al.* (1993a) for fructose addition to amylopectin at up to 40% fructose. Figure 4b shows a low-temperature transition (shoulder) in the sucrose-containing sample. In general, a comparison of all the samples in the water content range 7–11% (w.w.b.) showed that this second transition was more marked in sucrose-containing samples than in those without sucrose. The second transition was, however, never as well-defined as in the high ratio sugar–amylopectin samples of Kalichevsky *et al.* (1993a, b).

Figure 5 shows the variation of the bending modulus with water content determined at room temperature (20°C) for the eight samples. At any particular water content, the bending modulus, E, was lower in the presence of sucrose than for the sucrose-free samples except at lower water contents of 7–10% (w.w.b) where the modulus was approximately constant for the different samples. This confirms the effect of sucrose as a plasticizer in wheatflake-fabricated samples and is in general agreement with the changes in the room temperature Young's modulus measured by a three-

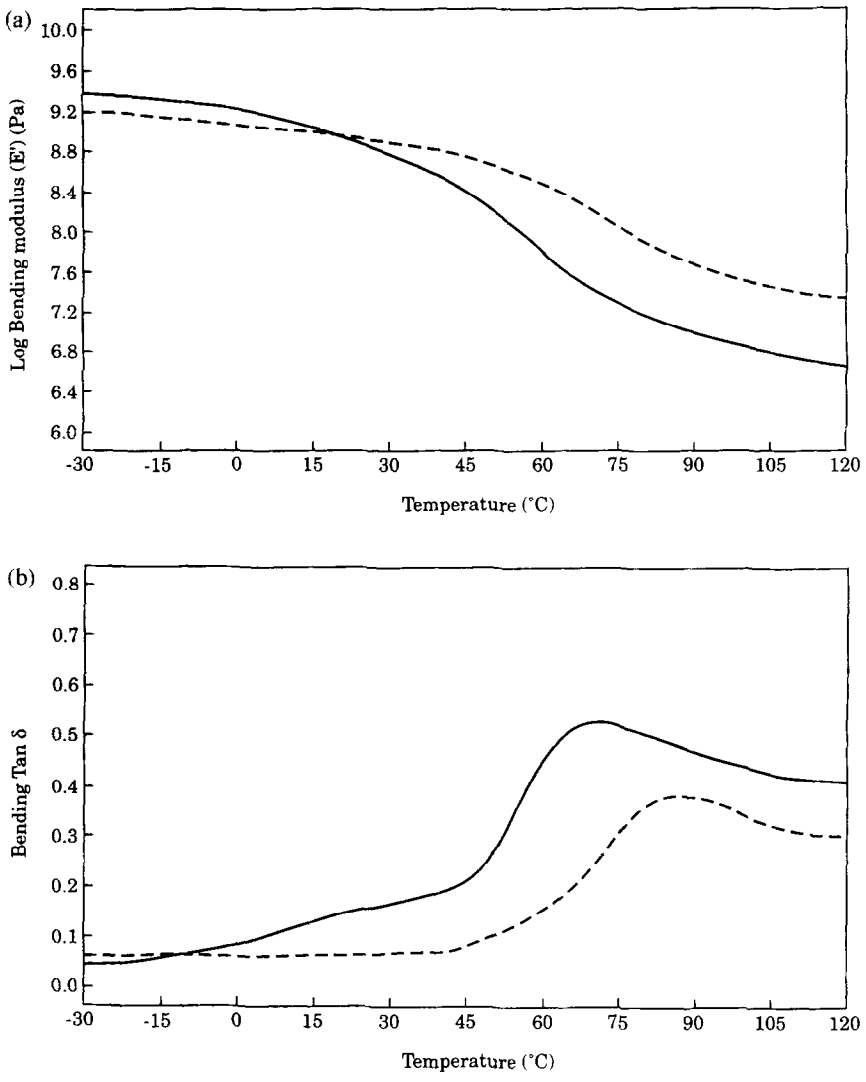

Fig. 4. (a) DMTA log E for the control formulation (1) (—); and without sucrose (4) (– –) at 9% water content (w.w.b). (b) DMTA tan δ for the control formulation (1) (—); and without sucrose (4) (– –) at 9% water content (w.w.b).

point bend test on gluten–fructose, amylopectin–fructose and starch–glucose mixtures observed by Kalichevsky *et al.* (1992b), Kalichevsky *et al.* (1993b) and Ollett *et al.* (1991), respectively.

