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Deformation and fracture behaviour of wheat starch plasticized with glucose and water

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The mechanical properties of wheat starch and the effects of plasticizers upon them are studied in flexure at 293 K. For compositions low in water and glucose the material is glassy, with a flexural modulus between 0.7 and 5.0 GPa. The addition of water and glucose to wheat starch plasticizes the material through its glass transition into a rubbery state. The flexural moduli of the rubbery samples are in the range 50 to 200 MPa, which is indicative of a partially crystalline polymer. For starch–water mixtures the glass transition occur in the water content range 18 to 20%. The addition of glucose progressively shifts the glass transition to lower water contents. At strains below 0.04 brittle failure is only observed in the glassy samples. The surface morphology of the fractured samples shows features typical of pure synthetic glassy polymers.

1. Introduction

The deformation and fracture behaviour of food biopolymers is important to both food processing operations and product texture. In a typical forming operation a feed material is shaped into a structured product by the application of the appropriate deformations whilst the material properties are manipulated using temperature and water content [1]. In sensory profiling textural attributes such as "chewiness', "hardness" and "fracturability" are defined which reflect the material properties of the food [2].

Starch is a major component of many foods. It is a polysaccharide with glucose as the monomer unit. In its natural state it occurs as a mixture of two polymeric components: amylose, a linear molecule, (MW $\approx 10^4$) and amylopectin, a highly branched molecule (MW $\approx 10^7$). Recent studies [3] have described the plasticization of starch in a composite material, a durum wheat pasta, in which granular starch is dispersed in a gluten matrix. In studies of starchy food foams [4] it was found that changes of water content achieved by drying or exposure to humid atmospheres resulted in changes in flexural modulus. These were interpreted in terms of the changing properties of the foam wall material as it was plasticized with water. Calorimetric measurements on amorphous wheat starch have shown that its glass transition temperature is depressed by the addition of water [5]. In humid atmospheres, sorption of water results in the glassy material passing through its glass transition into the rubbery region. A complication under these conditions is the potential for crystallization of the component polymers, amylose and amylopectin, and a corresponding increase in the modulus.

In this study the flexural behaviour of solid wheat starch is investigated. The effect of different concentrations of water and glucose on the modulus and fracture properties are studied. Since starch is known to be susceptible to macromolecular degradation during extrusion [6], intrinsic viscosity is used to give a measure of the mean molecular weight of the extruded material. The morphology of the fracture surfaces is investigated using scanning electron microscopy.

2. Experimental methods

2.1. Materials

The wheat starch was obtained from A. B. R. Chemicals Ltd., Corby, Northants. The glucose monohydrate was a gift from Tunnel Refineries Ltd, Greenwich, London. The water contents of these materials were 12.9 and 8.5% (wet weight basis), respectively.

2.2. Extrusion and sample preparation

Samples were prepared by first extruding narrow sheets using a Baker Perkins MPF50D co-rotating twin screw extruder fitted with a slit die. This is described in more detail elsewhere [7]. The starch and glucose were premixed to give the required proportions. The glucose was added at 0, 8.4, 17.4, 34.5 and 67.8%, expressed as mass percentage of the dry solids. This mixture was fed into the extruder together with additional water to give an overall feed rate of 6.0 kg h^{-1} and a water content of 30.0% (wet weight basis). The screw rotation speed was 250 r.p.m. The temperature profile along the extruder barrel was 25, 140, 140, 40, 30 °C (from feed zone to die). This ensured complete melting of the starch and glucose prior to cooling, which prevented the melt from boiling and gave a bubble-free extrudate.

Specimens of the size appropriate to the British Standard method for three-point bend tests on plastics [8, 9] were cut from the extruded sheets. The actual

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dimensions were dictated by the sheet thickness which varied slightly. Typical dimensions of the specimens were 3.0 mm thick, 12.0 mm wide and 100.0 mm long.

