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The mechanical properties of pressed processed wheat material

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Breakfast wheatflake materials, produced by two methods, were milled and different sieve fractions reconstituted by hot pressing into bar-shaped test pieces, to reduce the geometry and structure effects of flakes. The stiffness and fracture properties of these pressed bars of different particle size in ranges <0.5 mm, 0.5–1 mm, 1–1.4 mm, 1.4–2 mm and of different water content were compared. Dynamic mechanical thermal analysis showed that the bending modulus, E', superimposed as a function of temperature in the range −40 to 140 °C. The value of E' at 20 °C decreased with increasing water content corresponding to depression of the glass transition temperature. Microscopy of the test pieces revealed that starch was the continuous phase. The stiffness properties were similar in many respects to data published for pressed starch specimens. However, the energy to break samples at 7% water content (wet weight basis) was greater when a range of particle sizes was used compared to the results of narrow particle size ranges. This is consistent with published results on fracture toughness of particulate compacts. The energy to break samples increased with increasing water content.

1. 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.

Recently, mechanical properties and the glass transition, T_g, have been studied particularly in wheat starch and amylopectin [3–7] and gluten [5, 7–11] as a function of water content, together with the behaviour of the mixture of both components [12] and of their mixtures with sugars [10, 13, 14]. In these studies the specimens of simple geometry were generally obtained by hot pressing or extrusion. A recent study of the effects of formulation changes on the mechanical properties of ground wheatflakes hot pressed into bars was reported [15]. Flattened wheatflakes were deflected at the centre using a probe penetration technique [16] which showed a decrease of the Young's modulus with increasing water content.

This paper reports the mechanical behaviour of breakfast cereal flake materials which were milled and then moulded as bars and finally conditioned to different water contents. A hot-press technique was used to reconstitute the milled flake material as bar-shaped specimens to remove the geometry and structure effects associated with flakes and allow better comparison of the matrix properties. The bars were fabricated from milled material and different sieve fractions. Dynamic mechanical thermal analysis was used to compare the stiffness of the multiple component flake material as a function of temperature and water content with that published for simpler one- and two-component materials which were also in the form of hot-pressed bars. The impact failure in terms of the energy to fracture samples was compared with other published studies on the fracture toughness of compacted particulates and of filled polymers [17–19].

2. Experimental procedure

2.1. Sample preparation

Wheatflakes were processed following the procedure described by Fast and Caldwell [20], that is, wheat grains were first either processed in a pressure cooker (identified as type P) or in an extrusion cooker (type E) 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, sucrose and water.

Samples were ground using a laboratory grinder (Type A10 IKA Labotechnik, 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.). In addition to a standard ground sample, the ground powder was sieved to produce

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

	Unnotched	Notched
Particle size range (mm)	W^* (J)	G_c (J m^{-2})
< 0.5	0.025 ± 0.002[a]	50 ± 14[a]
0.5–1	0.019 ± 0.001[a]	84 ± 21[a]
1–1.4	0.018 ± 0.001[a]	74 ± 16[a]
1.4–2	0.019 ± 0.001[a]	62 ± 15[a]
Unsieved	0.028 ± 0.002[a]	117 ± 17[a]

[a] Standard error of the mean.

different size ranges as given in Table I. Sufficient water was mixed with 12 g of each specimen to give a 20% water content (w.w.b.) prior to moulding. The procedure was similar to that outlined by Kalichevsky *et al.* [6] and Livings [21] except that using liquid nitrogen to freeze the added water 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 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 they were smooth and parallel. They were then conditioned for 2–3 weeks over saturated salt solutions to give a water content range 7%–33% (w.w.b.). The higher water contents were achieved by leaving samples over water.

For the Charpy test, the same procedure was used, although 20 g 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 to various depths then conditioned over saturated salt solutions as described above.

The water content of the strips was determined by drying to constant weight in a fan oven at 130 °C (Gallenkamp, Hotbox oven with fan, size 1).

