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Properties of a plasticised starch blend. Part 1: Influence of moisture content on fracture properties

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Abstract

The effect of moisture content on tensile and fracture properties of a plasticised starch/high molecular weight polyol blend was investigated. A wide range of mechanical behaviour was achieved by varying slightly the water uptake of this material. At low moisture content, the Young's modulus was 3800 MPa and the yield stress, 54 MPa. When the moisture content reached 15 wt%, their values dropped, respectively, to around 1500 MPa and 21 MPa. As the material behaviour varies greatly over the moisture content range, two fracture mechanics techniques were employed: the linear elastic fracture mechanics approach to characterise brittle behaviour and the essential work of fracture method to investigate a more ductile material. At low moisture content, the measured strain energy release rate at fracture, J_Q was very low and showed little dependency on the moisture content. As the moisture content increases, the material becomes increasingly ductile and displayed a brittle-to-ductile transition at 12% of moisture content, which corresponded to the glass transition temperature of the added polyol.

Keywords: Plasticised starch; Starch blend; Moisture content; Tensile properties; Fracture behaviour

1. Introduction

Growing ecological concerns have resulted in the emergence of biodegradable plastics as alternative materials to petroleum-based polymers. Studies (Doane, 1994; Röper & Koch, 1990; Shogren, Fanta, & Doane, 1993) have shown that starch is a particularly interesting biodegradable substrate because it is sustainable, inexpensive and readily available in large quantities from sources such as cereals. Native starch can be transformed into thermoplastic material through disruption of its granular structure and plasticisation in the presence of plasticisers (e.g. water, polyols) by applying thermo-mechanical energy in a continuous extrusion process. This plasticised starch (PlS), also called thermoplastic starch, is processable using conventional plastic processing techniques including injection-moulding and thermo-forming. Unfortunately, there are some limitations to the commercialisation of PlS-based products. PlS materials based solely on starch are highly moisture sensitive and have rather limited mechanical properties, which, moreover, tend to vary with time (crystallisation due to ageing and plasticisation by water adsorption) (van Soest, 1996). Therefore, most of the commercial research has involved blending PlS with other polymers (Avérous, 2004).

Starch, as a hygroscopic material, absorbs varying amounts of moisture under different relative humidities. Previous works in our laboratory have quantified the water diffusion into a PlS blend under different conditions (Russo et al., 2007). Absorbed moisture introduces swelling stresses and also acts as a plasticiser, which lowers the glass transition temperature T_g. Consequently, the mechanical properties are affected and difficult to control under ambient environment conditions. Moreover, brittleness of PlS materials caused by relatively high glass transition temperature and lack of sub-T_g relaxation (Donovan, 1979) add

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another major issue to their development. Plasticisers are generally added to increase polymer chain mobility and thereby lower the T_g. Many studies (Avérous, Moro, Dole, & Fringant, 2000; Lourdin, Coignard, Bizot, & Colonna, 1997; Mathew & Dufresne, 2002) have looked at the combined effects of plasticiser concentration and relative humidity on the moisture content, T_g and mechanical properties of PlS-based plastics.

Although development of PlS-based plastics requires a full understanding of their performance, there has been little systematic work in the literature detailing exclusively the influence of moisture content on their mechanical properties in relation with their morphology and thermal properties. Determining their 'ultimate performance' properties such as their fracture properties over a large range of relative humidities will aid in controlling these effects. The literature regarding the fracture behaviour of PlS blends is still very limited. Some work has been done on amylose films thirty years ago by Even and Carr (1978) showing that surprisingly, moisture content does not greatly affect the energy required to advance a crack through an amylose specimen. This insensitivity was attributed to active interaction between absorbed water and amylose macromolecules.

The purpose of the present work is to investigate the influence of moisture content on the fracture behaviour of a plasticised starch-based plastic. The following section provides a brief introduction to the fracture mechanics techniques employed in this study.

2. Fracture mechanics: Theoretical background

Fracture mechanics techniques, traditionally designed for testing metallic materials, are now well established for characterising fracture behaviour of polymers (Williams, 1984). Linear elastic fracture mechanics (LEFM) methodologies have been applied to brittle polymeric materials (undergoing little plastic deformation) to characterise crack instability by examining the stress distributions in the vicinity of the crack tip. In tensile mode opening, the stress distribution at the tip of a crack is scaled by the stress intensity factor, K_I. K_I is related to the applied stress σ and the crack length a by the following equation:

$$K_I = Y\sigma\sqrt{\pi a}, \tag{1}$$

where Y is a dimensionless factor that depends on the crack and specimen geometries. At a critical value of K_I, the crack starts to propagate; this critical value is termed the fracture toughness, K_c. Under the condition of plane-strain, K_c is at a minimum and is known as the plane-strain fracture toughness, K_{Ic}. This is a specimen geometry independent material property that characterises brittle fracture in a material. In polymers, K_{Ic} is usually temperature and rate dependent. Several standard methods have been developed to measure K_{Ic}. In this work, according to the ASTM Standard D 5045 (1999), a compact tension (CT) specimen was used, as shown in Fig. 1, for which the stress intensity factor, K_I is given by:

