

The deformation and failure behaviour of wheat starch plasticized with water and polyols

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The mechanical properties of starch plasticized with water and glycerol or xylitol have been studied in flexure at room temperature. The addition of a polyol lowers the glassy modulus and the glass transition temperature of the starch. With the addition of polyols, the fall in modulus with increasing water content at the glass transition becomes less sharp and shifts to lower water contents. The high strain deformation shows that all samples fracture at a water content below 10% (wet weight basis), a proportion of which tears at water contents in the range 9%–10% and no fracture occurs in samples above about 10% water. Microscopy shows that there is evidence of permanent plastic deformation in fractured samples as the water content is increased to 10% water, although there is a negligible change in fracture stress and strain.

1. Introduction

Starch is a major component of many foods such as pasta, breakfast cereals, biscuits and various snack products and also non-food products such as biodegradable packaging materials. In common with synthetic semi-crystalline polymers, it has glass and melting transition temperatures and is plasticized by small molecules. The plasticization of starch, particularly by water, has been discussed by a number of authors. The majority of studies has used differential scanning calorimetry (DSC) to locate the transition temperatures [1–4] although thermomechanical techniques have also been used [5, 6]. Latterly, the stiffness and strength of moulded [7] and extrusion-formed [8] samples have been measured. The study of the mechanical properties of starch composites has included the Young's modulus of pasta as a function of water content [9] and the flexural modulus and strength of starch foams as a function of water content [10]. The compressive modulus and strength of sponge (wheat flour) cakes have been measured as a function of water activity, together with the establishment of a relationship between these mechanical properties and sensory hardness [11]. The glass transition temperature, T_g , is depressed by the addition of water [2] and, if sufficiently plasticized, a glassy material will pass through its transition and become rubbery [8]. Under these conditions, crystallization of the starch component polymers may proceed, leading to an increase in elastic modulus relative to the amorphous material.

Water content has a strong influence on the texture of starchy foods. The crispness of low water content starchy products decreases slowly with water content in the range 0%–6.5% (wet weight basis, w.w.b.) and then more rapidly at water contents above 7%–9% [12]. Katz and Labuza [13] describe a similar deteri-

oration in the crispness of maize snacks at 4%, though their definitions and methods were different. Even at 9%, the T_g of amorphous wheat starch is about 110 °C [2] and so it seems unlikely that the deterioration in crispness of starchy products is related to this transition. In any case the perception of crispness involves fracture, a large strain process, which will not necessarily be linked to transitions in small strain behaviour such as the glass transition [14]. Recently, Attenburrow *et al.* [7] have found a maximum in the fracture strain of moulded starch samples at about 10% water and a reduction of the acoustic emission signal from fracturing samples in the range 8%–12% water. Again, at these water levels the starch is in the glassy state. At large strains a number of deformation and failure modes are possible and a brittle–ductile transition may occur which is marked by differences in the force–displacement response and in the failure surfaces [14]. It was one objective of this study to investigate any changes in the large strain behaviour and mode of failure in this water content range.

In an earlier study [8], the mechanical properties in flexure of formed samples of wheat starch plasticized with glucose and water were studied. The flexural modulus of starch falls rapidly at a water content corresponding to the glass transition and the addition of glucose shifts the glass transition to lower water contents. The glassy samples exhibited brittle failure similar in some features to pure synthetic glassy polymers. It is well known that the lower molecular weight plasticizers will have lower T_g s and will depress the T_g of mixtures to a larger extent [15]. Recent tabulations of T_g s [16] show that low molecular weight polyols have low T_g s and should perform well as plasticizers. In this paper, the large strain deformation of starch plasticized by glycerol and xylitol is investigated and

the nature of the fracture surfaces examined using scanning electron microscopy and low-powered optical microscopy.

2. Experimental procedure

2.1. Materials

The wheat starch was obtained from A.B.R. Chemicals Ltd, Corby, Northants, UK. Glycerol (> 99% pure) and xylitol were supplied by the Sigma Chemical Co. Ltd, Poole, Dorset and Forum Chemicals Ltd, Redhill, Surrey, respectively.