2.2. Instrumentation

2.2.1. 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 $2^{1/2}$ (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 peak in tan δ.

2.2.2. Impact test

The impact properties were obtained using a Charpy test geometry with a Zwick 5102 testing machine generally with a 0.5 J hammer, although energies of up to 2 J were also used. 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 [22].

2.3. Microscopy

2.3.1. Scanning electron microscopy (SEM)

Test bars of type P samples at 7%, 14% and 19% (w.w.b.) were fractured. Each fracture surface was coated with a layer of gold, approximately 25 nm thick, in an Emitech K550 sputter coating unit, and examined and photographed in a Leica Cambridge 360 scanning electron microscope.

2.3.2. Light microscopy

Sections, approximately 3 μm thick, were cut from pieces of flake held, without infiltration, in polymerized Spurr resin. Sections were also cut directly from type P and E test bars without an embedding step. Small pieces sawn from each bar were held in the chuck of a Reichert Ultracut E microtome, and sections 1–2 μm thick were cut using glass knives. All sections were stained by placing them directly on to a drop of iodine in potassium iodide (1% wt vol^{-1} iodine and 1% wt vol^{-1} potassium iodide in water) allowing them to stretch before a coverslip was applied. Sections were examined and photographed using a Leitz Ortholux microscope.

3. Results and discussion

3.1. DMTA

3.1.1. Effect of particle-size range

Fig. 1 shows DMTA scans at one water content for the bars moulded from different sieve fractions of the type E flakes. The scans of E' for the different sieve fractions were almost coincident. The general features of the E' variation with temperature (Fig. 1a) are similar to those previously reported for a bar fabricated from unsieved type P wheatflake material [15] and for gluten and amylopectin polymers [6, 10] and their mixtures with each other [12] and sugars [10, 14]. The material underwent a glass to rubber transition, T_g, although the fall in modulus (by approximately 2.5 orders of magnitude) was less than that normally associated with synthetic polymers. The reduced decrease in E' may be attributed to crystallization or ordering of the molecules. For example, in studies of polyethylene terephthalate [23], the fall in modulus was 2.5 orders of magnitude in the amorphous sample

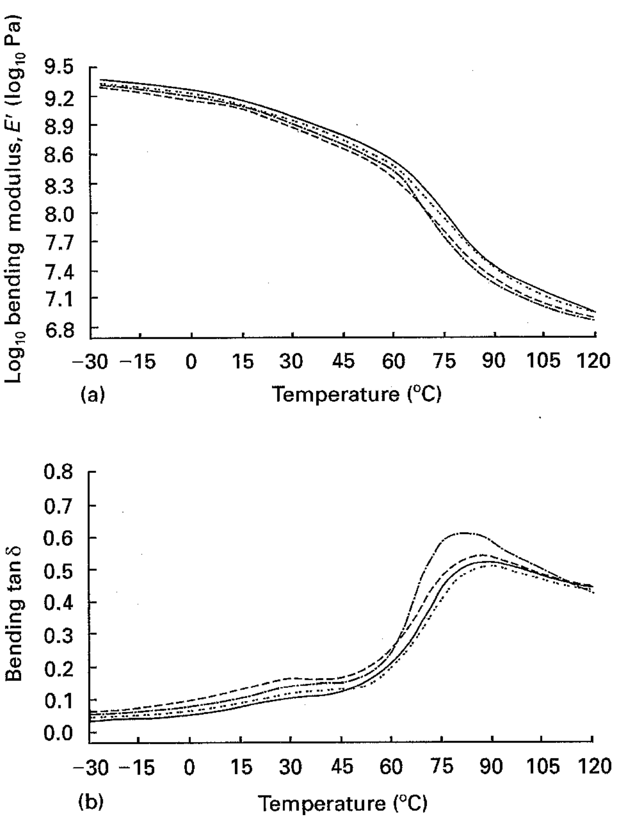

Figure 1 DMTA log E' and tan δ for E samples at an initial water content of 7.5%–8.0% (w.w.b.) as a function of temperature for different particle size fractions: (—·—) < 0.5 mm; (———) 0.5–1 mm; (· ·) 1–1.4 mm; (– – –) 1.4–2 mm.