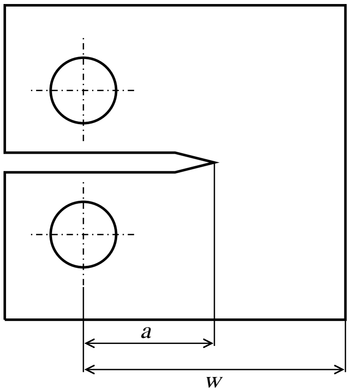

Fig. 1. Schematic diagram of a compact tension specimen.

$$K_I = \frac{Pf(x)}{B\sqrt{W}}, \tag{2}$$

where P is defined as the peak load under linear elastic loading, B the thickness of the specimen, W the width and $f(x)$ a geometry correction factor. For a compact tension specimen with $0.2 < x = a/W < 0.8$:

$$f(x) = \frac{(2+x)(0.886 + 4.64x - 13.32x^2 + 14.72x^3 - 5.6x^4)}{(1-x)^{3/2}}. \tag{3}$$

In the test method described above, for the results to be considered valid, plane-strain conditions are required for which the following size requirements must be satisfied:

$$B, (W-a),\ a > 2.5\left(\frac{K_I}{\sigma_y}\right)^2, \tag{4}$$

where σ_y is the uniaxial yield strength of the material. Plane-strain is the stress state that pertains to relatively thick parts for which one of the three principal strains, ε_{zz}, is equal to zero. If plane-strain conditions are not met, the K_I values measured are geometry dependent and will relate only to specimens of that thickness. In thin sheets, the normal stress, σ_{zz}, is zero and the specimen is said to be in a state of plane-stress.

The fracture toughness K_c can be related to the strain energy release rate G_c through the following equations:

$$G_c = \frac{K_c^2}{E} \quad \text{under plane-stress condition,} \tag{5}$$

$$G_{Ic} = \frac{K_{Ic}^2(1-\nu^2)}{E} \quad \text{under plane-strain condition,} \tag{6}$$

where E is the Young's modulus of the material and υ the Poisson's ratio.

While LEFM is effective for characterising fracture of brittle polymers, the assumptions of linear elastic behaviour and limited plasticity are violated by more ductile polymers. For ductile materials, two approaches have been used in order to characterise the fracture behaviour, namely the *J*-integral and the essential work of fracture. Techniques to measure the *J*-integral directly are specimen and labour intensive. On the other hand, the essential work of fracture approach provides a simple and rigorous alternative for evaluation of fracture toughness of ductile polymers.

The work of fracture technique was developed by Mai and co-workers (Cotterell & Reddel, 1977; Mai & Cotterell, 1986; Mai, Cotterell, Horlyck, & Vigna, 1987) based on the assumption, as firstly suggested by Broberg (1971, 1975), that the total work of fracture, W_f can be partitioned into two components: the essential work of fracture, W_e, which is the energy consumed in the inner fracture process zone where the actual fracture occurs, and the non-essential work of fracture, W_p, which is the energy dissipated in the outer plastic zone, where plastic deformation is necessary to accommodate the large strains. Fig. 2a shows the fracture process and outer plastic zones for a deep edge notched tension (DENT) specimen.

The applicability of essential work of fracture (EWF) methodology relies on the following conditions and assumptions: (i) the ligament should be completely yielded prior to fracture initiation; (ii) W_e is proportional to the fracture area, *BL*; and (iii) W_p is proportional to the volume of the plastic zone, BL^2. These concepts lead to the following expression for the specific work of fracture, w_f:

$$w_f = \frac{W_f}{LB} = w_e + \beta w_p L, \tag{7}$$

where *L* is the ligament length, *B* the specimen thickness, w_e the specific essential work of fracture, w_p the specific non-essential work of fracture and β the plastic zone shape factor.

Therefore, if a set of specimens with different ligament lengths are tested and w_f is plotted against *L*, a linear relationship can be obtained with the *y*-intercept giving w_e (Fig. 2b). The specific essential work, w_e is a material property for a given specimen thickness and has been shown to be equivalent to the critical *J*-integral value (J_c) for the fracture of ductile polymers (Mai et al., 1987; Mai & Powell, 1991; Paton & Hashemi, 1992; Wu, Mai, & Cotterell, 1993). Thus, the EWF technique can be used as an alternative to the *J*-integral analysis but it is much easier to perform experimentally.