In Fig. 6, the T_g is plotted against water content. For the different compositions, the T_g fell from 100°C to 15°C with increasing water content from 7 to 22% (w.w.b). Consideration of Figs 5 and 6 shows that sucrose appears to influence the T_g uniformly with water content but does affect the mechanical properties more at higher water contents. However, for 10:1 ratios of amylopectin–sucrose and gluten–sucrose, Kalichevsky *et al.* (1992b, 1993b) found that the T_g was lowered slightly more at water contents of 12–18% (w.w.b) than at higher values.

Charpy test

The energy to break unnotched and notched bars at a water content of 7% (w.w.b.) was consistently higher for the sample without sucrose (4) compared to that with sucrose (1) (Table 2 and Fig. 7). It is surprising that despite the absence of an imposed flaw, the standard deviation was small enough to enable the values to be considered as different. An estimate of the critical energy release rate, G_c, was made based on the energy to break, W^*, for different notch sizes as described by Plati and Williams (1975):

$$W^* = G_c BD\phi$$

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. Figure 7 is a plot of W^* against $BD\phi$ and the values of G_c are included in Table 2. An estimate of the fracture toughness, G_c, indicates that this was slightly higher for the sucrose-free samples. Ideally, a line through the data of Fig. 7 should pass through the

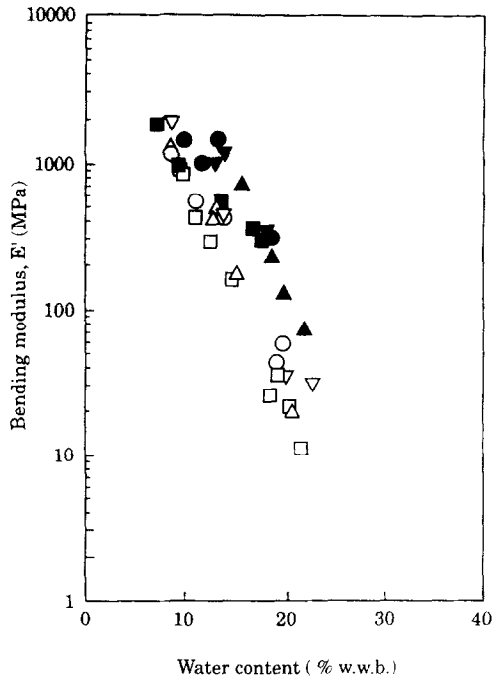

Fig. 5. E at 20°C as a function of water content for the different compositions (see Table 1): (■), wheat, NaCl, malt (4); (▲), wheat, NaCl (7); (●), wheat, malt (6); (▼), wheat (8); (□), wheat, malt, NaCl, sucrose (1); (○), wheat, malt, sucrose (2); (△), wheat, NaCl, sucrose (3); (▽), wheat, sucrose (5).

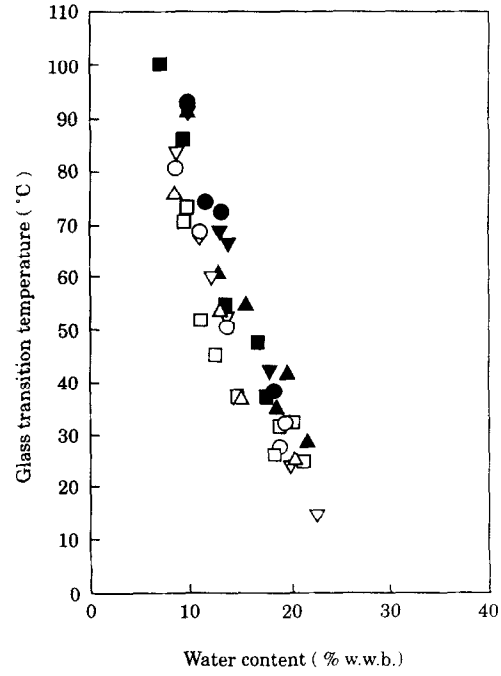

Fig. 6. T_g as a function of water content for the different compositions. Symbols as in Fig. 5.

origin. This was not the case, suggesting some incomplete compensation for the energy correction or some breakdown of the analysis for these samples (Marshall *et al.*, 1973).