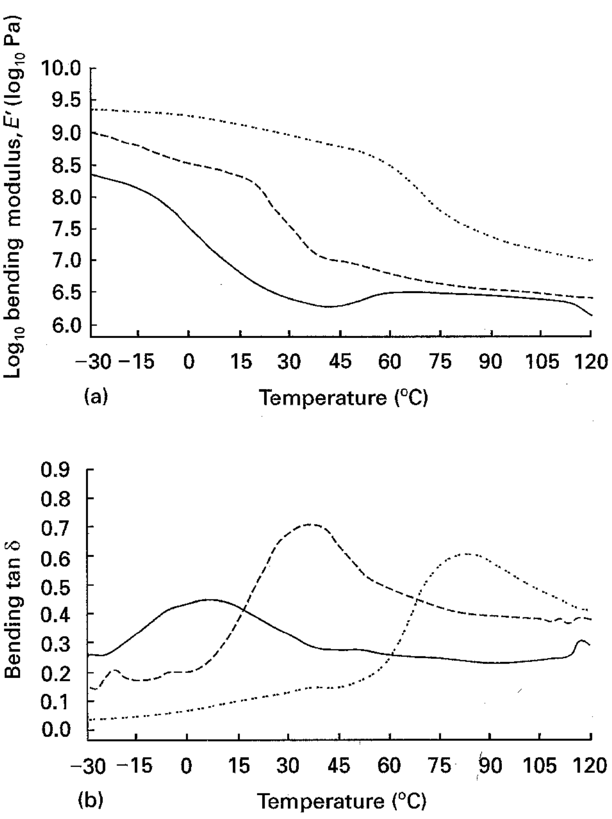

Figure 2 DMTA log E' and tan δ for E samples of particle size < 0.5 mm as a function of temperature for different water contents (w.w.b.): (· ·) 8%, (– – – –) 15%, (———) 26%.

and less than one order of magnitude in a sample of 50% crystallinity. In terms of the different sieve fractions, the scans were almost coincident.

The tan δ data (Fig. 1b) are again coincident for the different samples and indicate the T_g at 80 °C with evidence of a shoulder at 30–40 °C. Low-temperature transitions below the principal T_g have been observed before [6] for amylopectin. In mixed systems it may also be due to a low molecular weight phase such as a sugar. Kalichevsky *et al.* observed a second peak of this type in gluten–sucrose [10] and amylopectin–sucrose mixtures [14]. In previous studies on wheatflakes [15], it was more pronounced in formulations containing sucrose (in a ratio of 1 : 5.9 with wheat) than in those without sucrose. It is also interesting to note that two high-temperature DMTA peaks were reported by Kalichevsky and Blanshard [12] for amylopectin–gluten mixtures. The results reported here using a higher pressing temperature resulted in a single peak, consistent with the studies of Davies and Nicholls cited in [12]. Again with regard to the different sieve fractions, the data were very similar.

3.1.2. Effect of water content

DMTA scans were performed on all samples at different water contents. Fig. 2 shows the typical variation of the bending modulus, E', for the samples which were in the 9%–29% water content (w.w.b.) range at the start of the experiment. At low temperature the glassy modulus decreased with increasing water content. Kalichevsky *et al.* [10] and Kalichevsky and Blanshard [12] observed no effect of water content on the glassy modulus of gluten or gluten/amylopectin mixtures, respectively. However, Kalichevsky *et al.* [24] showed the effect of increasing water content was to reduce the sub-T_g stiffness in amylopectin. As with their data, the results of Fig. 2a indicate convergence of the glassy moduli at a temperature below the range studied. It is also interesting that in their studies of wood polymers, Kelley *et al.* [25] showed the glassy modulus to decrease with increasing water content.

