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The effects of the biaxial stretching of leather on fibre orientation and tensile modulus

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Leather has been subjected to different degrees of equal biaxial strain (up to 20%) during drying and its tensile modulus has been measured when dry. The collagen fibre orientation distribution in the dried leather has been assessed using wide angle X-ray diffraction. It was found that drying under biaxial strain caused the tensile modulus to increase markedly (by up to 400% at 20% biaxial strains) but with a dependence on the angle of test axis in relation to the principal axes of biaxial strain. The fibre orientation distribution in planes parallel to the surface was affected less by biaxial strain than in planes perpendicular to the surface and it is concluded that the latter type of fibre reorientation is the main factor responsible for the observed increases in tensile modulus. © *2004 Kluwer Academic Publishers*

1. Introduction

Leather is produced from animal hides and skins which is a bi-product of the meat industry. Because these raw materials are purchased by weight but leather is sold per square metre there is a continuing interest in how area yield from production may be maximised. One possible route to achieving this goal is to stretch leather at some stage during its manufacture [1] and it has been shown that an effective way of obtaining lasting increases in dimensions is to dry it whilst it is held under an applied strain [2]. However we have shown that drying under uniaxial strain can have a marked effect on the stiffness of the dried leather [3]. Increased stiffness may be a problem since in many applications leather is appreciated for its relative softness and suppleness. In practice biaxial stretching is better suited to achieving large area increases and it is one purpose of this paper to report on the effects on the tensile stiffness of leather of this mode of deformation applied during drying.

There have been a number of studies of the biaxial stretching of leather. Early investigations by Ward and Chinn [4] used pneumatically operated apparatus and examined the development of constitutive equations to describe the stress-strain response of leather in this mode of deformation. Butlin [5] studied the behaviour of leather when deformed by a sphere impressed on to a disk of leather clamped around its edge, he was particularly interested in the degree of area gain achieved under different conditions (temperature and moisture content). Lin and Hayhurst stretched leather along two orthogonal axes simultaneously using a system of pulleys attached to a conventional tensile testing machine [6]. None of these workers examined the mechanical behaviour of the leather after it had been deformed biaxially.

The structure of leather consists of a three dimensional network of chemically crosslinked collagen fibres. By using wide angle X-ray diffraction (WAXS) we have shown that as leather is subjected to increasing uniaxial strain these fibres tend to become progressively orientated along the axis of deformation. The degree of fibre orientation can be associated with the observed tensile modulus [3]. It is the other main aim of this present work to report on the use of WAXD to determine how biaxial stretching alters the fibre orientation and how such changes relate to the stiffness of the leather after stretching.

2. Experimental

2.1. Materials

Chromium tanned bovine hide was obtained from an UK tannery in a wet partially processed form (‘wet