Samples of different water contents were prepared by controlled drying. To obtain water contents in the range 17 to 25% samples were allowed to dry in the laboratory atmosphere for periods of 2 to 72 h and then wrapped in polythene film and stored for testing. Lower water contents in the range 7 to 17% were obtained by conditioning the samples in controlled humidity enclosures over a 30 to 35 day period. The relative humidity was controlled using slushes of different inorganic salts [10]. One set of starch samples was prepared using a double-pass procedure. Material which had been extruded at a low water content (about 20%), producing a foamed extrudate, was milled and then re-extruded into the unfoamed sheets for sample cutting.

2.3. Intrinsic viscosities

Intrinsic viscosities were measured with a kinematic suspended-level type viscometer at 25 °C with concentrations in the range 0.5 to 4.5 mg ml^{-1}. The solvent was a 90 wt % dimethyl sulphoxide–water mixture which had a flow time of 180 sec.

2.4. Vickers hardness

Some preliminary tests using the Vickers microhardness technique were used to ascertain whether samples were homogeneous, and over what time-scales surface drying had a measurable effect upon material properties. The technique involves measuring the dimensions of the impression left when a pyramid-shaped indentor is pressed against the specimen with a constant load for a specified time [11]. The mean length of the diagonal of the indentation and load are related to the hardness by using standard tables. In our work a Shimadzu microhardness tester (Shimadzu Corp., Kyoto, Japan) was used with a load of 100 g over a 10 sec indentation time.

2.5. Flexural testing

The force–deflection behaviour of each sample was measured in a three-point bend test using an Instron 1122. The span of the supports, l was set to be (16 ± 1) h, where h is the sample thickness, in accordance with the British standards [8, 9]. Both the supports and the load nose were cylinders of 5.0 mm diameter and were longer than the widest sample. The crosshead speed was 5 mm min^{-1}. The force–deflection data were logged using a Hewlett Packard 9122 and subsequently analysed after transfer to a DEC VAX computer.

The tensile stress, σ, and strain, ε, were calculated at the point on the lower sample surface opposite the load nose using the standard small deformation formulae [12]:

$$\sigma = \frac{3Fl}{2bh^2}$$

where F is the load and l, b and h are the load support span, sample breadth and height, respectively, and

$$\varepsilon = \frac{6hY}{l^2}$$

where Y is the deflection at the load nose. The samples were strained to a maximum of about 0.04. The flexural modulus, $E = \sigma/\varepsilon$, was calculated from the initial slope of the stress–strain curve. The measurement of the sample dimensions and the above calculations were performed on each sample individually.

A limited investigation of yielding was made by repeatedly loading samples to strains below the fracture strain. This enabled any deformation which remained after unloading to be measured.

2.6. Water content determination

The tendency of the samples to absorb or desorb water from or to the atmosphere meant that special care had to be taken to measure the water content at the time of testing. Samples were weighed immediately before and after testing, which established that negligible drying occurred during the test. The water content was determined gravimetrically by drying the samples in a two-stage process. First they were heated in a microwave oven for 2 min, which caused the samples to foam as water boiled off. Then drying was completed in a vacuum oven at 70 °C at a pressure of less than 5 mm Hg with a phosphorus pentoxide desiccant over a 24 h period.

2.7. Scanning electron microscopy

Samples were mounted on aluminium stubs with silver dag and were then coated with gold to a depth of about 20 nm using an Emscope E5100 sputter coater. The surfaces were viewed in a Philips 501B scanning electron microscope using a 15 kV accelerating voltage.

3. Results

3.1. Intrinsic viscosities

The intrinsic viscosity of the extruded starch was in the range 100 to 130 $\text{cm}^3\,\text{g}^{-1}$ as compared with 193 $\text{cm}^3\,\text{g}^{-1}$ for the native starch. These are typical levels of degradation for extruded wheat starch [13] and correspond to a limited degradation of both the macromolecular species present, amylose and amylopectin.