The fall in E' shifted towards lower temperatures with increasing water content as observed previously for gluten and amylopectin and their mixtures [6, 10, 12]. This confirms the expected role of water having a plasticizing effect on the fabricated wheatflake samples. A shoulder occurred after the transition (Fig. 2a) at the highest water content where the sample became stiffer as shown by a slight increase of the modulus. A similar response for amylopectin was reported by Kalichevsky *et al.* [24] 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.

The rubbery modulus was higher for the low water content bar than for the higher water content specimens as observed by Kalichevsky and Blanshard [12] for a gluten–amylopectin mixture, and Kalichevsky *et al.* [10, 24] for gluten and amylopectin, respectively. They attributed this trend to a decrease in cross-linking on addition of water. Unlike their data, the greatest decrease of modulus was observed for the driest type E sample in Fig. 2a, as also observed for other wheatflake formulations [15].

A maximum peak in tan δ occurs at the T_g which shifted towards lower temperature with increasing water content (Fig. 2b). Kalichevsky and Blanshard [12] and Kalichevsky *et al.* [24] found a marked increase in the height and narrowing of the tan δ peak with increasing water content in amylopectin/gluten (1:1) mixtures and amylopectin, respectively. This trend is not obvious here (Fig. 2b) and the reverse was observed in a previous study of wheatflake formulations [15]. Although plasticisers have been reported to broaden the loss peak for synthetic polymers [26], this may not be true for biopolymers and ionomers [24, 27]. MacKnight *et al.* [28] 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 work of Kalichevsky *et al.* [24] where multiple components, cross-linking and order were given as reducing the size of the transition.

At the highest water content the broadening of the peak in the tan δ coincided with its location near 0 °C. Kalichevsky *et al.* [14] mentioned the possible contribution of ice above water contents of 27% in amylopectin. Data for T_g and E' were not extracted from DMTA scans where there was this evidence for ice, owing to its effect on the water distribution.

In Fig. 3a, T_g is plotted against water content for E and P type samples and shows the T_g to decrease from 100 °C to 7 °C with increasing water content from 7% to 25% (w.w.b.), independent of particle-size fraction or whether extrusion or pressure cooking was used. Fig. 3b shows the variation of the bending modulus with water content determined at room temperature (20 °C) for the different samples. The data are independent of particle size or process route. They are in general agreement with the changes in the room-temperature Young's modulus measured by a three-point bend test on gluten–fructose, amylopectin–fructose and starch–glucose mixtures observed by Kalichevsky *et al.* [10, 14] and Ollett *et al.* [4], respectively.

3.2. Impact test

The energy to break unnotched and notched bars, W^*, at a water content of 7% (w.w.b.) was consistently higher for the standard ground sample compared to the narrower size fractions (Table I, Fig. 4a). 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 [29]:

$$W^* = G_c B D \phi \qquad (1)$$

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. Fig. 4a is a plot of W^* against $BD\phi$ for E samples of different particle-size fractions and the values of G_c are included in Table I. An