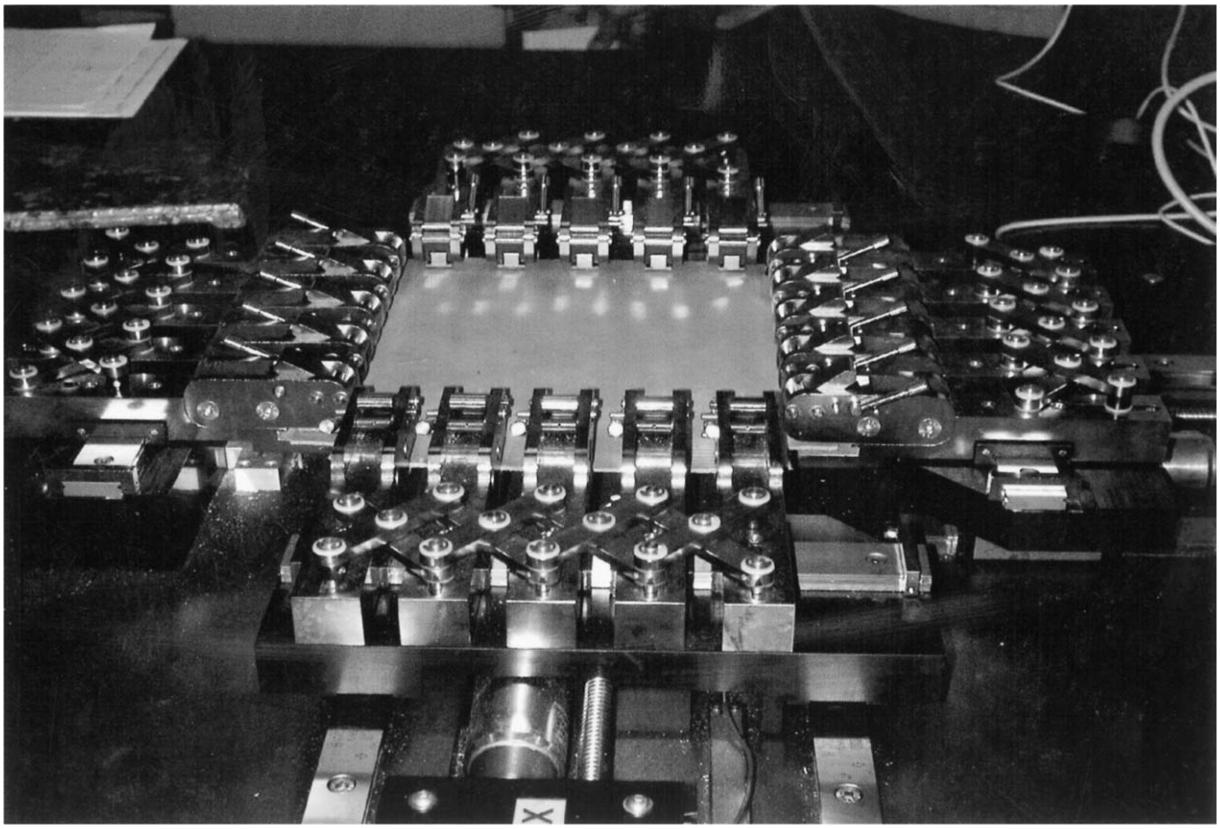

Figure 1 Biaxial testing machine.

blue'). The hide was cut along the backbone line to give two approximately equal sides. Five square (22 × 22 cm^2) samples were taken from one side in and around the official sampling location [7] and were dried under various degrees of biaxial stretch. Five such squares were also cut from the other side at the equivalent location.

2.2. Biaxial stretching and drying

The square shaped samples of wet leather were stretched on a biaxial testing machine supplied by Deben UK*. This machine consists of four sets of five jaws, which are at 90° to each other (Fig. 1). Each edge of the square sample is clamped in one set of jaws. Two sets of jaws on each of the orthogonal axes (X and Y) can be moved by a motorised screw. Each set of jaws is mounted on a slider and linked together by a concertina formation of links in order to allow a controlled lateral movement of the jaws to accommodate extension of the sample in this direction. Transducers allow the measurement of both load and extension along each axis.

Three square samples were simultaneously stretched in two orthogonal directions by 10, 14 and 20% strain. After the wet samples had been stretched they were left to dry under the applied strain for 48 h. After drying in this way, leather released from the grips retained the biaxial deformation. The five squares from the opposite side of the backbone line were allowed to dry without constraint.

2.3. Tensile testing

Rectangular shaped specimens (1.7 × 8 cm^2) were cut from the dried leather at various angles to the Y-axis (this axis was parallel to the backbone line). Following conditioning for 48 h at 65% relative humidity they were subjected to tensile testing on an Instron 1122 machine. The separation of the jaws at the start of the test was 5 cm and the crosshead speed was 5 mm/min. The maximum initial gradient of the resulting load-extension curve was used to calculate a tensile modulus.

2.4. Wide angle X-ray diffraction

Wide-angle X-ray diffraction patterns were collected at the Daresbury Synchrotron Radiation Source using a wavelength of 1.488 Å and a square 0.5 × 0.5 mm^2 beam cross section. X-ray diffraction profiles were taken either with the beam normal to the surface (direction of arrow 1) or through thickness (direction of arrow 2) as illustrated in Fig. 2. Normalised X-ray intensity profiles over the azimuth range $0° \leq \theta \leq 180°$ were obtained as described previously [8].

3. Results

3.1. Tensile modulus

Fig. 3 shows a graph of the tensile modulus at various angles to the backbone line. The material which was allowed to dry without constraint (referred to as the control sample) displayed a modulus which was around 15–20 MPa. It is apparent that such material is somewhat stiffer at the lower angles to the backbone line.

