DEFORMATION, YIELD, RELAXATION AND
RECOVERY IN PARTIALLY PROCESSED LEATHER

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Disclaimer.

This thesis describes original work by David M Wright which was completed during the period of registration. No part of this work has been submitted for a higher degree at this or any other university.
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Abstract.

The aim of this research was to understand better the rheological behaviour of part processed leather in order to improve area yield.

Rheological behaviour was characterised in uniaxial tests by measuring the stress-strain relationship, the immediate and recovered set and stress relaxation. The influence of moisture content, time under strain and applied strain were determined. The effect of drying under strain was also explored. Results were interpreted using rheological and structural models.

It was found that for wet leather the relationship between applied strain and long term set is nonlinear. Moreover, below a critical strain no set is imparted. At this critical strain there is a change from a bending to a tensile mode of fibre deformation. Long term set only occurs in wet leather when collagen fibres are subject to tension. In wet leather, recovery occurs because collagen fibres return to their initial bent configuration.

The long term set of partially processed leather at low strains increases with decreasing moisture content because collagen fibres permanently deform due to the rupture of intra-fibre adhesions. Inter-fibre adhesions formed on drying result in a yield point on the stress-strain curve. At the yield point the adhesions rupture and the mode of fibre deformation changes from stretching between adhesions to bending. A model, which views the structure of leather as adhesion nodes, joined by segments of fibres, has been used to predict increases in the initial modulus caused by drying under strain, in terms of the recruitment of straight fibre segments between nodes.

When material is held under strain, there is a proportionate decrease in stress and increase in the immediate set, which is shown to be consistent with the Maxwell model. The two stage recovery of set is fitted to a multiple Voigt model.

A novel way of achieving area yield without loss of tensile strength or softness is suggested, in which the leather's structure is relaxed whilst remaining wet and is then fixed by drying rapidly under strain.
CONTENTS

1 INTRODUCTION .................................................................................. 10

1.1 PROJECT AIMS ................................................................................. 10
1.2 MECHANICAL OPERATIONS IN LEATHER MANUFACTURE .......... 10
1.3 MECHANICAL PROPERTIES OF LEATHER ......................................... 14
   1.3.1 STRESS-STRAIN CURVE .............................................................. 14
      1.3.1.1 THE FIBRE ORIENTATION MODEL ........................................ 15
      1.3.1.2 THE FIBRE RECRUITMENT MODEL ....................................... 15
   1.3.2 RELAXATION and RECOVERY IN LEATHER ............................... 16
      1.3.2.1 THE DEFINITION OF SET ...................................................... 16
      1.3.2.2 BUTLIN'S WORK ON SET ...................................................... 17
      1.3.2.3 DEFINITION OF RELAXATION MODULUS and REDUCED STRESS ...................... 20
      1.3.2.4 STRESS RELAXATION IN LEATHER ..................................... 21
   1.3.3 HIDE VARIABILITY ..................................................................... 23
   1.3.4 SUMMARY .................................................................................. 25

1.4 THE STRUCTURAL HIERARCHY OF COLLAGEN-BASED BIOMATERIALS ............................................................................. 25
   1.4.1 THE TROPOCOLLAGEN MOLECULE ........................................... 25
   1.4.2 FIBRILS AND MICROFIBRILS .................................................... 27
   1.4.3 FIBRES, FIBRE BUNDLES, AND THE STRUCTURE OF SKIN .......... 29

1.5 THE MECHANICAL PROPERTIES OF SINGLE FIBRES ...................... 30

1.6 HYDRATION STATES OF WATER AND ITS EFFECT ON THE MOLECULAR RELAXATION OF COLLAGEN .................................................. 34

1.7 PROJECT OBJECTIVES ..................................................................... 40

2 METHODOLOGY ................................................................................ 42

2.1 MATERIALS ................................................................................. 42
   2.1.1 STANDARD LEATHERS ............................................................. 42
   2.1.2 LEATHERS WITH ELASTIN REMOVED ....................................... 43
   2.1.3 ISOLATED GRAIN AND CORIUM LAYERS ................................... 45