2.2. Sample preparation

Samples were prepared by extruding narrow sheets using a Baker Perkins MPF 50D co-rotating twin-screw extruder fitted with a slit die. The arrangement is described in more detail elsewhere [17], except the die was shortened to a length of 145 mm. Aqueous solutions of glycerol and xylitol at 85% wt/wt and 60% wt/wt, respectively, were prepared for pumping directly into the extruder barrel. Two pumps were arranged to feed independently the plasticizer solutions and water. During extrusion the pumps and solid feeder were set to give an overall feed rate of about 8.0 kg h^{-1} , a plasticizer concentration of 20% wt/wt (as a percentage of the non-aqueous components) and a water content of 30% wt/wt. The screw rotation speed was 150 r.p.m. and the temperature zones of the extruder barrel were, starting from the feed end, 30, 170, 170, 70, 50°C . This ensured complete melting of the starch prior to cooling, which prevented the melt from boiling and gave a bubble-free extrudate.

Specimens were cut from the extruded sheets to conform to the British Standards for three-point bend testing of plastics [18, 19]. The sheet thickness varied slightly and so sample dimensions were not identical. Typical specimens measured 5.0 mm thick, 10.0 mm wide and 100.0 mm long.

Samples of different water contents were prepared by controlled drying. The different water contents were obtained either by drying samples in the laboratory for periods of 5–50 h followed by wrapping in polyethylene film and storage prior to testing, or by conditioning the samples in controlled humidity enclosures over a period of 30–35 days. The relative humidity was achieved using standard inorganic salt solutions [20]. A summary of the water contents achieved after sample conditioning is given in Table I.

2.3. Mechanical properties

The force-deflection response of each sample was obtained using a three-point bend test in an Instron 1122 testing machine. The span of the supports, l , was set to be $(16 \pm 1)h$, where h is the sample thickness, in accordance with the British Standards. The two supports and load nose for the three-point test were cylinders of 5.0 mm diameter and were longer than the widest sample. The crosshead speed was 5 mm min^{-1} . The force data were logged using a Hewlett Packard

TABLE I Sample conditioning and resultant mean water contents

| Saturated salt solution | Mean water content (%) | |
|-------------------------|------------------------|----------------|
| | Starch-glycerol | Starch-xylitol |
| Potassium acetate | 6.5 | 8.1 |
| Lithium chloride | 7.2 | — |
| Phosphorus pentoxide | — | 8.6 |
| Magnesium chloride | 9.0 | 8.7 |
| Potassium carbonate | 9.9 | 9.1 |
| Wrapped after 5 h | 12.3 | 10.8 |
| Sodium bromide | 12.9 | 11.0 |
| Wrapped after 50 h | 13.2 | 11.5 |
| Sodium chloride | 17.8 | 14.6 |
| Ammonium sulphate | — | 17.7 |

9122 and transferred to a DEC VAX computer for analysis. Eight replicates were tested for each water content.

The tensile stress, σ , and strain, ϵ , were calculated at the point on the lower sample surface opposite the loading point using the standard small deformation formulae [21]

$$\sigma = \frac{3Fl}{2bh^2}, \quad (1)$$

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

$$\epsilon = \frac{6hY}{l^2} \quad (2)$$

where Y is the deflection at the loading point. The samples were strained to a maximum of about 0.04. The flexural modulus, $E = \sigma/\epsilon$, was calculated from the initial slope of the stress-strain curve.

2.4. Water contents

The water content of the xylitol-plasticized samples was determined gravimetrically using a vacuum oven and phosphorus pentoxide desiccant to dry them. The volatility of the glycerol meant that a Karl-Fischer titration [22] had to be used for the water determination of the glycerol-plasticized samples. Water contents are quoted on a wet weight basis throughout.

2.5. Microscopy

The surfaces were viewed at low magnification using a Wild Heerbrugg binocular microscope with photographs taken using the Photoautomat MPS45 accessory.