Looking at the material, which was biaxially strained prior to drying, it can be seen that the tensile modulus is increased as a result of the stretching. For any given biaxial strain there is a significant angular dependence of the modulus with the lower angles tending to give

TABLE I Tensile modulus anisotropy with and without the application of biaxial strain during drying

Biaxial strain (%)	E_0/E_{90}
0	1.44
10	1.68
14	2.21
20	1.44

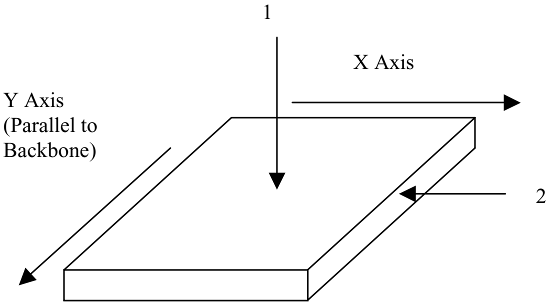

Figure 2 Orientation of sample with respect to the X-ray beam which was either (1) normal to the surface or (2) through thickness.

greater values. This anisotropy may be characterised by calculating the ratio of tensile modulus at 0° (E_0) to that at 90° (E_{90}) as shown in Table I.

Fig. 4 shows the modulus averaged over all test directions plotted against the degree of equibiaxial strain applied during drying. The results show that equal biaxial strains of 10% gave a mean modulus increase relative to the control of 114%, 14% biaxial stretching gave a mean modulus increase of 209 and 20% gave a 422% increase.

3.2. X-ray diffraction

Wide angle X-ray diffraction patterns from leather feature a single circular X-ray reflection, deriving from the regular array of rod-like molecules making up fibrous collagen. A typical diffraction pattern obtained with the X-ray beam directed normal to the surface of leather dried under biaxial strain is shown in Fig. 5. The backbone direction is indicated by an arrow. Because collagen fibres diffract X-rays in a plane normal to their long axis the intensity profile of the reflection contains information about the angular distribution of collagen fibres within the leather.

Fig. 6 shows the variation of relative normalised intensity with azimuth angle when the X-ray beam was normal to the surface of the leather. It is apparent that there is a marked angular dependence of intensity on the azimuth angle for the unstretched sample with intensity at a maximum at around 0/180° and a minimum around 90° indicating that more fibres were oriented parallel to the backbone direction. Equal strain biaxial stretching causes some changes in the intensity profile. Firstly the ratios of maximum intensity ($I_{\max}$) to minimum intensity ($I_{\min}$) differ somewhat and are compared in Table II. Secondly the minimum values occur at lower azimuth angle (70–80°) and for 10 and 20% strain the maximum is also shifted by 10–20°.

A typical diffraction pattern obtained when the X-ray beam was directed through the thickness of the sample dried under biaxial strain (direction 2, Fig. 2) is shown in Fig. 7. The backbone direction is indicated by an arrow which lies parallel to the sample surface.

The intensity profile results obtained with the sample in this orientation are shown in Fig. 8. The unstretched control sample gives a broad peak centred on an azimuth angle of 100° with the minimum value occurring at 0/180° indicating a preferred direction of fibre alignment inclined at 10° to the sample surface. Applying biaxial strain during drying has resulted in an increase in peak intensity and a reduction in minimum intensity (see Table III). Biaxial stretching during drying has also resulted in the peak position shifting to an azimuth angle of 90° as more fibres become aligned parallel to the sample surface.