A number of restrictions on specimen size have been suggested to establish the plane-stress state and appropriate yielding conditions in the ligament:

$$3B \text{ to } 5B < L < \min(W/3, 2r_p), \tag{8}$$

where *W* is the width of the specimen and $2r_p$ the plastic zone size, which may be estimated from:

$$2r_p = \frac{\pi E w_e}{8\sigma_y^2} \qquad \text{for a line plastic zone.} \tag{9}$$

These restrictions limit the plastic deformation to the ligament area, also ensure complete yielding of the ligament before the crack start to grow and avoid the plane-stress/plane-strain transition region where the theory breaks down (Fig. 2b).

In this present study, the EWF concept is employed to investigate ductile fractures, under plane-stress conditions, of a plasticised starch blend conditioned at high relative humidity. The LEFM method is used to characterise only the samples stored at lower relative humidity failing in a brittle manner. By applying both models, the entire range of fracture behaviour can be quantified.

3. Experimental

3.1. Materials and processing

Experiments were conducted on Plantic® R1 commercial grade supplied from Plantic Technologies Ltd

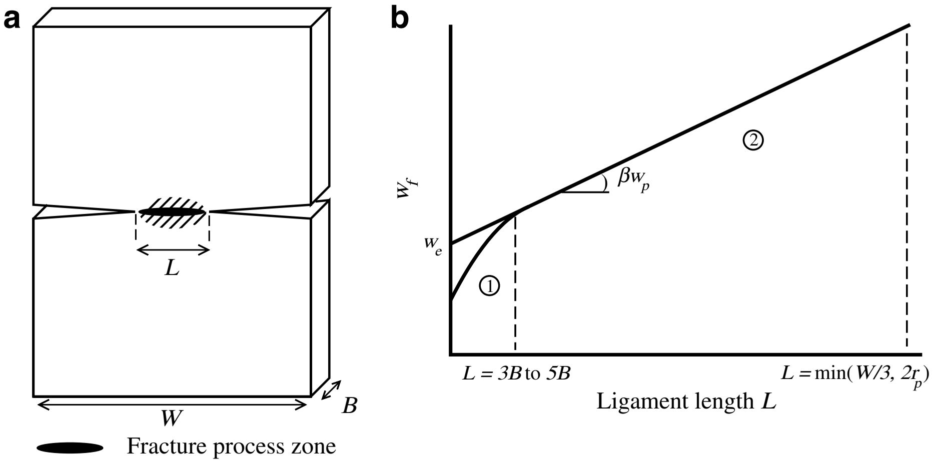

Fig. 2. (a) Schematic diagram showing the fracture process zone and the outer plastic zone in a DENT specimen. (b) Plot of specific total work of fracture, w_f, versus ligament length, *L*; (1) plane-stress/plane-strain region, (2) pure plane-stress region.

(Melbourne, Australia) in the form of pellets. It consists of a chemically modified high amylose maize starch to which a small amount (less than 10%) of a water-soluble high molecular weight polyol was added in accordance with the patents (Buehler, Casanova, Ernst, & Schultze, 1994; Buehler, Schmid, & Schultze, 1994). The pellets were extruded using water as the plasticiser. Pellets of this material were compression-moulded into sheets at 125 °C for 5 min under a pressure of 7.5 to 9 MPa and then rapidly cooled. Specimens for subsequent mechanical characterisation were cut out from several compression-moulded sheets.

3.2. Moisture content measurements

Because starch-based plastics absorb and desorb water, special care was taken to determine the moisture content (MC) of this material at different equilibrium relative humidities (ERH). Small square shaped (10 × 10 mm^2) samples cut out from the compression-moulded sheets were maintained at 20 ± 1 °C until equilibrium in desiccators containing saturated salts solutions. The salts used (with their corresponding ERH at 20 °C) were CH_3COOK (23%), K_2CO_3 (43%), $Mg(NO_3)_2$ (54%), KI (70%), $(NH_4)_2SO_4$ (81%) and K_2SO_4 (98%) (Greenspan, 1977).

Samples were considered to reach equilibrium at 14 days since weight variations overtime were negligible past that point as shown in Fig. 3. Although equilibrium was not completely reached after 14 days of conditioning, this period seemed to be optimal to avoid any possible changes occurring within the sample as X-ray diffraction spectra did not show any retrogradation or recrystallisation happening during this period.

MC was determined gravimetrically by drying out the specimens cut in small pieces at 70 °C under vacuum (less than 250 mBar) for 3 days, the time required to reach a constant mass. The moisture levels reported are the values averaged over 4 samples.