2.2 SAMPLING .................................................................................... 45

2.3 DRYING, CONDITIONING, and MAINTENANCE OF CONDITION ........ 46
   2.3.1 CONDITIONING ........................................................................ 46
   2.3.2 SOLVENT DEHYDRATION .......................................................... 47

5
4.3.1 IMMEDIATE SET, STRESS RELAXATION AND THE MAXWELL MODEL ........................................... 83
4.3.2 THE REQUIREMENT FOR THREE AND FOUR ELEMENT MODELS .............................................. 85
4.3.3 THE EXTENSION TO MULTI ELEMENT MODELS ................................................................. 88

5 THE INFLUENCE OF STRAIN ........................................................................................................... 102

5.1 EXPERIMENTAL ....................................................................................................................... 102
5.2 THE EFFECTS OF STRAIN ON SAMPLES OF STANDARD THICKNESS ........................................ 105
  5.2.1 VARIATION OF SET WITH APPLIED STRAIN ..................................................................... 105
  5.2.2 DEPENDENCE OF STRESS AND RELAXATION ON APPLIED STRAIN ................................. 107
  5.2.3 TOPOGRAPHICAL VARIATION OF THE SHAPE OF THE STRESS-STRAIN CURVE .............. 109
  5.2.4 THE VARIATION OF STRESS, RELAXATION AND SET WITH APPLIED STRAIN USING MATERIAL FROM ALTERNATIVE SAMPLING POSITION (NP) ........................................ 111
  5.2.5 THE EFFECTS OF ELASTIN FIBRE REMOVAL ..................................................................... 113
5.3 THE EFFECT OF STRAIN ON PARTIALLY PROCESSED LEATHER OF STANDARD THICKNESS IN COMPARISON WITH ITS EFFECT ON ISOLATED LAYERS OF GRAIN AND CORIUM .......................................................... 114
  5.3.1 STRESS-STRAIN BEHAVIOUR .......................................................................................... 114
  5.3.2 CHANGES IN LATERAL DIMENSIONS WITH APPLIED STRAIN ........................................ 116
  5.3.3 RELAXATION .................................................................................................................... 117
  5.3.4 THE RECOVERY IN GRAIN AND CORIUM IN COMPARISON TO STANDARD THICKNESS MATERIAL ............................................................................................................... 119
    5.3.4.1 WET MATERIAL .......................................................................................... 119
    5.3.4.2 DRY MATERIAL .......................................................................................... 121
  5.4 DISCUSSION ............................................................................................................................ 122

6 DRYING UNDER STRAIN .................................................................................................................... 138

6.1 EXPERIMENTAL ........................................................................................................................ 138
  6.1.1 DRYING STRIPS OF PARTIALLY PROCESSED LEATHER UNDER STRAIN .......................... 138
6.1.2 CUTTING AND TESTING SAMPLES FROM STRIPS DRIED UNDER STRAIN ........................................... 140

6.2 RESULTS ........................................................................................................................................... 142
6.2.1 THE SET RESULTING FROM DRYING UNDER STRAIN .............. 142
6.2.2 THE EFFECT OF DRYING UNDER STRAIN ON THE STRESS STRAIN CURVE ........................................ 143
6.2.3 THE EFFECT OF SOAKING BACK ON THE STRESS STRAIN CURVE ............................................... 145
6.2.4 RECOVERY OF SAMPLES DRIED UNDER STRAIN AFTER AN APPLICATION OF A FURTHER 10% STRAIN .............. 147
6.2.5 STRESS RELAXATION OF SAMPLES DRIED UNDER STRAIN AFTER AN APPLICATION OF A FURTHER 10% STRAIN .............. 148

