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The set and mechanical behaviour of partially processed leather dried under strain

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The stress-strain behaviour of partially processed leather which has been dried under a range of uni-axial strains has been investigated. It has been found that the dependence of the tensile modulus on the strain applied during drying is non-linear, increasing slowly at first then more rapidly later on. A two-dimensional microstructural model based on an idealised fibre network can describe this non-linear relationship and account for differences between samples. High values of set are produced by drying under strain and some of this set is retained even after soaking in water. It is suggested that this is due to the formation of stable crosslinks between the chemically modified collagen fibres that comprise leather.

1. Introduction

Leather is a material which continues to find wide application in the manufacture of shoes, clothing, upholstery, baggage etc. The principal raw materials for its manufacture are the hides and skins which are a bi-product of the meat industry. These are subjected to a range of chemical processes which remove unwanted material (e.g. hair, epidermis, ground substance) to leave a network of fibres composed of the biopolymer collagen. In the tanning process these collagen fibres are stabilised against microbial attack using chromium salts or tannins extracted from vegetable matter [1].

After tanning the partially processed leather may be subjected to various mechanical operations which exert a stretching action and which may leave residual strains in the leather and thus can influence the amount (as measured by area) of leather produced [2]. Since the tanner purchases hides and skins by weight but sells leather by area there is considerable interest in maximising the area yield of product for a given weight of raw material. There is however concern that too much stretching of leather during processing may affect some aspects its quality (e.g. its stiffness and strength).

The presence of residual strain in a material after it has been subjected it to an applied strain is termed set. There has, over the years, been interest in what factors influence set in leather. For example the early work of Butlin [3] was concerned with the shoe shaping operation (lasting) and it was reported that high values of set could be obtained when material was dried under strain at elevated temperatures. Recent work has been concerned with partially processed leather [4] and it was demonstrated that the moisture content at the time of stretching was a very important determinant of the amount of set produced in such material.

In spite of its importance for product quality there have been no publications concerned with how pre-stretching affects the mechanical behaviour of the leather produced. The work reported here is concerned with how drying under strain affects the degree of set imparted to part-processed leather and in particular how it affects its stiffness. Whilst mathematical models [5] have been developed to describe the mechanical behaviour of leather there does not appear to be any published work on the use of quantitative microstructural models for leather. The availability of such models is clearly desirable and a modification of a model developed for auxetic polymers is described.

2. Materials and methods

Chrome tanned, partially processed leather (“wet blue”) was obtained from a UK tannery. Details of the process used are given elsewhere [4]. This leather was of bovine origin and had not been subjected to the fatliquoring process.

Eight strips 25 by 300 mm were cut from within the standard sampling position [6] and in a direction parallel to the backbone. These samples were soaked in distilled water at 20 °C for at least 16 hrs. The surface of the samples was blotted and two benchmarks (spacing 100 mm) were drawn. Samples were stretched to various strains and then allowed to dry in an air conditioned room at 20 °C and 65% Relative Humidity; such leather had a moisture content of 25% (dry weight basis). The strains applied were from 0 to 35% in 5%

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intervals. After drying the leather strips were released and the separation of the bench marks was measured one day after release. Set was calculated as follows:

$$\text{Set}(\%) = \frac{\text{Lr} - \text{Lo}}{\text{Lo}} \times 100$$

where Lo = Original separation of bench marks and Lr = Separation of bench marks after release.

Dumb-bell shaped tensile test pieces and narrow strips (2 mm wide) were cut parallel to the long axis of the strips which had been dried under strain. The dumb-bell sample was subjected to tensile testing at a rate of 100 mm min^{-1} using an Instron 1122 machine housed in the air conditioned room and the stress-strain relationship was recorded. Changes in the dimensions of the narrow strip were measured after it was immersed in distilled water for one week and subsequently allowed to re-dry (without constraint). Initial modulus values after drying under strain were also measured for strips cut from the official sampling position (and perpendicular to the backbone) of another partially processed hide from the same batch.

3. Results

Fig. 1 shows a typical plot of the variation of stress with strain during tensile testing of the initial part processed leather before drying. The test piece was cut close to and parallel to the long axis of the strips (from hide 1) which were dried under strain. This curve displays a low slope region at low strain and a high slope region at high strain. Test pieces from hide 2 gave a similarly shaped stress-strain curve.

Fig. 2 shows a plot of set (measured one day after release) against the strain applied during drying of the large strips. It can be seen that the values of set are close to the line representing set equal to applied strain. The effect of immersing material in water for one week (followed by re-drying) is also shown and it is clear that this procedure has resulted in a reduction in set. However it is apparent that at 10% applied strain and above the amount of set retained by the re-wetted leather is a large proportion of the initial set.