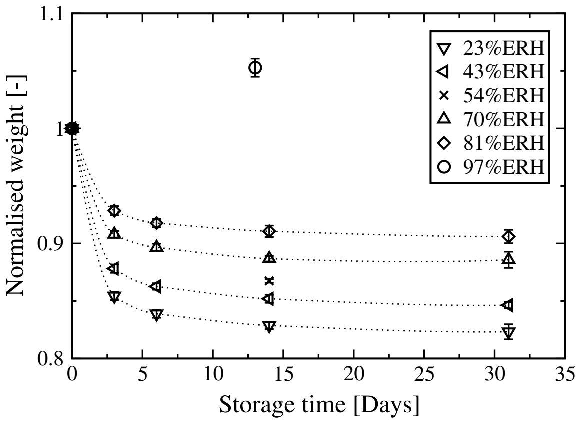

Fig. 3. Weight variations of the PlS blend over storage time at different ERH. (Data are plotted with their 95% confidence interval and lines are only included as visual aids to highlight trends.)

3.3. Tensile tests

Dumbbell-shaped specimens were punched out from five 1.5-mm thick compression-moulded sheets using an ASTM Standard D 638M (1996) Type M-III die and randomised before conditioning for 14 days at 20 °C in different ERH environments as described previously. Tensile tests were carried out on an Instron 4505 equipped with pneumatic grips to avoid slippage. Young's modulus, E and yield stress, σ_y, were measured at a crosshead speed of 5 mm min^{-1} using a 10 mm-gauge length extensometer for accurate monitoring of the tensile strain. The Young's modulus was calculated using the initial slope of the stress–strain curves. Due to the lack of a clearly defined yield point, the yield stress was determined as the stress at an arbitrary plastic strain of 1% (offset yield stress). Six replicates were tested for each storage condition.

3.4. Fracture tests

The essential work of fracture method was performed on DENT specimens cut out from twenty 0.9-mm thick compression-moulded sheets with a width of 30 mm, a length of 40 mm. Samples were randomised. The side notches were cut to a nominal depth (5, 7 or 10 mm; at least 5 samples for each depth) and sharpened with a sharp razor blade. Actual remaining ligament lengths were measured using a travelling microscope after testing giving ligament lengths ranging from 3 to 9 mm ($L \leqslant W/3$ to avoid edge effects). Specimens were then stored at constant ERH (43, 54, 70, 81 and 97% ERH) for 14 days. After conditioning, the samples thickness was about 0.8 mm due to shrinkage. For each ERH condition, at least 15 DENT specimens were tested to complete failure with an Instron 4505 at a rate of 5 mm min^{-1} using pneumatic clamps with a gauge length of 25 mm. Load–displacement plots were recorded for each sample, from which the maximum load P and the total fracture energy W_f were measured.

The linear elastic fracture mechanics approach was applied to 2.6-mm thick CT specimens with $W = 20$ mm (Fig. 1). This geometry was consistent with those recommended by the ASTM Standard D 5045 (1999). They were cut out from five compression-moulded sheets, randomised and stored at constant ERH (23, 43 and 54% ERH) for 14 days. Notching was done prior to testing using a sharp razor blade in one motion under a fixed load of 100 N with a Dynamite Instron 8841. The notch length range was measured accurately after testing using a travelling microscope and was $0.45 < a/W < 0.55$ as required by the ASTM Standard. For each ERH condition, 8 CT specimens were tested on an Instron 4505 at 5 mm min^{-1} using pins for loading. Load–displacement plots were recorded for each sample, from which the maximum load P was measured.

All mechanical testing reported in this section were performed at room temperature (23 ± 1 °C) and all specimen dimensions such as thicknesses were measured just prior to testing.

4. Results and discussion

4.1. Moisture content versus equilibrium relative humidity

Fig. 4 shows the MC reached after equilibration for 14 days in constant ERH environments. It illustrates the ability of PlS blend when stored under different ERH conditions, to absorb or desorb varying amounts of moisture. This is also demonstrated in Fig. 3. Just after processing (compression-moulding) this material has a MC of approximately 20%. Therefore, samples conditioned at 81% ERH and below desorb moisture and can reach a MC of 6.5% at 23% ERH. Samples conditioned at 97% ERH absorb moisture to achieve a MC of about 32%.

It is important to note that the drying technique used here does not measure the true water content (Isengard, 2001; Ruckold, Grobecker, & Isengard, 2000). Tightly bound water cannot be detected with this technique and moreover some other volatile substances can be released by the heating process. The low pressure applied in the vacuum oven during drying was aimed at reducing the production of volatile decomposition compounds. Nevertheless, the drying method used gave reproducible results as shown by the error bars in Figs. 3 and 4, even though these may differ slightly from the true water content.

Although in this study the parameter controlled accurately was the ERH, results will be discussed from now on as a function of MC since the changes observed in the material properties were directly caused by the adsorption or desorption of water as a result of the surrounding environment relative humidity.

4.2. Tensile properties

The Young's modulus, E, and the yield stress at 1% strain, σ_y, are shown, respectively, in Fig. 5a and b as a function of MC. The modulus and yield stress plots follow similar decreasing trends with increasing MC.