6.3 DISCUSSION ................................................................................................................................... 149
6.3.1 THE ROLE OF WEAVE ANGLE CHANGES .............. 151
6.3.2 PREDICTIONS OF A NODE FIBRIL MODEL .............. 153
6.3.2.1 THE RE-ENTRANT NODE FIBRIL MODEL AND ITS APPLICABILITY TO LEATHER .............. 153
6.3.2.2 THE NON-RE-ENTRANT NODE FIBRIL MODEL AND ITS APPLICABILITY TO LEATHER .............. 154
6.3.2.3 THE ZERO NODE SIMPLIFICATION .............. 155
6.3.2.4 MODES OF FIBRIL DEFORMATION .............. 156
6.3.2.5 RELATIONSHIP BETWEEN FIBRIL ANGLE AND STRAIN .............. 158
6.3.2.6 PREDICTIONS OF ZERO DIMENSION NODE FIBRIL MODEL .............. 158
6.3.2.7 COMPARISON OF THE PREDICTION OF THE NODE FIBRIL MODEL WITH EXPERIMENTAL OBSERVATIONS .............. 159
6.3.2.8 THE RELATIVE IMPORTANCE OF BENDING AND STRETCHING DEFORMATION MODES .............. 163
6.3.3 MODELLING THE HIGH STRAIN MODULUS .............. 166
6.3.4 EXPLANATION OF RELAXATION AND RECOVERY FOLLOWING APPLICATION OF A FURTHER 10% STRAIN .............. 169
1 INTRODUCTION

1.1 PROJECT AIMS

This research investigated the rheological properties of partially processed leather in order to develop a comprehensive understanding of how leather responds to those mechanical operations used in its manufacture. The main focus was on those aspects of rheology and processing that may be related to area yield. Optimising area yield is of prime importance to the tanner since raw hides and skin are bought by weight and finished leather is sold by area. Maximising area yield means maximising profit. This project has therefore concentrated on how the nonlinear viscoelastic properties of leather relate to its plasticity. A major theme involved an attempt to interpret the plasticity of leather in terms of its microstructure at both fibre and molecular levels.

1.2 MECHANICAL OPERATIONS IN LEATHER MANUFACTURE

Mechanical operations in leather manufacture fall into two categories:

i. Operations, such as wet drumming, that use mechanical action to speed up either the removal from or penetration of substances into a hide. These processes are not intended to change directly the properties of the material by the application of mechanical stress. Indeed in some cases the intention is to try to minimise stress as for example during liming when slow drum speeds are used because the alkali swollen hide is fragile;

ii. Operations, such as staking and setting out, which apply
deliberate mechanical stress to alter the structure and physical properties of the final leather;

Many of the latter processes are believed to influence area yield. However, mechanical operations that affect area yield also influence mechanical properties such as strength and softness. Tight toggle drying of leather may improve yield, but gives the leather a "boardy" feel. Staking may result in increased softness and a gain in area but over staking results in a looser structure with a lower tensile strength [HEIDEMANN(1993), COVINGTON and ALEXANDER].

Typical results from a technological investigation reported by SYKES on the area changes that occur during processing after the leather has reached the wet blue stage of manufacture are shown in figure 1.1. The leather, after removal from the tanning drum is dripping wet (about 70% moisture wet weight basis^). The cheapest and fastest way of removing this water is to squeeze it out using the samming operation. A typical hydraulic samming machine applies a compressional load to the leather by squeezing it between two felt-covered rollers whilst simultaneously applying uniaxial strain to the leather using a third blunt bladed slicker roller. The slicker roller has two helical blades with opposing pitch directions that meet half way along the length of the roller in a "V" arrangement [SHARPHOUSE]. The "V" bladed roller, figure 1.2, is a common feature of many machines used in leather manufacture including, as well as samming, shaving, setting and fleshing machines. The applied strain depends on the pitch of the helix and the speed of rotation of the blade.

^All moisture contents are, unless otherwise stated, quoted on a wet weight basis. Appendix III shows how to convert between this basis and a dry weight basis often quoted in other studies.
Figure 1.1
Percentage area (relative to trimmed weight at start) of a pack of wet blue hides during mechanical operations in leather manufacture according to SYKES
a) Pack average, b) Pack maximum c) Pack minimum
Figure 1.2
a) The "V" bladed roller [SHARHOUSE] b) The arrangement of roller in a typical setting machine [JARRETT and SYKES].