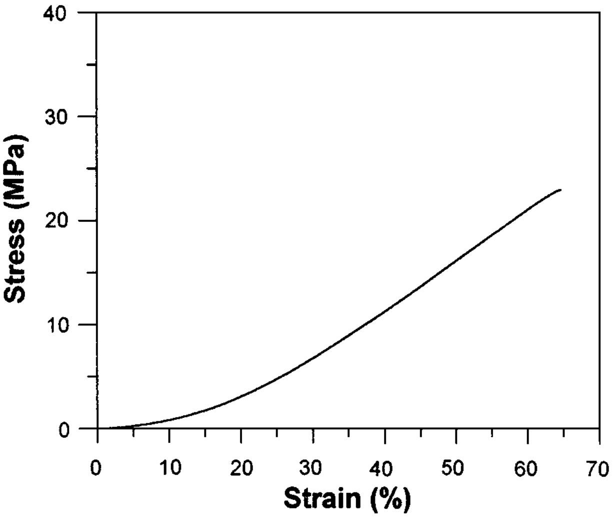


Figure 1 A typical stress-strain curve for wet partially processed leather.

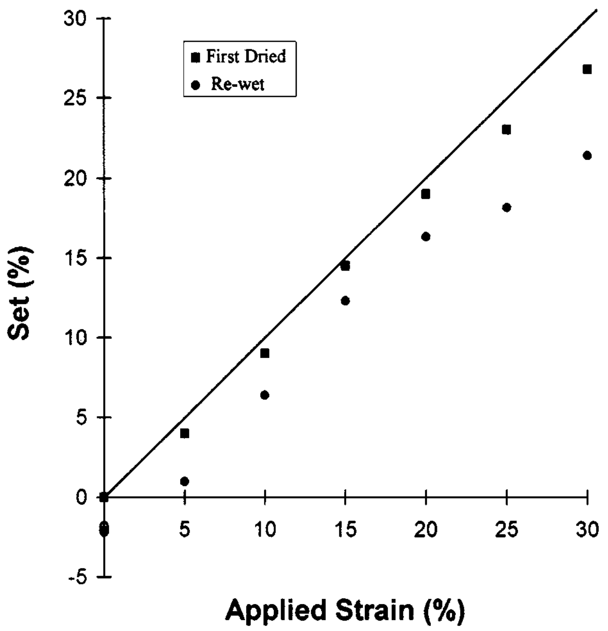


Figure 2 Set plotted against the strain applied during drying of leather strips from hide 1. Squares represent set measured after first drying. Circles represent set measured after re-wetting and then drying again. In this second re-drying samples were not constrained. The solid line represents the relation set = applied strain.

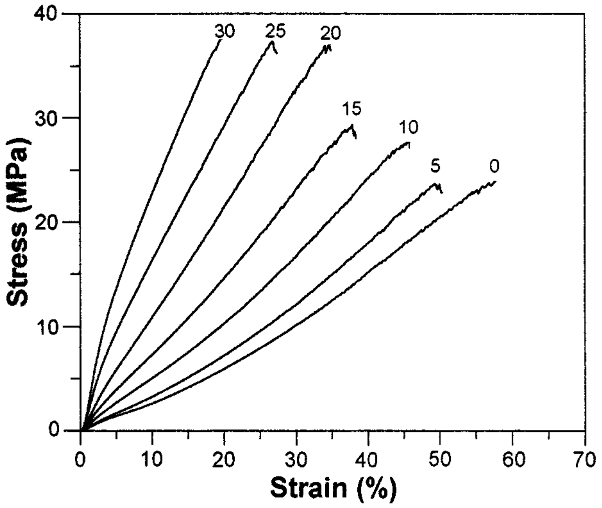


Figure 3 Stress-strain curves from tensile tests of leather strips (from hide 1) dried under an applied strain (%). The value of applied strain applicable to each curve is indicated.

The influence of the strain applied during drying on the subsequent stress-strain behaviour of the dried strips is shown in Fig. 3. The curves show that as applied strain increases the strips display an increasing stiffness with a decrease in the strain at break and an increase in the stress at break.

The stiffness of the dried strips was characterised by measuring the slope of the curves at 2% strain to give a tensile modulus and Fig. 4 shows a plot of this modulus against set. In the case of leather from the first hide the increase in modulus is over ten fold as the applied strain during drying increases from 0 to 30% and it is clear that most of this increase occurs above 10% applied strain. For leather from the second hide the increase is only four fold over the same range of set.