3.2. Hardness testing

Some initial tests were made using a Vickers microhardness test to check that samples were homogeneous and stable over experimental time-scales. The standard deviation of the hardness of a cut surface reduced from 3.2 on the day of extrusion to 2.4 after two days, and a final figure of 1.1 after four days for the high water-content samples wrapped in polythene. This can be interpreted as inhomogeneities in the

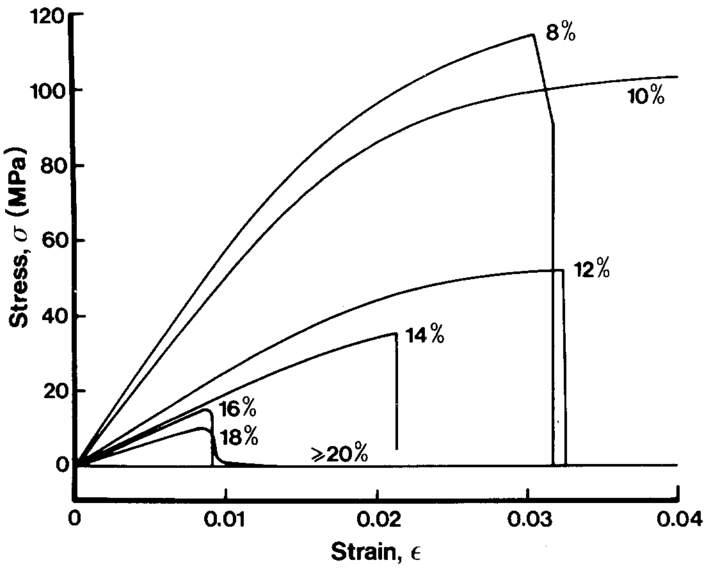

Figure 1 Stress–strain behaviour of starch plasticized with different levels of water.

water content distribution diffusing out within a four-day period. Samples were stored for at least four days prior to flexural testing. Another test on high water-content samples showed an initial linear increase in hardness with time at a rate of $0.13\,\mathrm{min}^{-1}$. The Instron three-point bend procedure was such that the test was complete within 2 min of the samples being removed from their controlled environment, which means that negligible surface hardening occurs during the tests.

3.3. Flexural properties

Some typical stress–strain plots for the wheat starch–water mixtures are shown in Fig. 1. The plots are essentially linear at low strains (< 0.01) and curve towards the strain axis at higher strains. As each sample has a different water content, representative samples in 2% bands are included. The initial slope (which gives the flexural modulus) decreases with increasing water content. Fracture was usually marked by a rapid decrease in stress (< 30 msec, the logging period). However, the 18% water-content sample showed a slower drop in stress during the fracture process which could be followed by the data acquisition system.

The behaviour of samples with added glucose at a water content of 12% are shown in Fig. 2. These are qualitatively similar to the starch–water samples, with increasing glucose concentrations decreasing the initial slope. A summary of the flexural moduli is shown in Fig. 3. Each curve exhibits a sharp change of modulus at a water content which is dependent upon the glucose concentration. At lower water contents the modulus rises steadily from a shoulder ($E >$ 700 MPa) and reaches 5000 MPa at the lowest water contents. The position of the shoulder is lowered by increasing the glucose concentration. At higher water contents the modulus varies less regularly with composition. The modulus falls to a plateau value of 50 to 150 MPa, with increasing water content causing a further decrease. At the highest glucose concentration, 67.8%, the sharp decrease is replaced by a more steady decrease in modulus with increasing water content.

The repeated loading tests were made on samples with 17.4% glucose. At 8.0% water content repeated straining to 0.01 resulted in a residual strain of less than 0.0002 after the load was removed. Fracture was occurring with negligible yielding in these samples. At 12.0% water content, straining a sample to 0.035 resulted in a residual strain of 0.001. Straining a sample to 0.05 resulted in a 0.0067 residual strain, which indicates that yielding is occurring in the layers close to the lower surface. It should be noted that this strain is higher than in the typical test.