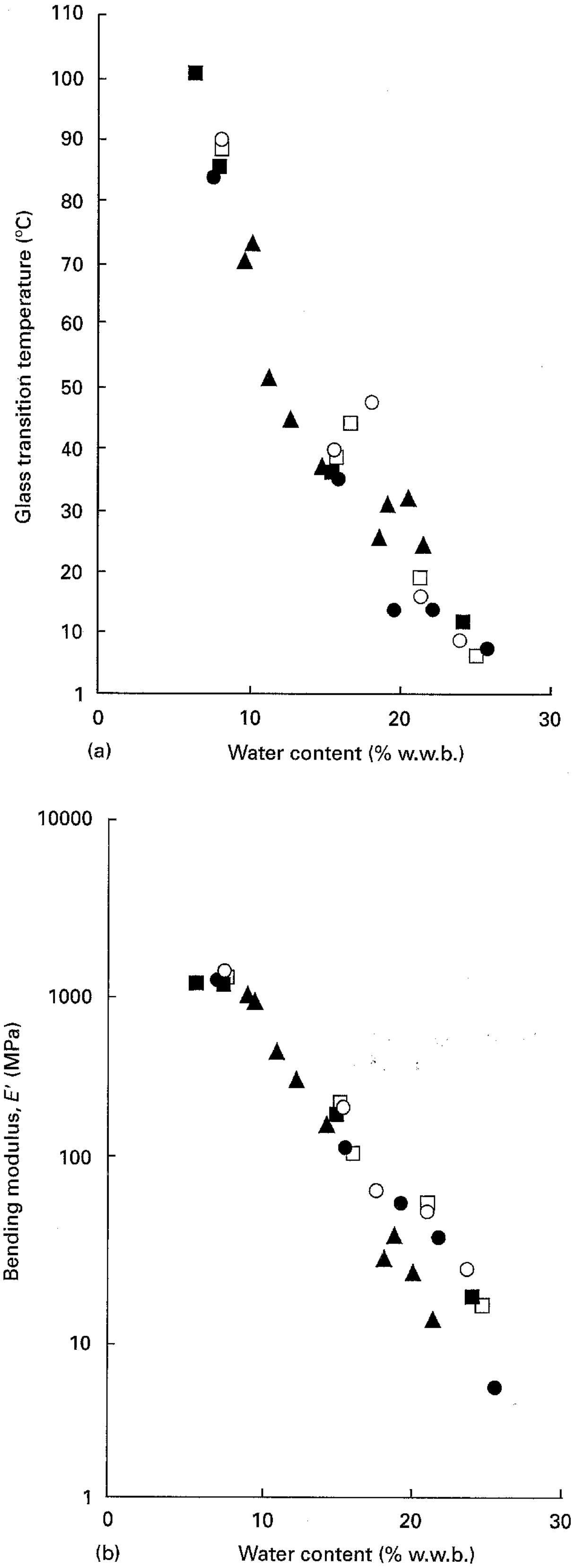

Figure 3(a) T_g and (b) E' at 20° C, as a function of water content for the E samples of Fig. 1; (●) < 0.5 mm; (○) 0.5–1 mm; (☐) 1–1.4 mm; (■) 1.4–2 mm, and (▲) P samples.

estimate of the fracture toughness, G_c, indicates that this was higher for the sample comprising a range of particle sizes (Table I). This was also concluded by Adams *et al.* [18] in their study of sand-filled polyvinyl pyrrolidone. A line through the data of Fig. 4a should pass through the origin. This was not the case,

TABLE II The energy to break, W^*, and the critical stain energy release rate, G_c, determined for unnotched and notched P samples, respectively, as a function of water content (w.w.b.)

	Unnotched	Notched
Water content (% w.w.b.)	W^* (J)	G_c (J m^{-2})
7	0.034 ± 0.001[a]	157 ± 17[a]
14	0.11 ± 0.02[a]	1 132 ± 257[a]
19	1.35 ± 0.01[a]	11 890 ± 2010[a]

[a] Standard error of the mean.