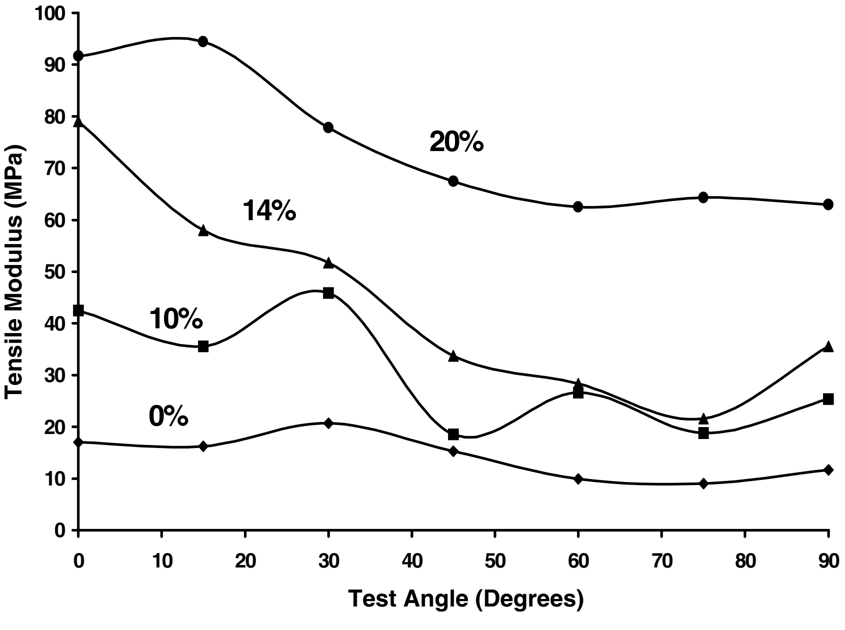

Figure 3 A plot of tensile modulus against test angle for leather dried under equal biaxial strains of 10, 14 and 20% as indicated. Also shown are results for a control sample dried without constraint (0%). Angles are measured with respect to the Y-axis as defined in Fig. 2.

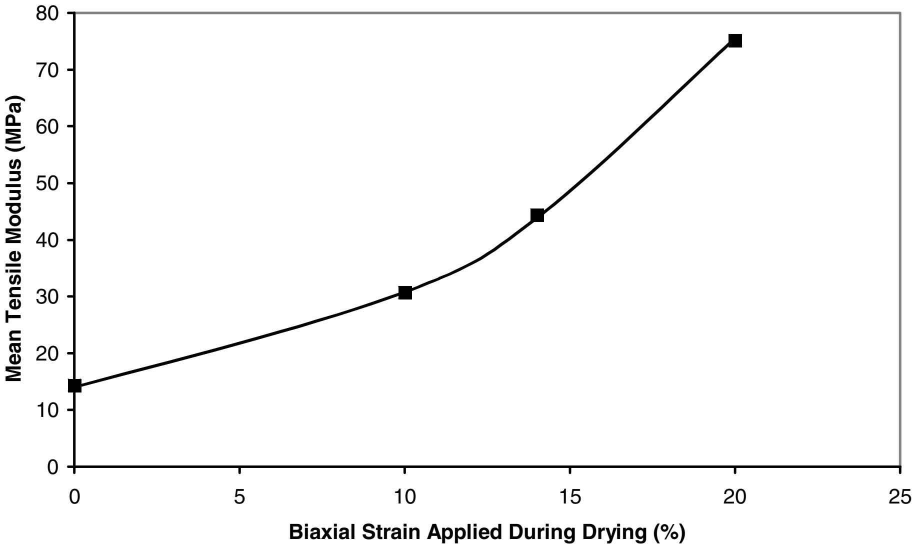

Figure 4 A plot of mean tensile modulus against the biaxial strain applied during drying.

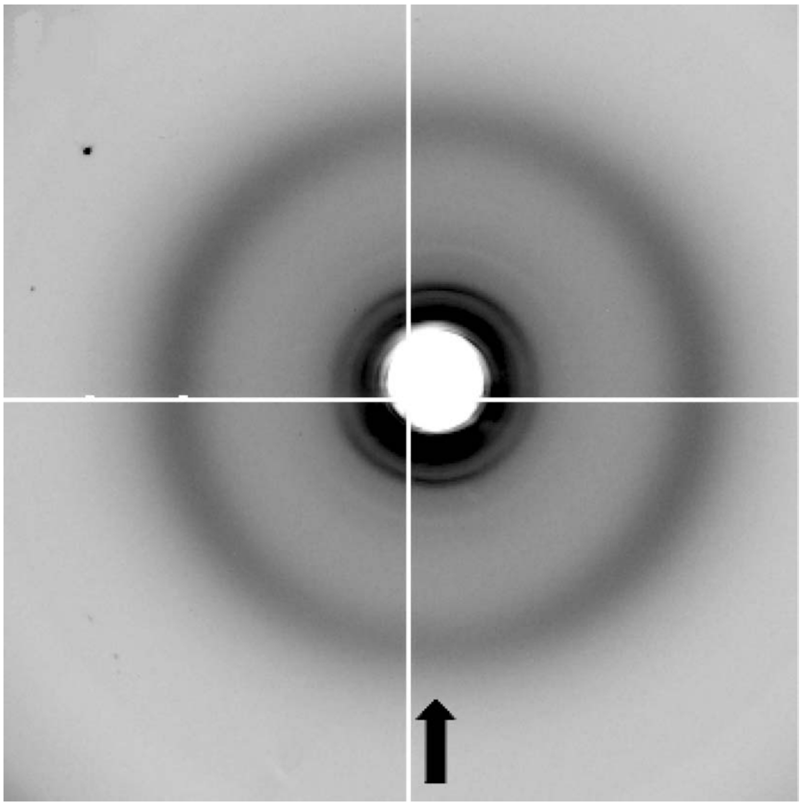

Figure 5 A wide angle X-ray diffraction pattern obtained with the beam directed normal to the surface of leather dried under a 14% biaxial strain. The backbone direction is indicated by an arrow.