The occurrence of fracture was not demarcated by a sharp composition boundary. Under certain conditions a proportion of the samples would fracture whilst others remain intact to the maximum strain, $\varepsilon = 0.04$. The different failure processes are summarized in histograms in Fig. 4. With no added glucose the samples did not fracture until the water content was reduced below 19.0%. At 18.0% some samples fractured rapidly whilst others exhibited a slower fracture as shown in Fig. 1; this is termed a "tear" in Fig. 4. With the addition of glucose the onset of fracture was

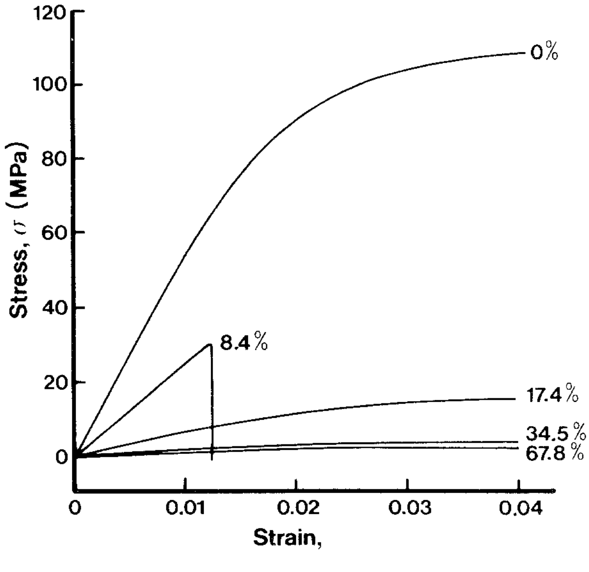

Figure 2 Stress–strain behaviour of starch plasticized with different levels of glucose. Water content = 12%.

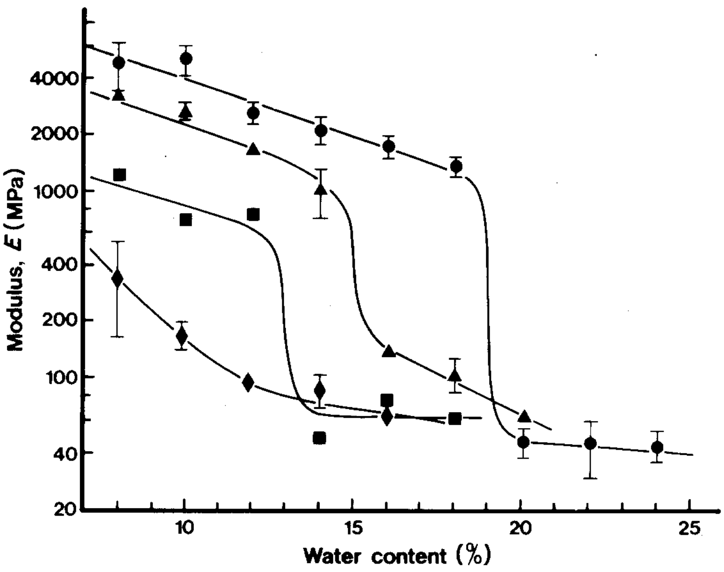

Figure 5 Fracture stress, σ_f (●) and strain, ε_f, (○) for 8.4% glucose–starch mixtures at different water contents.

reduced to lower water contents, i.e. at 8.4% glucose, to 14.0%, and at 17.4% glucose, to 8.0%. This coincides with the modulus drop for the lower glucose concentrations, though for the 17.4% glucose samples fracture only occurred at about 4% lower water contents. The samples with no added glucose (Fig. 4a) showed a second region where fracture tended not to occur. In the water content range 9 to 11% only 20% of the test samples fractured. The stochastic nature of the fracture process makes quantitative results difficult to report. Fig. 5 shows the fracture stresses and strains for the 8.4% glucose samples. There is a relatively small drop in the fracture strain with increasing water content (0.02 to 0.01) compared with the drop in fracture stress from 50 to 8 MPa.