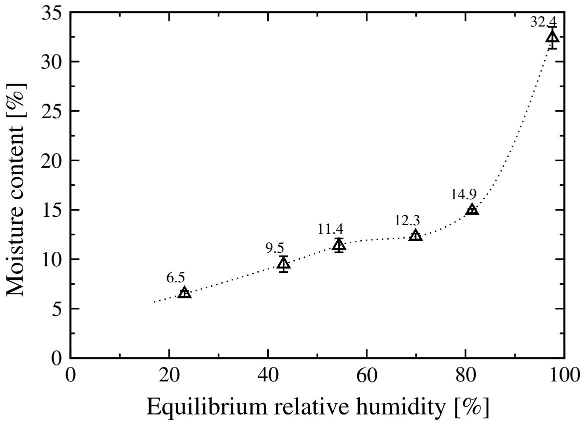

Fig. 4. Moisture content variations of the PlS blend according to the ERH after 14 days of storage. Data labels display the moisture content values. (Data are plotted with their 95% confidence interval and line is only included as visual aid to highlight trend.)

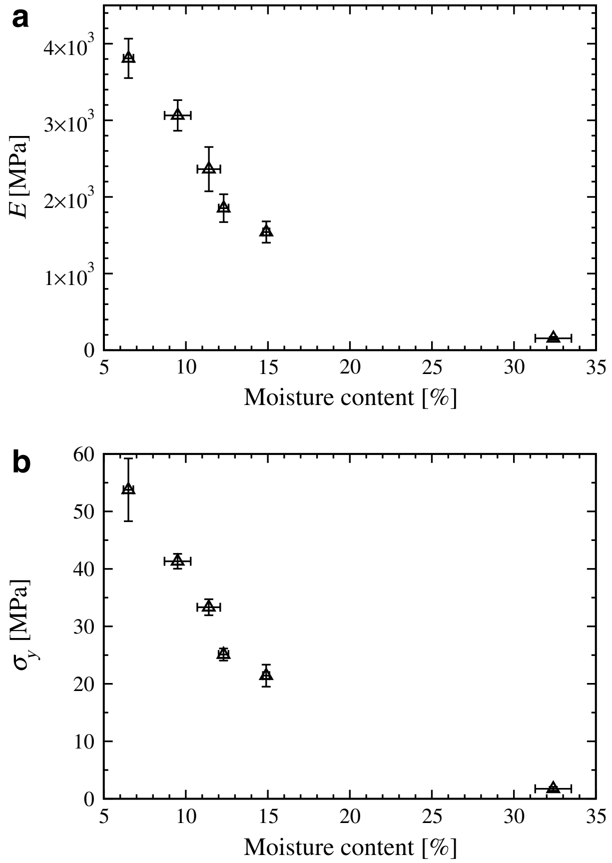

Fig. 5. Tensile properties of the PlS blend stored in various ERH environments for 14 days: (a) Young's modulus, E, and (b) yield stress, σ_y, versus the equilibrium moisture content. (Data are plotted with their 95% confidence interval.)

The MC clearly has a strong influence on the mechanical properties of this PlS blend and a wide range of mechanical behaviour can be achieved just by varying slightly the water uptake of this material. At very low MC (~6.5%), E was 3800 MPa and σ_y, 54 MPa. When the MC reached 15%, their values dropped, respectively, to around 1500 MPa and 21 MPa. When the material was stored between 43 and 70% ERH, its MC varied only 3%, from 9% to 12%, but the tensile properties exhibited a large variation: E and σ_y drop by 40%.

It is worth noting that the material studied here is a blend in which the plasticised starch is the main component. Dynamic mechanical thermal analysis has revealed the occurrence of two glass transitions in this material indicating the presence of a two-phase system (Chaléat, Michel-Amadry, Truss, & Halley, in preparation). The T_g of the PlS phase was found to vary between approximately 145 °C and 45 °C when the MC changed from 6.5% to 15%. The other T_g observed was related to the water-soluble high molecular weight polyol. It varies from 53 °C to about 1 °C in the same MC range. At 11.4%, the T_g of this phase is around 27 °C. Therefore, at ambient temperature, the polyol phase goes through its glass transition when the overall MC is changing between 9% and 15% and even though this phase is rather small, this change in T_g influences the overall mechanical properties of the blend.

As tensile testing was performed with an extensometer to get an accurate measurement of E and σ_y, the elongation to break was difficult to evaluate correctly because the extensometer blades slightly notched the specimens and so failure occurred prematurely altering the true value of strain at break. Nevertheless, it could be observed that elongation increased with increasing MC. Indeed, samples failed in a brittle manner when the MC was lower than 9.5% indicating reduced chain mobility. As the MC increased, ductile behaviour was observed from the material. On most samples with a MC above 12%, stress whitening occurred around the failure zone revealing some plastic deformation (such as crazing or cavitation) and strain at break could be evaluated at around 10–15%.