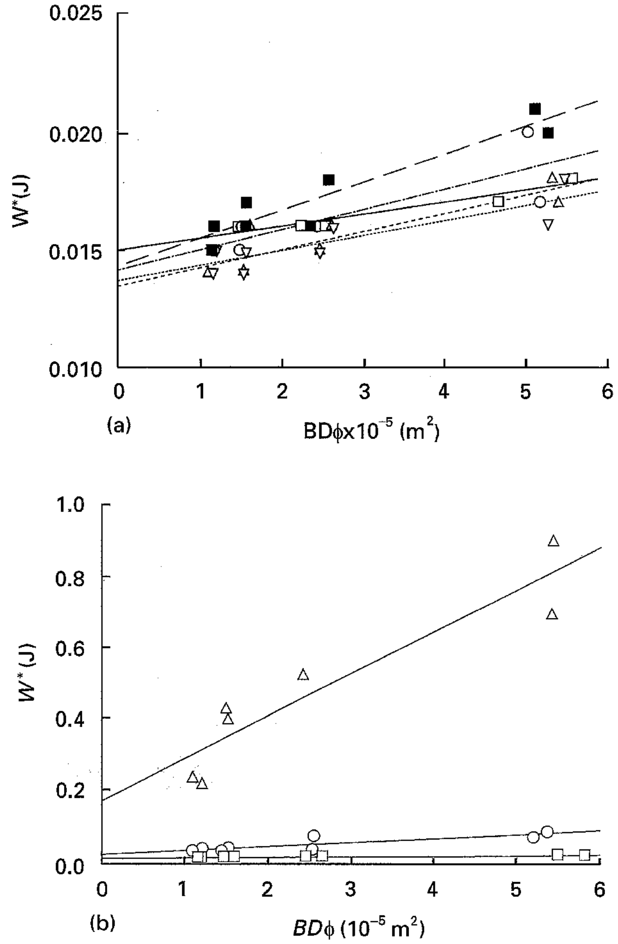

Figure 4(a) Energy to break, W^*, for E samples as a function of $BD\phi$ at 7% water (w.w.b.) for different particle size fractions: (□) —— < 0.5 mm; (○) – · – 0.5–1 mm; (△) --- 1–1.4 mm; (▽) ···· 1.4–2 mm; (■) — — — — unsieved, where B is the sample width, D is the sample depth and ϕ is a calibration factor [29]. (b) Energy to break, W^*, for the P samples as a function of $BD\phi$ for different water contents (w.w.b.): (□) 7%, (○) 14%, (△) 19%; where B is the sample width, D is the sample depth and ϕ is a calibration factor [29].

suggesting some incomplete compensation for the energy correction or some breakdown of the analysis for these samples [30].

Fig. 4b is a plot of W^* against $BD\phi$ for P samples of different water content, and the values of G_c are included in Table II. Whilst E and P samples have similar values of E' (Fig. 3a) they were just distinguishable by the values of W^* and G_c (Tables I and II). An estimate of the fracture toughness, G_c, indicates that this was notably higher for the samples at a water content which would depress the T_g to about ambient temperature. Again, a line through the data of Fig. 4b did not pass through the origin.

The experiments by Adams *et al.* [17, 18] are noteworthy in considering these data. They found values of $G_c = 1$–45 J m^{-2} for glass- and sand-filled polyvinyl pyrrolidone. Phillips and Harris [19] reported values of $G_c = 100$–300 J m^{-2} for glass-filled polyester and Powell [31] gave values of $G_c = 400$–5000 J m^{-2} for polyester and polystyrene. Plati and Williams [29] gave J_c (generalized G_c) equal to 15 800 and 49 000 J m^{-2} for high-impact polystyrene and acrylobutadiene styrene, respectively. Recent data on the impact properties of starch–synthetic polymer composites showed an increase in the impact energy with increasing water content [32].

3.3. Structure

Sections cut from flakes for light microscopy, although fragmented, revealed that the flakes consist of a matrix of gelatinized starch in which pieces of endosperm and bran are embedded. At high magnification (Fig. 5a), partially gelatinized starch granules (s), cell-wall material (w) and globules of wheat protein (p) can be recognized within the matrix (m) by their staining properties. Sections cut directly from hot-pressed bars were held together by the matrix, and swelled anisotropically in staining solution, by 40% in the direction of compression of the bar and by 20% in the plane of sectioning. This reflects the anisotropy of moulding stresses, which are frozen-in on cooling and dehydration and then released when the sample is hydrated. Despite the grinding, sieving and pressing procedures involved in the preparation of bars, structures identical to those in the flakes could be observed. Fig. 5b shows fragments of endosperm cells and bran (e) in the continuous matrix (m) of gelatinized starch in a bar pressed from material passing through the 0.5 mm sieve. In Fig. 5c a section of a bar pressed from material in the particle size range 1.4–2 mm, the close adhesion of the matrix (m) and endosperm cells (e) containing partially-gelatinized starch, can be seen. Protein (p), swollen starch granules (s) and wall material (w) are also present within the matrix. However, adhesion between the matrix and cuticles of the bran layers was poor, often resulting in a tear in the section (not shown).