Comparing Tables II and III it is apparent that the increases in $I_{\max}/I_{\min}$ after biaxial stretching are substantially greater when the beam is edge on (increases in the range 39–79%) compared with when the beam is normal to the surface (increases in the range 7–24%).

4. Discussion

4.1. Leather dried with no stretching

The X-ray intensity profiles indicate that there are preferred fibre orientations within the unstretched material. Firstly Fig. 6 suggests that when viewed normal to the surface the predominant direction of fibre orientation is parallel to the line of the backbone. This observation is reasonably consistent with the work of Osaki [9] who used a method based on absorption of polarised microwaves to determine preferred collagen fibre orientations in different regions of a whole calfskin leather. He showed that within the region termed the official sampling position [7] from where we took our samples, the principal axes of fibre orientation were at low angles to the line of the backbone.

TABLE II Ratio of maximum to minimum diffracted X-ray intensity for different biaxial strains applied during drying. Incident X-ray beam normal to surface

Biaxial strain (%)	$I_{\max}/I_{\min}$
0	1.44
10	1.79
14	1.63
20	1.54

TABLE III Ratio of maximum to minimum diffracted X-ray intensity for different biaxial strains applied during drying. X-ray beam incident on sample edge

Biaxial strain (%)	$I_{\max}/I_{\min}$
0	2.39
10	3.33
14	4.29
20	3.50

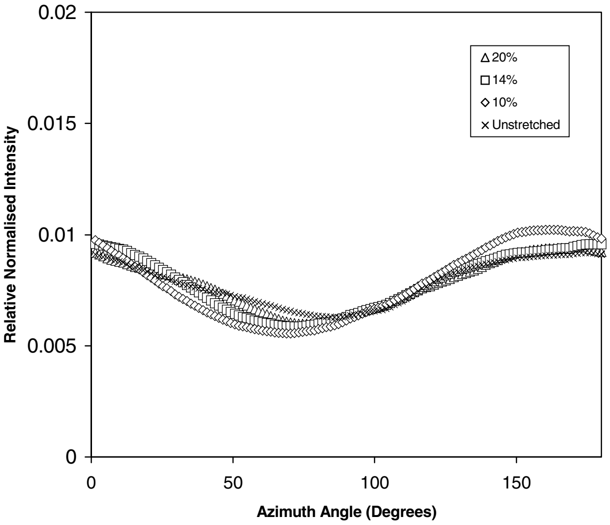

Figure 6 Averaged X-ray intensity profiles for leather dried under different degrees of biaxial strain. X-ray beam incident normal to surface (direction 1 in Fig. 2).

The unstretched material also displays non-uniform fibre orientation when viewed edge on (Fig. 8). The results show that the majority of fibres are aligned at small angles to the surface. A preferred orientation of fibres in hide when viewed edge on has been observed using optical microscopy and has been described as the fibres having a preferred 'angle of weave' [10].

The greater tensile modulus values observed at lower test angles for unstretched material (Fig. 3) is consistent with the finding that fibres lie predominantly along or at low angles to the backbone line. Shoe manufacturers have been aware of tensile modulus anisotropy in leather for many years and refer to the phenomenon as 'lines of tightness' in the leather [11].

4.2. Leather dried under biaxial strain

Fig. 6 shows that the after the application of biaxial strain during drying the fibre orientation distribution in planes parallel to the surface is broadly maintained although the results suggest a degree of increased fibre alignment along the two principal strain axes. Considerably more realignment of fibres occurs when the leather is observed through thickness (Fig. 8). In view of these findings it is reasonable to assume that it is the through thickness reorientation of fibres occurring during the application of biaxial strain that in the main accounts for the large increases in tensile modulus which occur after drying leather under biaxial strain.