4.3. Fracture behaviour

Fracture mechanics analysis was used to characterise the fracture resistance of the PlS blend conditioned under various ERH. Depending on whether the fracture was ductile or brittle, the essential work of fracture (EWF) analysis or the linear elastic fracture mechanics (LEFM) analysis was used, respectively.

4.3.1. Essential work of fracture method applied on DENT specimens

The EWF was performed on DENT specimens conditioned at various ERH ranging from 43 to 97% ERH resulting in a MC varying between 9.5% and 32.4% as shown in Fig. 4. Fig. 6 depicts load–displacement diagrams which exemplify the types of fracture behaviour observed. These traces indicate that specimens with a MC of 9.5% demonstrated a brittle failure, with fast crack propagation before yielding of the ligament area occurred. Consequently, the EWF method could not be performed on these specimens.

DENT specimens with a MC of 11.4% and above displayed a typical load–displacement curve where stable crack propagation occurred after the ligament had completed yielding at the maximum load. Fig. 7 is a photo of a DENT specimen taken during loading. It demonstrates the full yielding of the ligament and the elliptical shape of the plastic zone developed. After testing, the fracture area exhibited a whitened zone indicating that the polymer may have cavitated or crazed under the load. DENT specimens with a high MC of 32.4% failed by ductile tearing where fracture commences before the maximum load was reached. The plastic deformation zone was not clearly visible and so, it was not possible to establish visually whether complete ligament yielding had occurred.

Fig. 8a shows w_f versus L plots for the different MC. According to Eq. (7), w_e and βw_p were evaluated for each ERH condition from the linear regression lines drawn in Fig. 8a and are shown in Table 1 along with the related coefficients of determination, R^2. w_e reaches a maximum at 12.3% MC and decreases with increasing MC. This clearly reveals a strong dependence of the fracture behaviour on the MC of this PlS material. Another finding is that the slope of the regression lines, e.g. βw_p, decreases with increasing MC. βw_p is related to the energy dissipated in the outer plastic deformation zone. If one assumes that β (the factor related to the shape of the plastic zone) stays constant over the different MC, w_p then seems to decrease with MC. This was probably due to the plasticisation effect of the increasing MC, which would decrease σ_y, and thus lower the energy absorption. However, the explicit determination of w_p requires knowledge of the shape of plastic zone β.

It is necessary to check the validity of the EWF tests. Net section yielding can be experimentally verified by measuring the maximum net section stress σ_n (maximum load divided by the original ligament length and thickness). According to Hill (1952), if σ_y is the yield stress of an unnotched specimen, then a DENT specimen in plane-stress will yield at $1.15\sigma_y$ due to a greater notch constraint effect in this geometry. In Fig. 8b, the maximum net section stress is plotted as a function of ligament length for each MC and confirms that this prerequisite was met.

A further validity check is needed on the specimen size criteria given by Eq. (8). Using w_e results and the E values from Section 4.2, the maximum ligament length $\hat{L}$, for

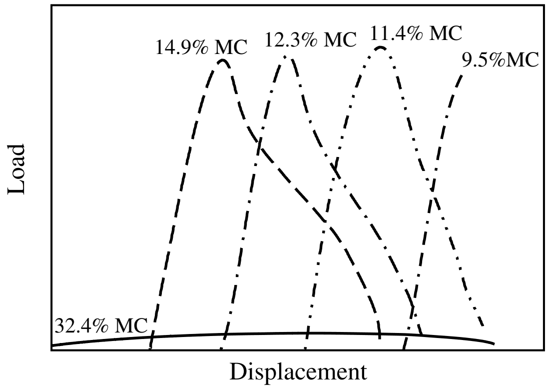

Fig. 6. Different types of load–displacement curves for DENT specimens with various moisture contents and the applicability of the EWF method.

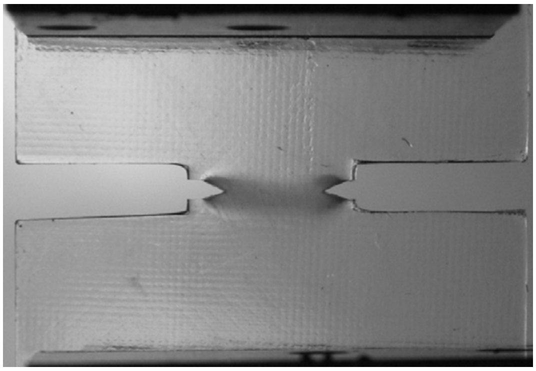

Fig. 7. DENT specimen under loading.