3.4. Fracture surface morphology

The fracture surfaces of the 8.4% glucose samples were examined using electron microscopy. The same features occurred throughout the water content range 8.9 to 14.9%. An area of each was a smooth reflective mirror centred around the point at which the crack initiated. If this was at the centre of the lower face the mirror would extend over more than 70% of the surface. Cracks initiating at the corners resulted in a smaller mirror area and multiple faces, as shown in Fig. 6. At high magnification the mirror surfaces show some roughness over a 1 μm length scale (Fig. 7). Where faces meet, steps often occurred on each face (Fig. 8). The crack growth was initially perpendicular to the sample surface and bent away from this plane as the crack neared the top surface. Bands of forked lines running parallel to the crack direction marked these curved surfaces (Fig. 9). A feature of the multiple-faced surfaces which occurred on highly curved sections close to the top surface were steps with filaments attached (Fig. 10). The mirror area on a slowly fractured sample (14.6% water) was particularly small ($<$ 10% of area) and centred at a corner, while a stepped area covered the remainder with some filaments attached (Fig. 11).

4. Discussion

The variation of the flexural modulus with increasing water content is characteristic of a polymer being plasticized through its glass transition [14]. At low water contents when $E > 0.8$ GPa the material is glassy, and at higher water contents when $E \simeq 60$ MPa it is rubbery (in food terminology this corresponds to a stiff gel). The modulus drops steeply in the region centred around the glass transition. The effect of replacing starch by glucose is to shift the glass

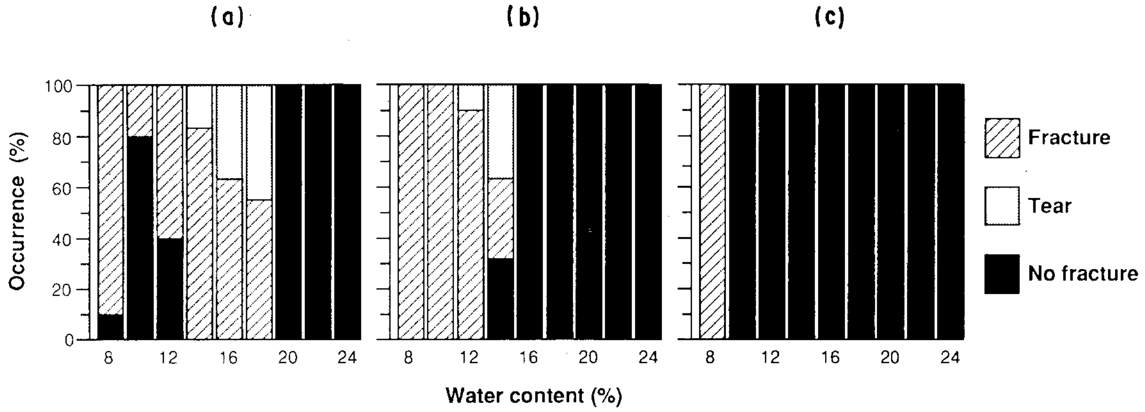

Figure 4 Histograms of the occurrence of fracture at different water contents. Glucose contents: (a) 0%; (b) 8.4%; (c) 17.4%.

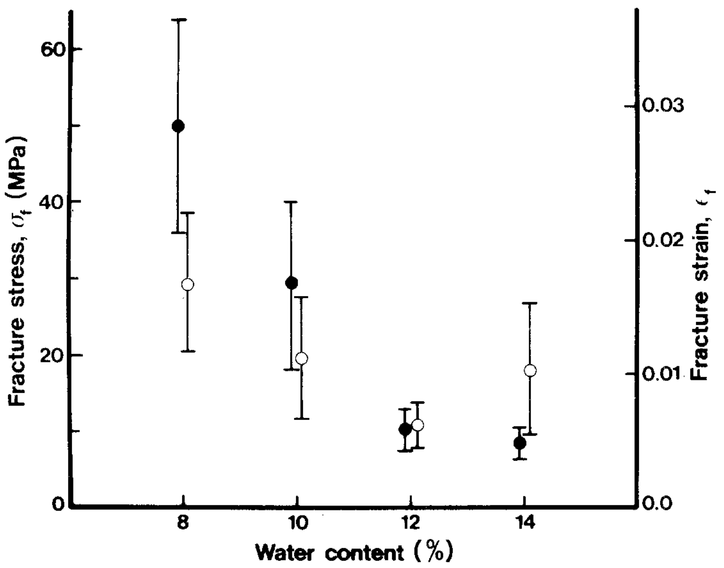

Figure 5 Fracture stress, σ_f (●) and strain, ε_f (○) for 8.4% glucose–starch mixtures at different water contents.