Figure 1.3
The pin action of the CARTIGLIANO Staking machine
The setting machine flattens out the naturally barrelled shape of leather and is believed to increase area yield. JARRETT and SYKES showed that area strains as high as 40% are applied in a typical setting operation but that after a period of 5 minutes the typical area increase has dropped to 10%. The mode of operation of the setting out machine is similar to the samming machine and in modern machines these two operations are combined. Little information is published regarding the optimum rotational speed of the rollers, pitch of the helical blade or hydraulic pressures involved (typical loads applied to the rollers of the samming machine at the British School of Leather Technology (B.S.L.T) are about 10 tonnes). Machine manufacturers are unforthcoming with this type of information and often say it is the job of the tanner to determine the required settings on a machine for the particular raw material.

After samming and setting, the moisture content of leather drops to around 50%. The area gained in samming and setting out is lost during the period in which drying occurs figure 1.1. This loss is due to both viscoelastic recovery and shrinkage which is a direct result of drying. In this investigation the variables, moisture content and recovery time, are investigated independently. Area increases again when the leather is conditioned for staking. Conditioning is often done either by spraying with water or packing the leather in damp sawdust. In this way a moisture content around 35% is achieved.

In the staking process leather is subjected to cyclic stresses principally to soften the leather and even out differences in mechanical properties due to hide variation. SHARPHOUSE has reviewed the methods of staking. The "Molissa" and "Cartigliano" staking machines have a conveyor which feeds the leather between two parallel plates vibrating with a typical frequency of ~10 Hz in the direction perpendicular to plane of the leather. Pins
are attached perpendicular to the surface of the lower and upper plates of the "Molissa" staking machine. The lower plate of the "Cartigliano" staking machine contains recesses into which the pins attached to the upper plate vibrate (Figure 1.3). The resulting geometry of deformation is similar for both machines. Namely, a combination of bending and multi-axial straining. In some recently introduced cartigliano machines, the plates have a rocking motion in the plane parallel to the surface of the leather which move the sheet of material through the machine. The Slocomb staker is often used in conjunction with a vibrational staking machine to tighten the loose fibre structure in the belly and flank regions by applying uniaxial strain to the leather.

In nearly all mechanical operations the leather is only subjected to stress for a short time. For example, with the three roller arrangement each part of the leather is only pinched along the line of contact of the rollers for less than a second. In fact HEIDEMANN (1993) calculates that with a feed through rate of 40 m min⁻¹, as is often used, the nipping pressure is only exerted for about 0.1 s. This calculation is based on the fact that, at anytime, the broadest width of material pinched along the line of contact between the rollers is roughly 5 cm. This is calculated from the roller diameters and the thickness of the material.

The time taken to feed hide through the Cartigliano staking machine at B.S.L.T is roughly 20 s and this machine is approximately two metres long. Therefore, any portion of a two metre long bovine hide can at best be under cyclic deformation for 20 s and it is only under the maximum deformation exerted by the cyclic action of the pins for a very small amount of time. The only operation in which the leather is under long term mechanical stress is toggle drying.
1.3 MECHANICAL PROPERTIES OF LEATHER

The previous section emphasised that partially processed leather with various moisture contents is subject to a range of deformations. But how does the material respond to the deformation? Previous work on the rheology of leather is now reviewed to establish how well this question has been answered. In particular the extent to which the stress-strain, stress relaxation and strain recovery of leather has been characterised is assessed. In addition, some of the concepts used to describe the experimental results reported in this investigation are introduced. Also, outlined are the simple models accepted as descriptions of the stress-strain curve.

1.3.1 STRESS-STRAIN CURVE

ATTENBURROW recognised that in general the tensile stress-strain curve for leather is "J" shaped. A typical "J-curve" for finished leather has three discrete regions: figure 1.4

i. The low strain, or toe, region of the curve where there is little resistance to deformation as characterised by the low modulus, defined as the local slope of the curve, is small;

ii. The region where the slope of the stress-strain curve is continuously increasing;

iii. The high strain region where the curve is linear and the modulus is large;

In this thesis the strain at which the slope of the curve changes from a low to high value is designated, the "turnup" strain. The "turnup" strain is defined as the intercept of the secant modulus fitted to the low strain region and the secant modulus fitted to the high strain (i.e. the intercept of the dotted lines in figure 1.4).