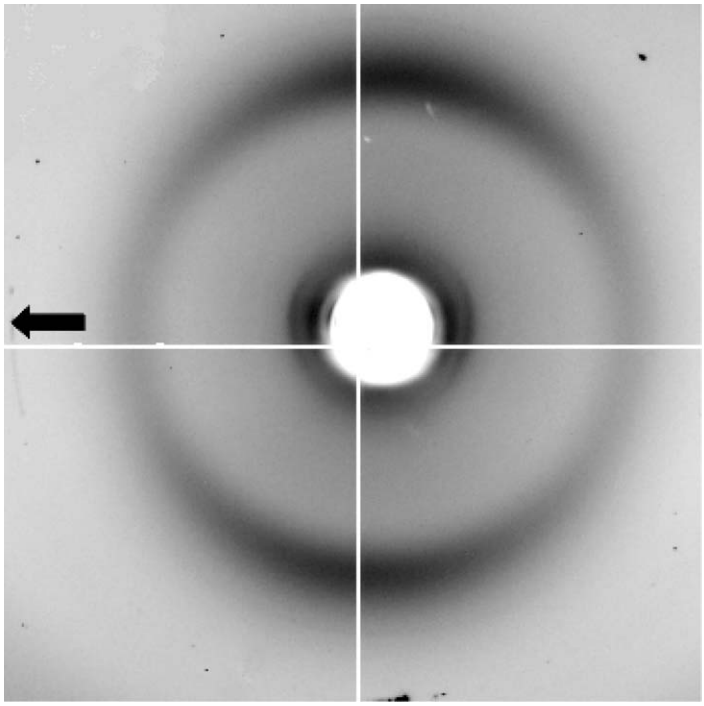

Figure 7 A wide angle X-ray diffraction pattern obtained with the beam directed parallel (i.e. through thickness) to the surface of leather dried under a 14% biaxial strain. The backbone direction is indicated by an arrow: this arrow is parallel to the sample surface.

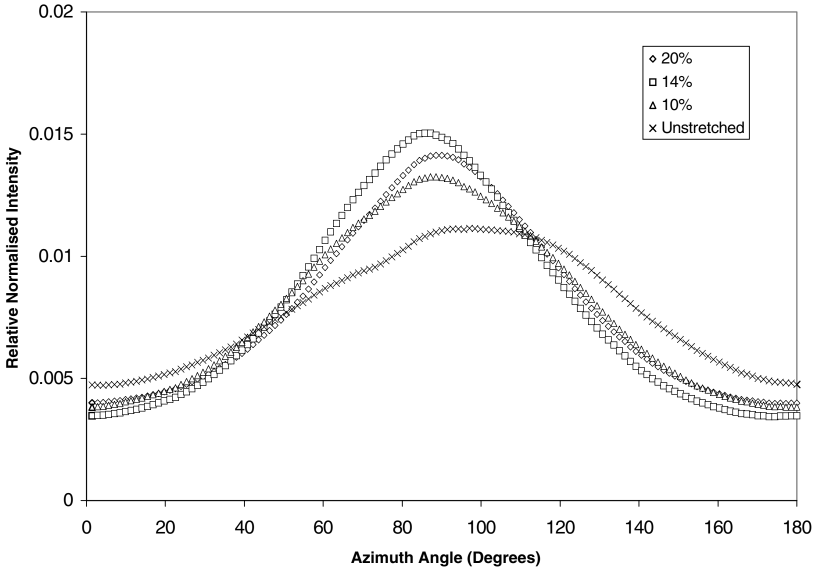

Figure 8 Averaged X-ray intensity profiles for leather dried under different degrees of biaxial strain. X-ray beam incident normal to edge (direction 2 in Fig. 2).

The data in Fig. 8 indicate that following the application of biaxial strain the angle between any given collagen fibre and the Y-axis is reduced. In the simplified collagen network model proposed by Wright and Attenburrow [2] it is shown that reducing the angle between the fibre axis and the tensile test axis may be expected to result in an increased tensile modulus. Leather is derived from animal skin and it is interesting to note that the importance of though thickness reorientation of collagen fibres during the biaxial deformation of porcine skin has been predicted by Hepworth *et al.* [12]. However it must be pointed out that leather is different from skin in a number of ways, one of which is that the gel like matrix (ground substance) which is present between the collagen fibres in skin is removed during leather manufacture.

5. Conclusions

It is concluded that the application of biaxial strain during the drying of leather leads to substantial increases in its stiffness. This increase is mainly due to a reorientation of collagen fibres in planes perpendicular to the surface. The tensile modulus anisotropy found in unstretched leather is maintained after biaxial stretching.

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