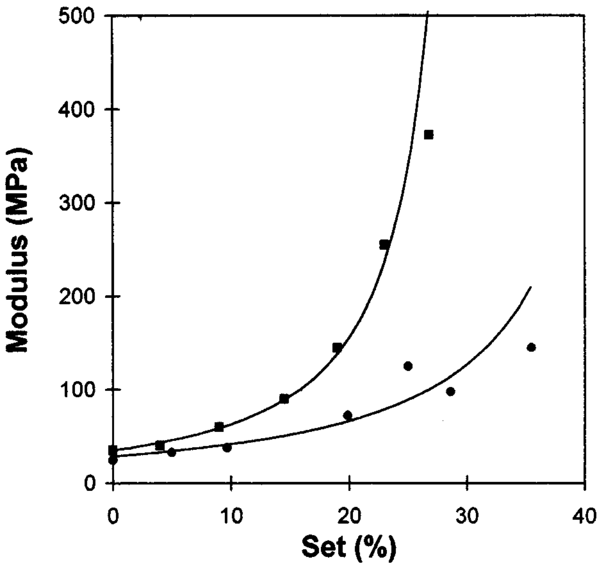
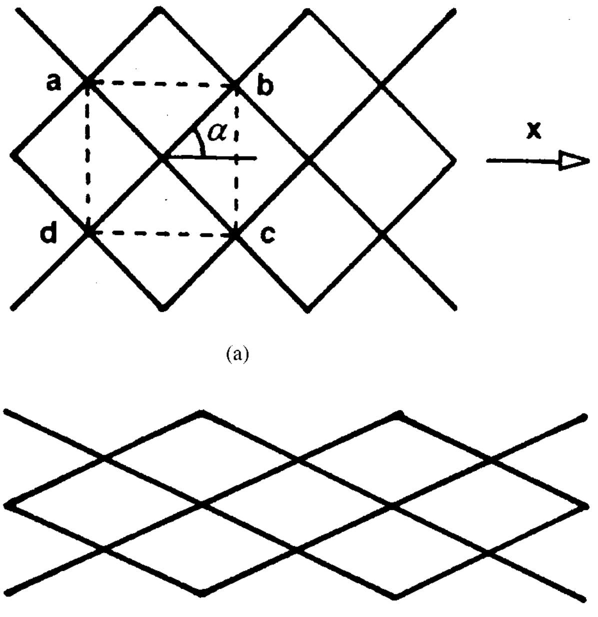


Figure 4 The tensile modulus of leather strips dried under strain plotted against their set. Squares represent data from hide 1, circles data from hide 2. The solid lines are theoretical curves arising from the microstructural model (fibril hinging).

4. Microstructural modelling

The question arises as to whether the observed non-linear dependence of modulus on pre-strain (Fig. 4) may be analysed in terms of a quantitative microstructural model. Dried leather may be considered to be an assembly of more or less straight fibres which are connected together at junction points such that they form a network. A simplified two dimensional representation of such a structure is given in Fig. 5a. The unit cell is defined by the square abcd. After drying under a uniaxial strain it is assumed that fibres have rotated towards the strain axis so that the angle α is reduced as shown in Fig. 5b.



(a)

(b)

Figure 5 The proposed microstructural model for dried leather in which straight fibres form a network as illustrated in (a); the unit cell is defined by the square 'abcd'. When the strain along the x-axis is increased fibril hinging leads to a reduction in the angle α as illustrated in (b).

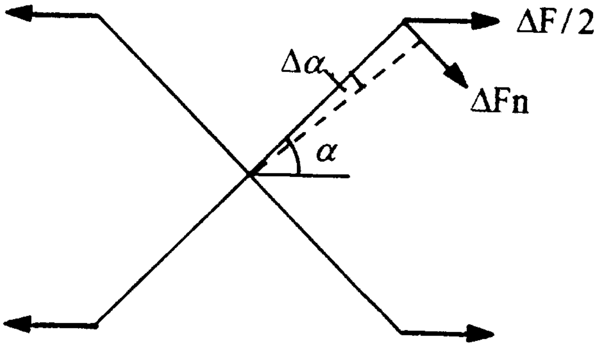


Figure 6 Deformation of the unit cell during fibril hinging. An increase in the force (ΔF) acting on the unit cell causes the angle α to reduce by $\Delta\alpha$.

The problem of calculating elastic constants for materials with a fibrous microstructure has been addressed by Alderson and Evans [7] and the structures drawn in Fig. 5 are a special case of their node-fibril model in which the node dimensions are zero and the sign of the angle α is reversed. The node-fibril model was developed to account for the behaviour of auxetic microporous polymers but here we show it has wider application.