transition to lower water contents. This is an example of a polymer being plasticized by its monomer; the glass transitions of the pure components have been estimated to be 500 and 303 K, respectively [15]. The modulus of the rubber is indicative of a material which is partially crystalline. A purely amorphous polymer, e.g. linear polystyrene, shows a decrease in modulus by a factor of about 10^3 in the region of the glass transition, whereas this is considerably narrowed by network formation, in this case by microcrystalline regions [16]. Although qualitatively similar to the starch results, the moduli of the glucose-plasticized

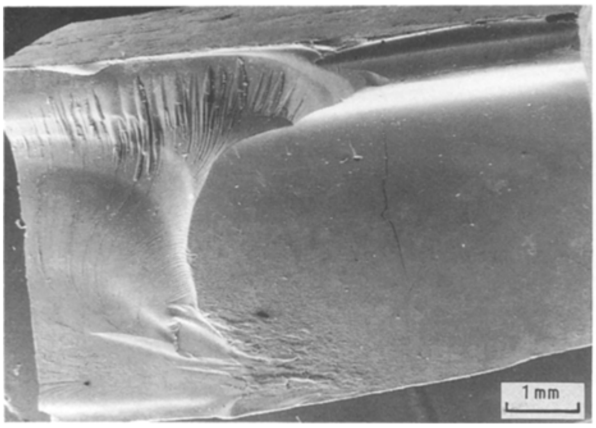

Figure 6 Fracture surface showing mirror area resulting from crack initiating at the right-hand corner of the lower face. Length bar = 1 mm.

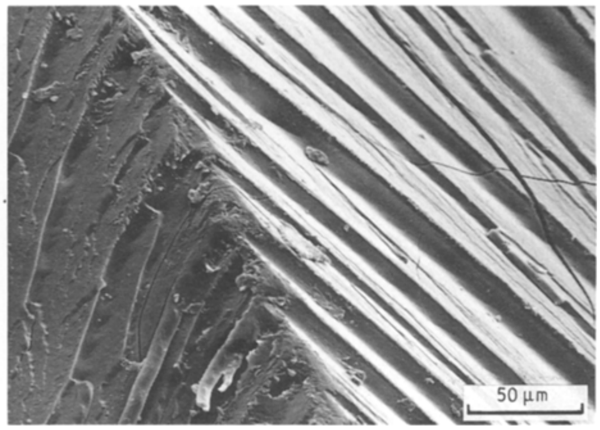

Figure 8 Step feature at two intersecting faces. Length bar = 50 µm.

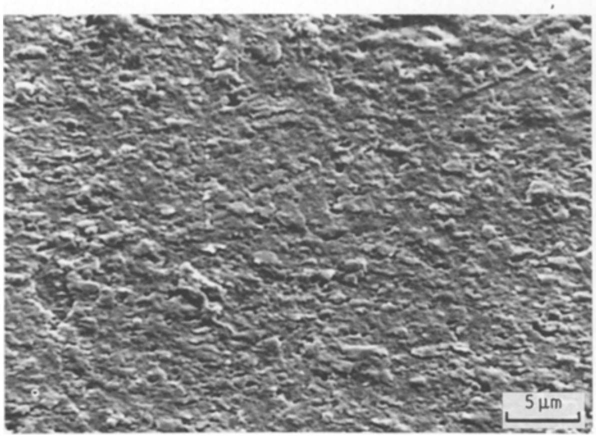

Figure 7 Mirror surface at high magnification. Length bar = 5 µm.