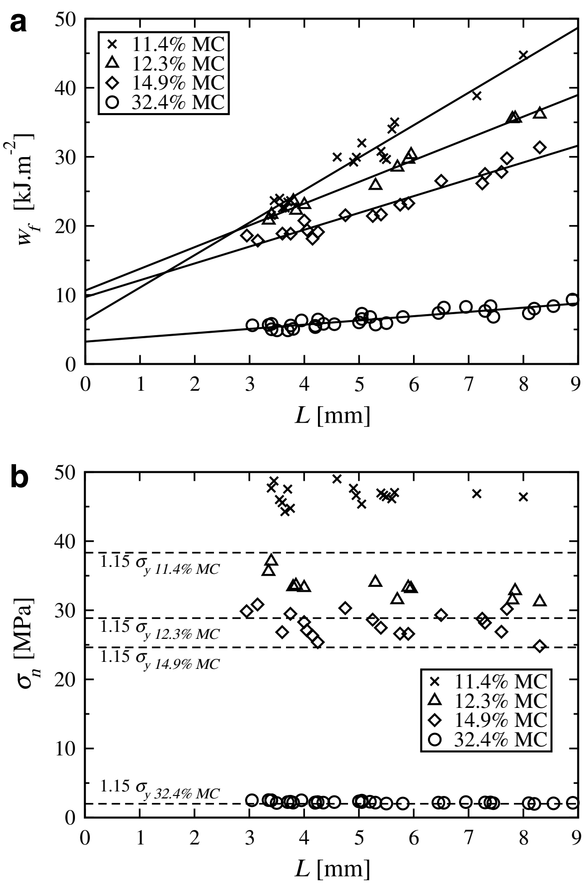

Fig. 8. Plots of specific total work of fracture w_f (a) and the maximum net section stress σ_n (b) versus ligament length L for materials with a moisture content varying between 11.4% and 32.4%.

Table 1
Essential work of fracture parameters (w_e and βw_p) and the related coefficients of determination (R^2)

MC (%)	w_e (kJ m^{-2})[a]	βw_p (kJ m^{-3})[a]	R^2
11.4	6.4 ± 2.6	4.7 ± 0.6	0.95
12.3	10.6 ± 1.4	3.1 ± 0.2	0.99
14.9	9.7 ± 1.6	2.4 ± 0.3	0.94
32.4	3.2 ± 0.6	0.6 ± 0.1	0.80

[a] Values given with their standard errors (95% confidence limits).

complete yielding, was estimated for a line plastic zone using Eq. (9). For the DENT specimens with a MC of 12.3% and above, $\hat{L}$ was restricted by the alternative width criterion (i.e. $W/3 \approx 10$ mm) and all the ligament lengths tested were shorter than this upper ligament limit. For the DENT specimens with a MC of 11.4%, the estimated size of the plastic zone, $2r_p$, based on w_e of 6.4 ± 1.3 kJ m^{-2}, E of 2.3 ± 0.1 GPa and σ_y of 33.3 ± 0.7 MPa, is about 5.3 ± 1.5 mm. The majority of the ligament lengths tested at this MC exceeded this value. Despite failing to satisfy the validity condition, it should be noted that within this pure plane-stress region, the proportionality of w_p with L^2 was still maintained along with an acceptable R^2 value (≈0.95). Previous studies employing the EWF method on various polymers (Arkhireyeva, Hashemi, & O'Brien, 1999; Hashemi, 1997, 2000; Karger-Kocsis, Czigány, & Moskala, 1998) have led to the same conclusion that this size requirement is too restrictive; especially when considering, that the ligament region of all DENT specimens was fully yielded. These results support this proposition.

4.3.2. Linear elastic fracture mechanics applied on CT samples

In this study, the LEFM approach was employed for the material failing in a brittle manner, which was stored below 54% ERH achieving a MC lower than 11.4%. The values of the measured K at fracture, K_Q, determined on CT specimens are displayed in Table 2. For the K_Q values to be considered as the plane-strain fracture toughness K_{Ic}, the size criterion given in Eq. (4) must be satisfied. The critical size for the thickness parameter B summarised in Table 2 demonstrates that the plane-strain conditions were not fulfilled with the specimen size used (∼2.6 mm). The K_Q values were in fact obtained for a mixed-mode state of plane-strain/plane-stress. This implies that the K_Q values measured are geometry dependent and will relate only to specimens of that same thickness. For this specimen thickness, K_Q was very low and showed very little dependency on the MC. This result is consistent with Even and Carr's work (1978), which shows a very mild dependence of fracture toughness on MC for amylose films. However, they observed this behaviour for a large range of MC (0–30%), which, in the present study, was only true for MC below 11.4%.

It should be noted that to determine the plane-strain fracture toughness K_{Ic} for this PlS material, samples whose size satisfy the size requirement would have to be moulded. The large critical thickness values required could not be achieved in this work.