If we consider the unit cell in isolation (Fig. 6) then an increase ($\Delta F/2$) in the force acting on the fibre in the x direction may be resolved into an increase ($\Delta\mathrm{Fn}$) in force acting normal to the fibre axis. This normal force acts to rotate the fibre into the direction of stretch by an angle $\Delta\alpha$.

We then have:

$$\Delta\mathrm{Fn} = \frac{\Delta F}{2\sin\alpha} \qquad (1)$$

Alderson and Evans define a hinging coefficient Kh such that

$$l\Delta\mathrm{Fn} = \mathrm{Kh}\Delta\alpha \qquad (2)$$

where l is the fibre length

This equation is equivalent to Equation 6 in reference 7. Following exactly the line of Alderson and Evans' analysis in reference 7 the following expression for the Young's modulus (E) measured along the x axis is obtained:

$$E = \mathrm{Kh}\frac{\cos\alpha}{l^2\sin^3\alpha} \qquad (3)$$

This equation is equivalent to Equation 14 in reference 7 with the node dimensions set to zero. Alderson and Evans' derivation assumes that the unit cell has unit thickness and this allows ΔF to be related to changes in applied stress. Geometrical analysis is then used to relate $\Delta\alpha$ to the change in strain. Finally E is calculated as $\mathrm{d}\sigma/\mathrm{d}e$ where $\mathrm{d}\sigma$ is the (infinitesimal) change in stress producing an (infinitesimal) change in strain, $\mathrm{d}e$.

If the material with zero set has a modulus $E\mathrm{o}$ and is characterised by a model fibre network where $\alpha = \alpha_0$ and the material with a set S has a modulus Es and is characterised by a model fibre network with $\alpha = \alpha_s$ then we may write:

$$\frac{\mathrm{Es}}{E\mathrm{o}} = \frac{\cos\alpha_s \sin^3\alpha_0}{\sin^3\alpha_s \cos\alpha_0} \tag{4}$$

If the length of the unit cell along the x-axis is $X\mathrm{o}$ at zero set and Xs at set S we have:

$$X\mathrm{o} = 2l\cos\alpha_0$$

$$\mathrm{Xs} = 2l\cos\alpha_s$$

$$\frac{S}{100} = \frac{(\mathrm{Xs} - X\mathrm{o})}{X\mathrm{o}} = \left(\frac{\cos\alpha_s}{\cos\alpha_0}\right) - 1 \tag{5}$$

The change in modulus, Es, with S as predicted by Equations 4 and 5 is shown in Fig. 4 (solid curves). The curves were generated assuming $\alpha_0 = 41^\circ$ for hide 1 and $\alpha_0 = 50^\circ$ for hide 2 and were fitted to the experimental data at $S = 0$ (where $E\mathrm{o} = 35$ MPa for hide 1 and 25 MPa for hide 2). Good agreement with the experimental data is obtained in both cases.

Alderson and Evans also consider two further modes of deformation. The fibril bending mode leads to an equation of the same form as Equation 4 above and predicts the same dependence of Es on α. The fibril stretching mode predicts the following relation:

$$\frac{\mathrm{Es}}{E\mathrm{o}} = \frac{\cos\alpha_0 \sin\alpha_0}{\cos\alpha_s \sin\alpha_s} \tag{6}$$

Curves generated from the use of Equations 5 and 6 cannot provide a good fit to the data for any selected value of α_0 (Fig. 7).

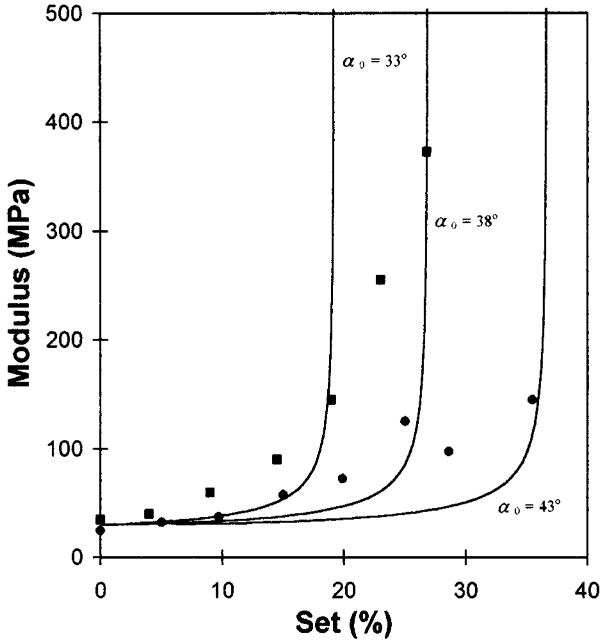


Figure 7 Theoretical predictions for tensile modulus (solid curves) arising from the microstructural model with fibril stretching using the values of α_0 indicated. The experimental data are the same as in Fig. 4.