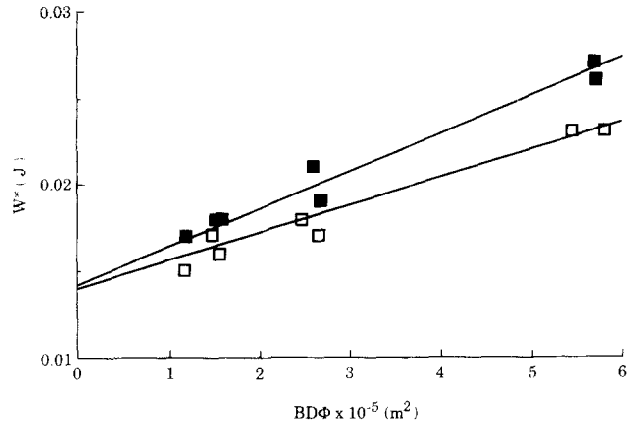

Fig. 7. Charpy test data of energy to break, W^*, for the control formulation sample (1) (□); and without sucrose (4) (■) as a function of $BD\phi$ at 7% (w.w.b.) water, where B is the sample width, D is the sample depth and ϕ is a calibration factor.

Table 2. The energy to break, W^*, and the critical stain energy release rate, G_c, determined for unnotched and notched samples, respectively, at 7% (w.w.b.) water

Samples	Unnotched (W^*/J)	Notched (G_c/J/m^2)
With sucrose (1)	0.034±0.004[a]	157/0.936[b]
Without sucrose (4)	0.047±0.004[a]	214/0.969[b]

[a] Standard deviation.
[b] r^2 = coefficient of determination.

The present study shows that although both samples were brittle at ambient temperature, the removal of sucrose made the samples harder to break or tougher. In the context of sample breakage, Kalichevsky *et al.* (1992b, 1993b) reported that the addition of fructose (at the 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 (1993) also reported that the maximum force to break or yield was much greater for amylopectin alone than in the presence of sugars. Comparing the present results of Table 2 with the stiffness data, Fig. 5 shows that the moduli of samples with and without sucrose were generally similar at a water content of 7% (w.w.b). However, Fig. 4a indicates that at 9% water (w.w.b.), the effect of sucrose was to increase the stiffness at temperatures below ambient. It is therefore possible that this may occur at ambient temperature for lower water contents.

CONCLUSION

The stiffness of hot-pressed test pieces of ground wheatflakes 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 glass transition of flaked wheat, and also a

more complex formulation of wheat, sucrose, salt and malt, fell approximately within the envelope of results found by Kalichevsky *et al.* (1992a, b) for amylopectin and gluten. The general features of the gluten and amylopectin systems were exhibited by the more complex samples, although water content affected the rubbery modulus less than previously reported. The tan δ peak was smaller and broader at high water content in contrast to that observed for amylopectin (Kalichevsky *et al.*, 1993a) and amylopectin–gluten (1:1) mixtures (Kalichevsky & Blanshard, 1992). The decrease in the bending modulus at the glass transition was greatest at lower water content, contrary to the results for the simpler systems. The breadth of the principal tan δ peak for the wheatflake materials indicates the heterogeneity of the mixture and the immiscibility of the components. The subtraction of sucrose (added to wheat in the ratio 1: 5.9–6.1) from any of the wheat mixtures, regardless of whether or not they contained salt and malt, was the only compositional change studied here to affect the temperature-dependent bending modulus. At 20°C, addition of sucrose increasingly reduced the stiffness as the water content was increased from 7 to 22% (w.w.b). Some evidence was obtained from Charpy impact tests that the energy to break and the toughness at 7% (w.w.b) water decreased on adding sucrose.

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