Scanning electron microscopy of fractured surfaces was carried out using a Philips 501B microscope operating at an accelerating voltage of 15 kV. Samples were mounted on aluminium stubs with silver dag and then coated with gold to a depth of about 20 nm using an Emscope E5100 sputter coater.

3. Results

The samples exhibited different types of stress-strain behaviour; Fig. 1 shows what are termed "fracture",

“bend” and “tear”. The plots are linear at low strains (< 0.015). Fracture was marked by a rapid decrease in the stress in a time period of less than 30 ms (the minimum time between logged forces). Tearing, a slow fracturing process, was characterized by a broad maximum in the stress followed by a rapid decrease in stress with failure occurring at a strain larger than that for fracture. The bending mode was typified by a curvature of the stress-strain plot towards the strain axis with no fracture.

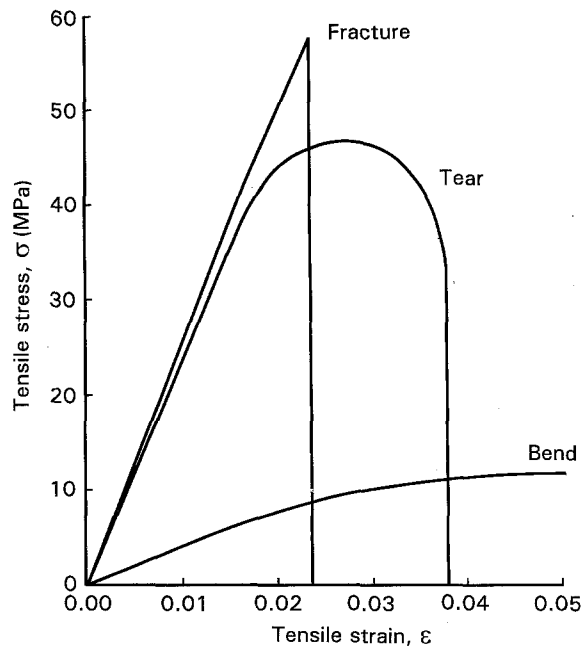


Figure 1 Typical stress-strain curves from the three-point bend tests.

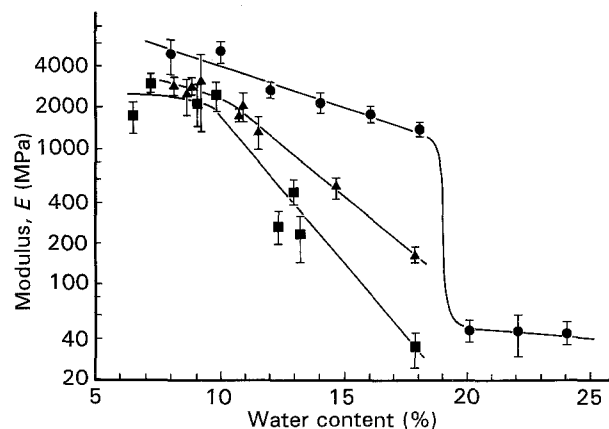


Figure 2 The flexural moduli of starch and starch-polyol mixtures for a range of water contents. Composition: (●) starch; (▲) starch-xylitol; (■) starch-glycerol.

imum in the stress followed by a rapid decrease in stress with failure occurring at a strain larger than that for fracture. The bending mode was typified by a curvature of the stress-strain plot towards the strain axis with no fracture.

The flexural moduli, derived from the initial slope of the stress-strain plot, are shown as a function of water content in Fig. 2. Whilst the pure starch-water system exhibited a sharp change in the modulus at a water content of 18%–20%, the addition of a polyol caused a more gradual decrease in modulus with increasing water content. At the lowest water content of study (6%–8%) the modulus reached a value of order 2–5 GPa and fell to a value in the range 30–150 MPa at a water content of 17%–20%. The addition of the polyol shifts the fall in modulus to lower water contents and decreases the magnitude of all moduli. The change is more marked for glycerol than xylitol.