5. Discussion

The stress-strain curve for the wet leather (Fig. 1) is markedly non-linear having a low slope at low strains which increases progressively as strain increases. Stress-strain curves of this shape are very characteristic of mammalian skin [8–11] and may be explained in two ways. In the first [9] it is assumed that the progressive orientation of collagen fibres along the strain axis leads to the observed increase in stiffness. The analysis developed for high strain fibre reinforced materials [12] provides a sound theoretical base for this approach. In the second [11] it is assumed that in undeformed skin the fibres are not straight. During straining more and more become taut thus causing a non-linear build up of stress. This approach has been underpinned theoretically by the work of Lanir [13] who assumed that the elastomeric elastin fibres present in skin [1] are linked to the collagen fibre network causing individual fibres to adopt a buckled ("wavy") conformation.

In spite of the theoretical work noted above we have chosen to use the approach of Alderson and Evans [7] to provide a microstructural model for dried leather. We feel that this is justified because in leather manufacture interfibrillar material present in raw skin is removed and so leather is not a genuine composite material with a matrix phase. In addition whilst elastin fibres may survive the leather production process [14] their elastomeric nature will be lost on drying since elastin will then be below its glass transition temperature [15].

The observation that the analysis based on fibril stretching does not fit the data very well (Fig. 7) implies that this mode of deformation was not the predominant one in the range of pre-oriented leathers examined. If a high enough degree of leather fibre alignment could be achieved then presumably the modulus of the material would approach that of dried collagen fibre. This latter modulus has been reported to be 10 GPa [16] which is an order of magnitude greater than the highest value reported here (0.375 GPa) for pre-orientated leather implying that although the leather had been pre-stretched some 26% the fibre structure was still some way from perfect alignment.

If it is assumed that fibril hinging (or fibril flexure) is the dominant mode of deformation then the model can successfully describe the data (Fig. 4). However in spite of this it is recognised that the fibre network depicted in Fig. 5a is a considerable oversimplification and in practice leather will have a distribution of fibre orientations.

There is evidence that during drying collagen fibres become adhered to each other [17] and this explains why the stress-strain curves for the dried leather are different in shape from wet leather. For leather dried under low strains the curve has an initial high slope which turns to a lower slope region at around 3% strain and then turns up again between 20% and 30% strain. For leather dried under higher strains a similar inflection at 3% strain is seen but the later upturn is absent. It has been observed [17, 18] that on first extension, there is a significant amount of acoustic emission as strain increases beyond ~3% which suggests that the adhesions start to become ruptured at this stage and so the material becomes softer.

Samples taken from the two hides were cut at different orientations (paralell to backbone line in hide 1 and perpendicular to the backbone line in hide 2). The mechanical properties of leather often display anisotropy [19] and this can be explained by local variations in the organisation of the undeformed fibre network. It therefore seems reasonable to assume that the contrasting behaviour we have observed between the samples from the the two hides (Fig. 4) are due to differences in initial fibre orientation with respect to the test axis requiring the use of different values of α_0 (41° for hide 1 and 50° for hide 2).

The high values of set obtained after drying under strain are consistent with the early work of Butlin [3] using finished leather. What is surprising perhaps is the relative stability of this set when the leather is re-wet and then dried. One hypothesis that may be advanced to explain why drying under strain produces high values of set is that the strained fibre network is held in its deformed configuration by means of the above mentioned adhesions which are postulated to occur within and between fibres during drying. Although it might have been expected that on soaking in water many of these adhesions would be softened sufficiently to allow gross relaxation of the fibre network this does not appear to be the case and that some inter and intra fibre connections made during drying survive re-wetting and are sufficiently strong to effectively hold the fibre network in its deformed state. This argument is supported by the work of Komanowsky [20] who concluded that drying allows new contacts between collagen molecules which were not present when the leather was fully wet. He stated that the consequent closeness of amino acid residues could lead to the occurrence of crosslinking reactions.

6. Conclusions

When leather is dried under uni-axial strain the dependence of its tensile modulus on the amount of strain applied during drying is markedly non-linear. A microstructural model based on a two dimensional fibre meshwork can describe this non-linear behaviour. The chemically modified collagen fibre network produced during leather manufacture is fixed in its deformed state by the formation of adhesions/crosslinks which occur during drying.

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