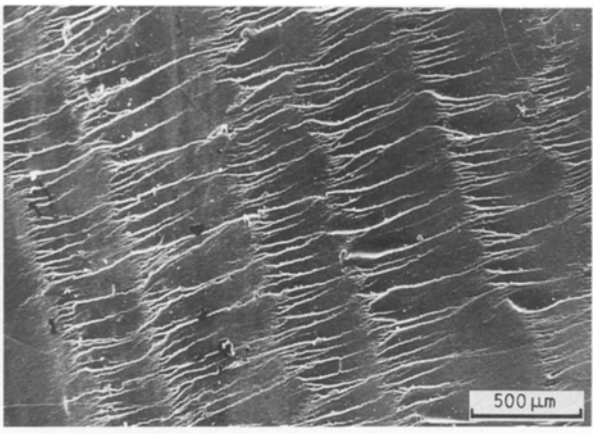

Figure 9 Bands of forked lines running parallel to the crack direction. Length bar = 500 µm.

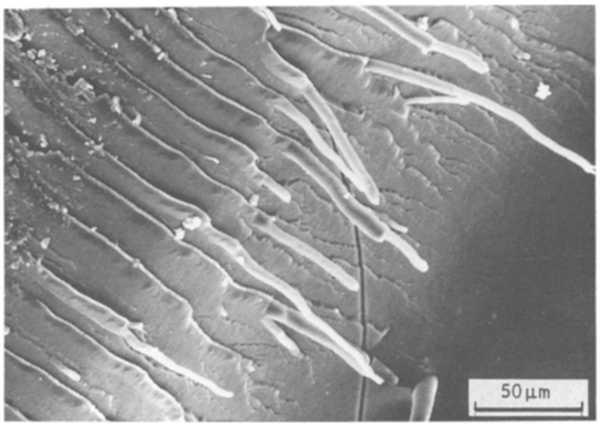

Figure 10 Steps with filaments attached. Length bar = 50 µm.

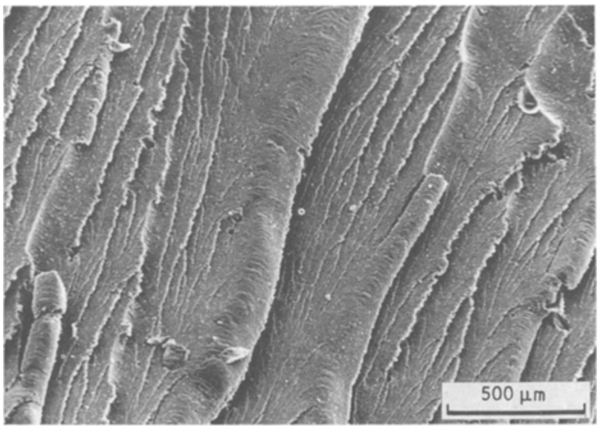

Figure 11 Steps with filaments attached on a slow fracturing sample. Length bar = 500 µm.

starch do show minor differences. With increasing glucose content the fall in modulus at the glass transition and the height of the glassy plateau are both decreasing. At the highest glucose content (66%) the sharp decrease in modulus is absent in the water-content range studied.

The occurrence of brittle failure coincides with glassy behaviour for the 0 and 8.4% glucose samples. It is difficult to establish whether yielding or ductile behaviour occurred in any of the samples. The strain field in the three-point bend test is such that tensile yielding can occur close to the lower surface, whereas the upper surface does not exceed its compressive yield stress. The complicated strain as compared with, say, a tensile test means that the form of the stress–strain curve does not enable a yield stress to be identified. The curves do show strong curvature once the strain exceeds 0.01. Several factors lead to curvature at large deformations, even for ideal Hookean materials [12]. A stress maximum or "apparent yield point" occurs at $\varepsilon = 0.089$ ($l/h = 16$, $Y/l = 0.236$). This is more than double the strain limit of our stress–strain curves and demonstrates their non-Hookean behaviour. The repeated loading tests showed only limited yielding below the typical strain maximum of 0.04. The higher-strain repeated loading test showed a higher residual strain and the existence of a yield strain below 0.05.

The fracture surfaces show all the features typical of glassy polymers. The mirror area centred around the crack-initiating flaw (Fig. 6) is common to most descriptions [17–19]. Fig. 9 is aptly described as "ribs" of "river markings" by several authors, typically in studies of polymethyl methacrylate [18, 19]. The features of Figs 10 and 11 have recently been described as "steps" and "welts" and are also found to occur in both network and borosilicate glasses [20].

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