The stress-strain behaviour changed from the failure processes (fracture and tear) to remaining intact (bend) at a distinct water content. Whereas for starch-glycerol all the samples below 12% water failed, all the samples of starch-xylitol below 10% water failed. The tearing occurred at compositions close to these critical water contents. In contrast, samples of starch alone failed below 20% water, although some samples remained intact in the range 8%–12% water. These data are summarized as histograms in Fig. 3. The mean stress and strain at failure are given in Table II for starch-polyol mixtures at different mean water contents. There was relatively little variation in the mean failure stress and strain with water content.

The fracture surfaces of the starch-glycerol samples were viewed with both scanning electron microscopy

TABLE II Mean failure stresses and strains

| Samples | Mean water content (%) | Mean failure stress (MPa) | Mean failure strain |
|-----------------|------------------------|---------------------------|---------------------|
| Starch-glycerol | 6.5 | 47 | 0.022 |
| | 7.2 | 52 | 0.019 |
| | 9.0 | 35 | 0.020 |
| | 9.9 | 32 | 0.023 |
| Starch-xylitol | 8.1 | 59 | 0.029 |
| | 8.6 | 53 | 0.035 |
| | 8.7 | 60 | 0.033 |
| | 9.1 | 51 | 0.028 |

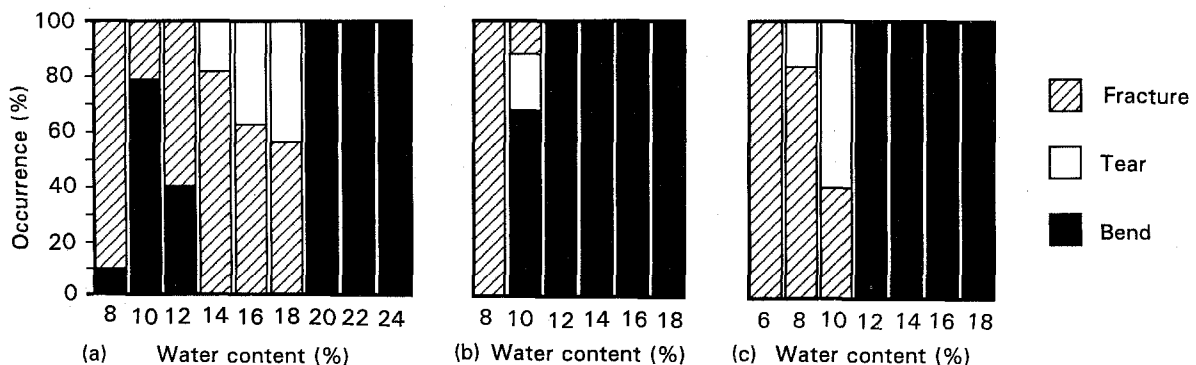


Figure 3 The occurrence of different types of stress-strain behaviour. Composition: (a) starch; (b) starch-xylitol; (c) starch-glycerol.

and optical microscopy. At the lowest water content (6.5%) a V-shaped wedge of material from the fracture zone fragmented into small pieces and was not recovered. In Figs 4 and 5, the two remaining pieces are fitted together in their original configuration. In the contact area, the pieces fit together perfectly indicating

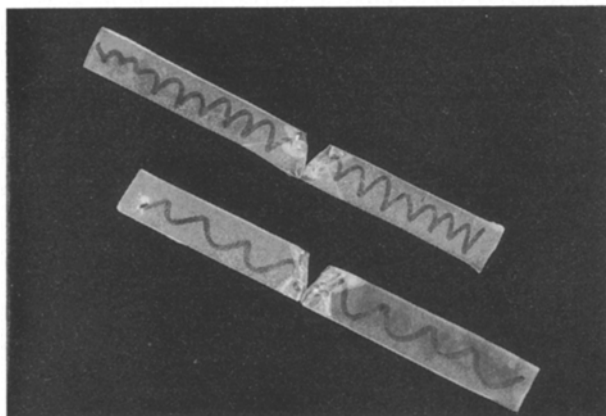


Figure 4 The upper surfaces of starch-glycerol samples fractured at a water content of 6.5%.