The failure surface of a pressed type P wheatflake bar containing 7% (w.w.b.) water appeared comparatively featureless and glassy by SEM (Fig. 6a). At higher magnification (not shown), the fracture plane can be seen to run through small pieces of endosperm and bran, or at the junction of bran cuticles and matrix. Fig. 6b shows the failure surface of a pressed wheatflake bar containing 14% (w.w.b.) water, and at higher magnification (not shown) the features of the failure surface are similar to those of the 7% (w.w.b.) water content bar. However, at 19% (w.w.b.) water content (Fig. 6c), the failure surface is less glassy, the roughness being due to endosperm and bran fragments projecting from the surface. Again, the fracture plane runs through the starchy matrix and the endosperm

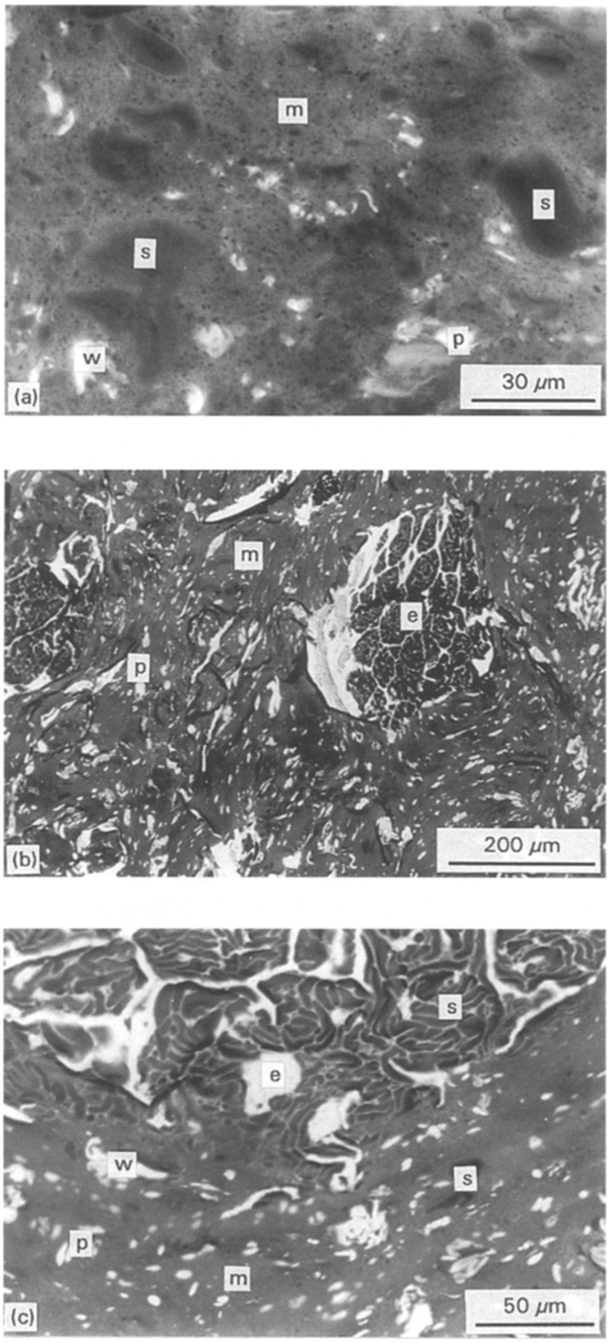

Figure 5 Optical micrographs of sections of (a) wheatflake, (b) pressed bar of particle size less than 0.5 mm, (c) pressed bar of particle size 1.4–2 mm. All were stained in iodine/potassium iodide. *m*, gelatinized starch matrix; *s*, swollen starch granule; *w*, cell wall; *p*, wheat protein; *e*, endosperm cells.