4.3.3. Influence of the moisture content on the fracture behaviour – summary

To be able to compare the two sets of results, obtained from the EWF and LEFM methods, w_e and K_Q need to be converted into the same fracture parameter. As explained in Section 2 the essential work of fracture w_e can be equated to J_c, the energy release rate for plastic deformation. Using Eq. (5), K_Q can also be related to G_Q and J_Q is equivalent to G_Q in the elastic case. As the plane-strain state was not achieved, the plane-stress relationship was preferred

Table 2
Linear elastic fracture mechanics results

MC (%)	K_Q (MPa m$^{1/2}$)[a]	Critical size for B (mm)	E (GPa)	J_Q (kJ m^{-2})[a]
6.5	1.9 ± 0.2	3.0	3.8	0.9 ± 0.2
9.5	2.1 ± 0.3	6.4	3.0	1.4 ± 0.5
11.4	2.1 ± 0.2	10.1	2.3	1.9 ± 0.5

[a] Values given with their standard errors (95% confidence limits).

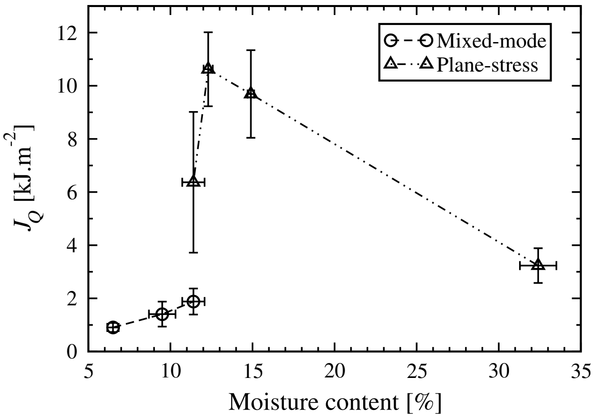

Fig. 9. Variations of the strain energy release rate, J_Q for plane-stress and mixed-mode conditions with the equilibrium moisture content. (Data are plotted with their 95% confidence interval).

although the difference is not great. The J_Q values resulted from the LEFM data are detailed in Table 2.

All fracture results are summarised in Fig. 9 plotting the strain energy release rate J_Q as a function of MC. The plane-stress J_Q values resulting from the EWF method applied to material with a high MC (11.4–32.4%) as well as the mixed-mode J_Q values obtained from the LEFM approach performed on material with a lower MC (6.5–11.4%) are presented on this graph. The lines through the data points are only included as visual aids to highlight trends.

Most polymers have G_{1c} values of 1–10 kJ m^{-2}, so the J_Q values obtained for this PlS blend are comparable. At low MC, J_Q is quite low showing that the material is in a glassy state displaying a very brittle behaviour. While the MC increases, the yield stress decreases and J_Q increases slightly since water plasticises the material allowing more movement between the chains.

Fig. 9 clearly indicates the presence of a brittle-to-ductile transition at around 12% MC. This sudden change in behaviour occurs when the T_g of the high molecular weight polyol drops below ambient temperature as explained in Section 4.2. At an overall MC of 11.4%, DMTA data have shown that the T_g of this phase is around 30 °C. Although this component was present in a very small quantity in this blend, it did induce a very dramatic change in its fracture behaviour when this phase went from a vitreous to rubbery state. It is speculated that the effect of the rubbery polyol was to toughen the PlS in a similar manner to the effect of small rubber inclusions in glassy synthetic polymers such as in ABS or epoxy (Bucknall, 1967; Bucknall & Smith, 1965; Kinloch, Shaw, Tod, & Hunston, 1983). These materials are also known to undergo a decrease in toughness with decreasing temperature when their second phase rubbery particles are below their T_g.

At higher MC, the resistance to fracture also dropped. Water is known to act as a plasticiser for both phases. Around 12% MC, the high molecular weight polyol phase was in a rubbery state while the main, probably continuous, PlS phase was still glassy. This is probably the reason why there was a maximum in toughness at this stage. However, with increasing MC above 12%, the matrix PlS phase became increasingly plasticised. As shown by the tensile data this had the effect of both increasing the ductility of the material but also decreasing the maximum stress on the material. This had the combined effect of reducing the energy to break the sample. Eventually, with increasing MC, the starch phase would also transition through its T_g. At an overall MC of 14.9%, the T_g of this phase was around 55 °C.

5. Conclusions

The moisture content was shown to strongly affect the tensile properties of a plasticised starch/high molecular weight polyol blend due to changes in the glass transition temperature. As the moisture content increased, there was a reduction in the Young's modulus and yield stress.

By means of commonly employed fracture mechanics techniques, it was shown that changes in moisture content also altered significantly the fracture properties of this plasticised starch blend. At low moisture content, the measured strain energy release rate J at fracture, J_Q, was very low, and showed very little dependency on the moisture content. As the moisture content increased, the material became increasingly ductile and displayed a brittle-to-ductile transition at 12% of moisture content due to the glass transition temperature of the high molecular weight polyol phase dropping below ambient temperature.

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