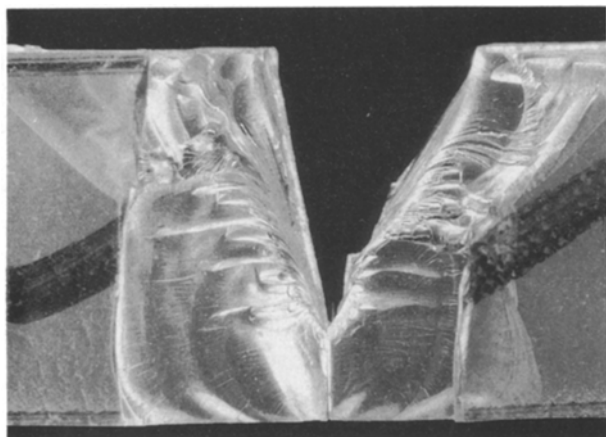


Figure 5 The V-shaped wedge left by fragmentation in the fracture zone. Starch-glycerol sample fractured at a water content of 6.5%.

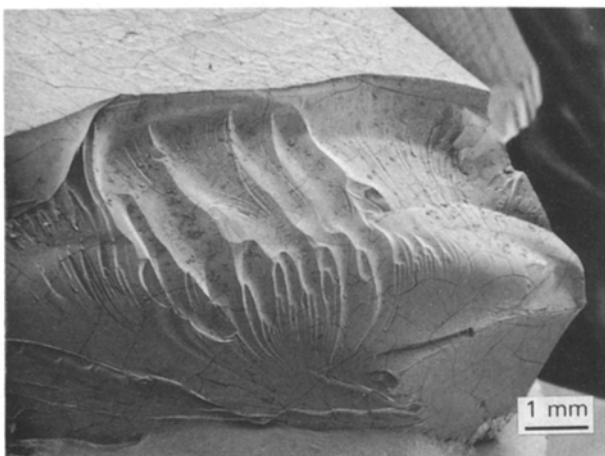


Figure 6 The heavily grooved fracture surface with mirror area in the bottom right. Starch-glycerol sample fractured at a water content of 6.5%.

a brittle fracture. The fracture started from a crack on the lower surface at one edge. A small mirror area resulted which can be seen in the bottom right-hand corner of Fig. 6. Otherwise the fracture surfaces are curved and quite heavily grooved. The faces are highly reflective and glassy-looking. At higher water contents (9.0%) the fragmentation in the fracture zone did not occur and the two fractured halves could be pieced together (Fig. 7). The crack is initially perpendicular to the bottom surface then bends through 90° before reaching the upper surface. The curved surface was heavily ribbed (Fig. 8). The ribs sometimes showing limited self-similarity under high magnification (Fig. 9). The highest water content samples which fracture (9.9%) showed different surface features. The pieces no longer fitted together (Fig. 10) due to permanent deformation, i.e. yielding in the area where the fracture was initiated. Fig. 11 shows a rounding of the lower surface and stress whitening. At high magnification the surface of the area which has yielded is seen to be coarse textured (Fig. 12, bottom right) in contrast to the mirror area of Fig. 6. No features could be found which correlated with the occurrence of a tear type stress-strain curve rather than a fracture type.

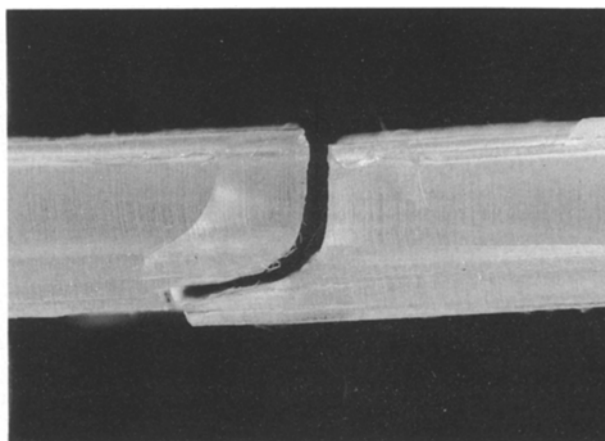


Figure 7 Side view of the two halves of a starch-glycerol sample fractured at a water content of 9.0%.