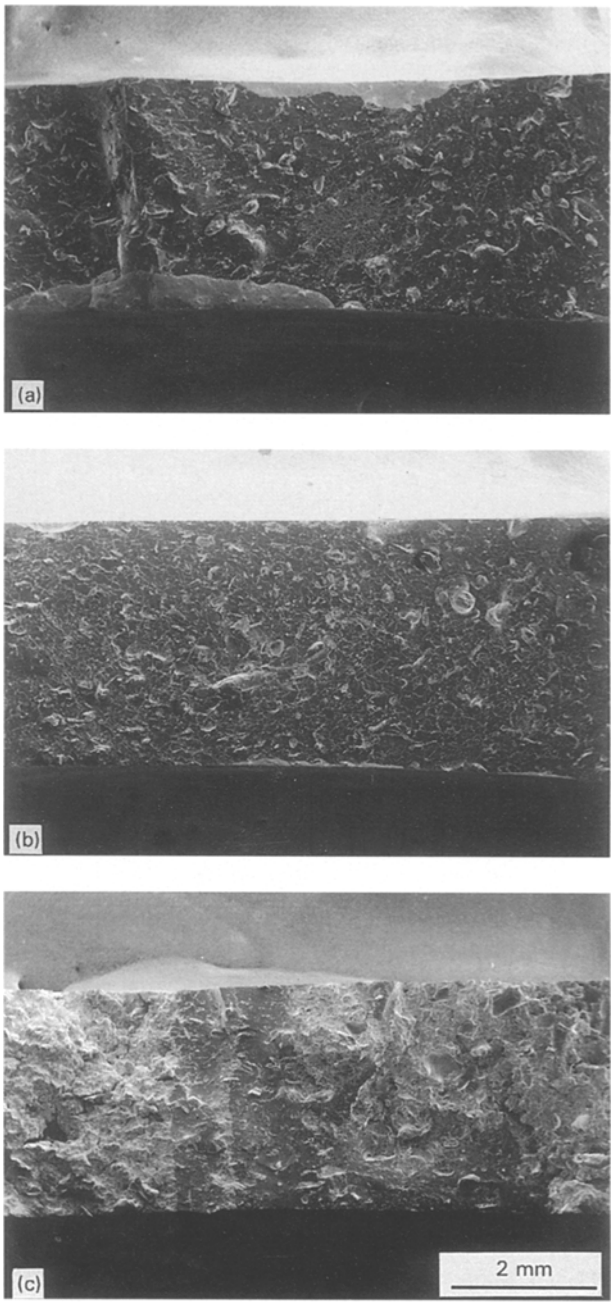

Figure 6 Scanning electron micrographs at the same magnification of failure surfaces of wheatflake bars at different water contents (w.w.b.): (a) 7%, (b) 14%, (c) 19%.

particles, except where there is a poorly adhering cuticle–matrix interface. A similar change in the surface topography was observed in fractured bars of extruded starch–glycerol mixtures [33] between water contents of 6.5% and 9.9% (w.w.b.).

4. Conclusion

The stiffness and glass transition of hot-pressed test pieces of ground wheatflakes varied with water content in a similar way to those of amylopectin and gluten, the principal components. The tan δ 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 the results for the simpler systems. The breadth of the principal tan δ peak for the wheatflake materials is consistent with the heterogeneity of the mixture. At 20 °C, addition of water in the range 7%–25% (w.w.b.) reduced the stiffness from 1 GPa to 10 MPa. Some evidence was obtained from impact tests that the energy to break and the toughness at 7% (w.w.b.) water decreased on narrowing the size distribution of particles. A comparison with published data on other particulate compacts shows a similar trend and broad agreement in G_c values. The effect of increasing water content was to increase the energy to break samples or the fracture toughness.

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