GRASSMAN and ZESCHITZ (1954) report that the stress-strain behaviour of dry leather (unlike polymeric, poromers and
Figure 1.4
A typical stress-strain curve for finished upper leather.
rubbers) is independent of temperature over the temperature range -70°C to 60°C. Closer analysis of their results for chrome tanned gloving leather suggests that the toe region is absent from a sample tested at -70°C despite the similarity in high strain modulus over the range -70°C to 60°C.

According to Atttenburrow the two accepted models that describe the "J-curve" are the fibre orientation model and the fibre recruitment model. In their simplest form both models treat the collagen fibre as an elastic element. These models may describe the nonlinear stress-strain curve but need to be modified to describe the viscoelastic behaviour of leather.

1.3.1.1 THE FIBRE ORIENTATION MODEL
The fibre orientation model is illustrated in figure 1.5 where the leather is represented by a trellis of elastic rods freely hinged at junction points. As the trellis or feltwork deforms, the fibres become progressively aligned along the direction of the applied strain. Hence, more of the resolved load is borne by the fibres. The stress-strain curve for leather using this model can be described by a cosine curve. The model in figure 1.5 is a two dimensional simplification. In reality the fibres have an angular distribution with respect to the applied strain. A more realistic model is conceivable consisting of layers of trellises with different orientations. Mitton originally developed this model for leather to explain why the extensibility of leather was at least twice the elongation to break of the individual fibres.

1.3.1.2 THE FIBRE RECRUITMENT MODEL
The fibre recruitment model is illustrated in figure 1.6. The initial number of slack fibres decreases as the strain increases and consequently the resistance to deformation increases because the number of taut load bearing fibres increases. Kronick and Buechler (1986) found that the variation in the elastic component
Figure 1.5
The fibre orientation model

Increasing Strain
Figure 1.6
The fibre recruitment model

Increasing Strain
of the dynamic tensile modulus of untanned wet calf skin over the range 0 to 20% strain could be predicted using the results of small angle light scattering tests to determine the distribution of taut and slack fibres. They used a simplified version of a model original developed by LANIR to model collagenous membranes under biaxial strain. KRONICK and BUECHLER(1988) later found that the predictions of the fibre recruitment model did not fit the variation in modulus recorded for solvent-dried calf corium.

1.3.2 RELAXATION and RECOVERY IN LEATHER

Information on the phenomena of stress relaxation and strain recovery in whole leather is limited. Investigations, carried out in the sixties and early seventies, were primarily concerned with the optimisation of the lasting process in shoe manufacture rather than with the optimisation of processes that control area yield in leather manufacture.

1.3.2.1 THE DEFINITION OF SET

Two definitions of percentage set are often used in the literature [ATTENBURROW].

i. The residual strain $S_{rs}(t) = e_r(t)$ is defined as the recovered length, $l(t)$, or area, $A(t)$, a time $t$ after release divided by the initial length $l_0$ or area $A_0$. Equation 1.1a for linear samples is the definition used in most of the experimental sections and discussions of this thesis. Equation 1.1b is the corresponding equation for area strain (or area gain) which is a quantity of considerable interest to the tanner.

$$S_{rs}(t) = e_r(t) = \frac{l(t) - l_0}{l_0} \times 100$$  \hspace{1cm} (1.1a)
\[ S_{rs}(t) = e_r(t) = \frac{A(t) - A_0}{A_0} \times 100 \]  

(ii) The comparative set \( S_{comp}(t) \) defined as the residual strain \( e_r(t) \) divided by the applied strain \( e_s \). This division results in equation 1.2a for the linear case where \( l_{max} \) is the maximum length of a sample during uniaxial deformation and equation 1.2b for the area case where \( A_{max} \) is the maximum area of a sample during multi-axial deformation. Equations 1.2 are useful when comparing the relative recovery after application of differing amounts of strain. Equation 1.2a is a definition preferred by many workers on single fibres probably because their experimental design measured the deformation produced by an applied load, i.e. a creep-recovery rather than a relaxation-recovery investigation.