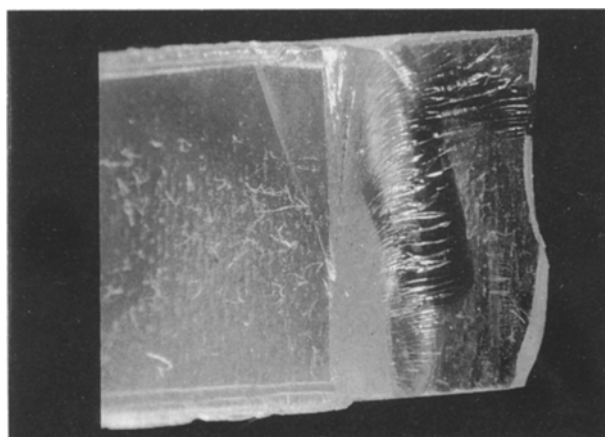


Figure 8 Curved fracture surface showing heavy ribbing. Starch-glycerol sample fractured at a water content of 9.0%.

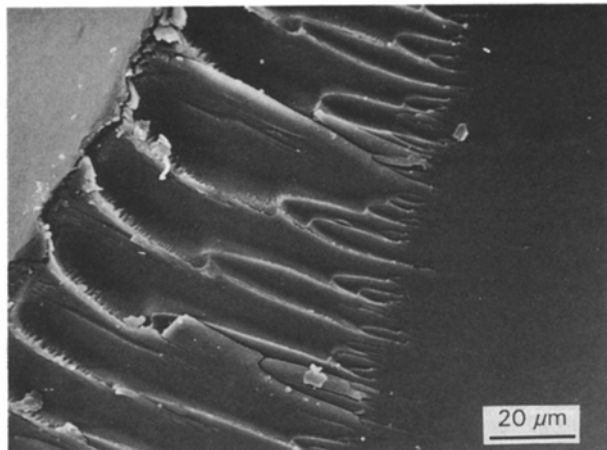


Figure 9 A band of "river-like" markings. Starch-glycerol sample fractured at a water content of 9.0%.

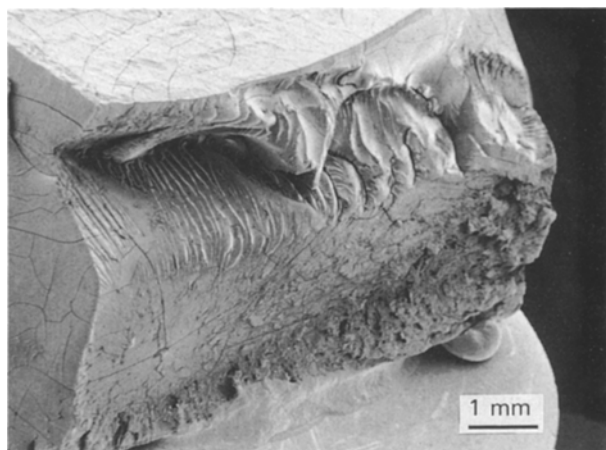


Figure 12 The fracture surface showing coarse-textured plastically-deformed zone where the fracture initiated. Starch-glycerol sample fractured at a water content of 9.9%.

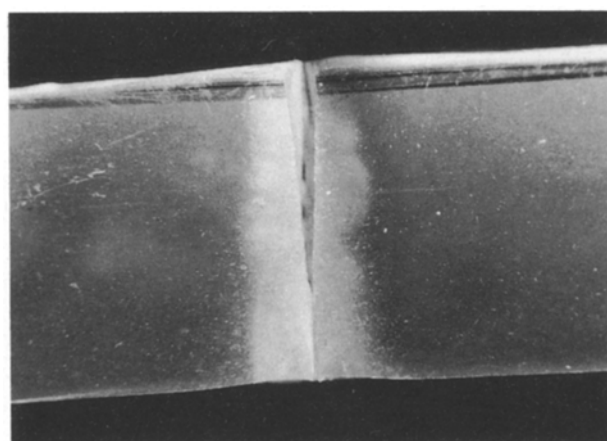


Figure 10 The pieces of a starch-glycerol sample fractured at a water content of 9.9% showing plastic deformation.

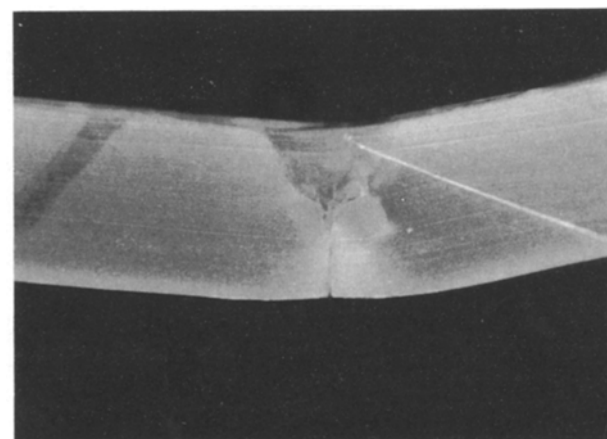


Figure 11 A side view showing plastic deformation on the lower surface and stress whitening. Starch-glycerol sample fractured at a water content of 9.9%.

4. Discussion

The fall in modulus from about 1 GPa to less than 100 MPa (Fig. 1) with increasing water content is characteristic of a polymer being plasticized through its glass transition [23]. The addition of the polyols shifts the glass transition to lower water contents. The

data confirm that the addition of a plasticizer with a lower glass transition temperature (glycerol, -85°C [24], xylitol, -19°C [25]) depresses the glass transition of the mixture to a greater extent. For purely amorphous polymers such as polystyrene, the modulus of the rubbery material, i.e. above T_g , is typically about 1 MPa. This is considerably increased by the formation of microcrystalline regions. This would appear to be the case for starch in this study, i.e. crystallization has taken place during the sample conditioning after extrusion. The glass transitions of the polyol-starch systems are relatively broad. Dynamic mechanical thermal analysis has shown that this is indicative of the plasticizers being relatively poor solvents for the polymer [14]. The polyols are less good solvents for starch than water. The breadth of the transition reflects the more heterogeneous structure of the mixture and the greater tendency of the components to segregate.

In this study, well-defined fracture events become less common in favour of tearing failure with increasing water content, and failure no longer takes place at water contents above about 10% for the starch-polyol systems. The evidence from microscopy indicates that the mechanism of fracture changes with increasing water content up to 10% although there are no corresponding changes in the failure stress and strain. Some permanent deformation occurs in the samples fractured at this water content. The elastic moduli of the starch-glycerol and starch-xylitol samples when they cease to fail (tear or fracture) are about 1500 and 800 MPa, respectively. This indicates they are just above the glass transition as can be seen in Fig. 2. In these systems there is evidence for limited ductile behaviour during failure when the materials are close to the glass transition. The unplasticized starch ceases to fail by fracture or tearing at a water content of 20% corresponding to its glass transition. However, some samples did not fail in the water content range 8%–12% which is consistent with the results of Attenburrow *et al.* [7] where the fracture strain of moulded starch reached a maximum at similar water contents, implying a reduced tendency to

fail at lower strains. In the case of starch, examination of the fracture surfaces provided no evidence for plastic deformation.

5. Conclusions

1. The solubility of glycerol and xylitol in starch is lower than that of water, leading to a relatively broad glass transition in polyol-plasticized starch.

2. In this study, the failure of glassy materials ceases in the region of T_g .

3. A slow tearing fracture was observed as glassy materials approached T_g .

4. Microscopic examination of the fracture surfaces revealed a series of changes in the mechanism of fracture. With increasing water content there is a move from purely elastic fracture to the inclusion of limited plastic flow.

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