\[ S(t)_{comp} = \frac{e_r(t)}{e_s} = \frac{l(t) - l_0}{l_{max} - l_0} \times 100 \]  

(1.2a)

\[ S(t)_{comp} = \frac{e_r(t)}{e_s} = \frac{A(t) - A_0}{A_{max} - A_0} \times 100 \]  

(1.2b)

1.3.2.2 BUTLIN'S WORK ON SET

BUTLIN investigated how the three variables of (i) time, (ii) initial moisture content and (iii) drying regime influenced the area set of finished leather. From a scientific viewpoint his experiments compounded the effects of time temperature and moisture content. Technologically, however his ideas revolutionised the shoe industry and led to a reduction in lasting times from months to hours. Using the SATRA dome plasticity apparatus (SLP 11) he applied a multi-axial area strain to circular samples for various durations. Unfortunately with this apparatus it is not possible to measure the load when
the strain is applied or the decay of the load during relaxation. In pilot experiments he showed that the recovery of a sample after having been strained continuously for four hours at 15% area strain was identical, within the limits of experimental error, to that of a sample held at 15% area strain for four separate one hour periods between which samples were unloaded and allowed to recover for five minute intervals. His inference that intermittent and continuous loading are equivalent was pivotal to the design of a full scale experiment that investigated the effect of initial moisture content and drying procedure on area set. This allowed him to overcome the problem of hide variability by allowing him to strain a sample more than once. However, in a nonlinear viscoelastic material, that does not comply to the Boltzmann superposition principle [WARD] such inference may not be entirely justified since each incremental loading step may not be assumed to make an independent contribution to the final deformation. Even BUTLIN's own results comparing the residual area strain produced by intermittently straining one sample with that produced by straining similar individual samples to a maximum load challenges the precision of an approach using intermittent straining. These results show that the residual area strain is linearly related to the applied area strain for continuous loading over the range 0 to 25%. However, intermittent loading produced higher residual strain, especially at strains greater than 15%, and a parabolic relationship exists between residual and applied strain. BUTLIN suggests that this deviation is observed because the intermittently loaded sample is cumulatively under load for a longer time than the continuously loaded samples.

In the same test BUTLIN also measured the pressure-area strain curve for dry leather. This curve had the familiar nonlinear "J" shaped form. The curve obtained by intermittently loading (with a periodic five minute recovery interval) a single sample to increasing values of strain is identical to the curve obtained
by continuously loading a number of similar samples to one load. He did not relate the load-area strain curve to residual area strain produced by multiaxial strain despite being able to characterise both experimentally.

**BUTLIN** showed that the set of uniaxially strained samples of finished chrome tanned leather conditioned at 20°C and 65% RH increased linearly with the logarithm of time under strain (for times under strain longer than 5 minutes), and that below 15% applied strain the comparative set increased with increasing linear strain below 15% applied strain. A similar relationship was found by him to exist between time and comparative area set.

**BUTLIN**'s results also show that after 30s the recovery of both area and linear samples was linear with the logarithm of time. Moreover, he observed that if a sample is under strain for a short period (1-120s) then recovery is almost complete after about two hours whereas for long periods (>16 hrs) under strain, recovery continues even after six months. All these results were obtained for one type of chrome tanned bovine leather at one moisture content and over a limited range of strains. No indication of the mechanical operations used to produce the leather is given by **BUTLIN** but it is safe to assume that the leathers had been set out or staked.

**BUTLIN** went on to investigate the influence of drying on leathers conditioned to a range of moisture contents. He achieved a slow drying rate by air drying samples in a conditioned atmosphere (20°C, 65 RH), intermediate drying rates by oven drying and, high rates by a stream of hot air. Re-analysis of his data shows that these drying rates differ by a factor of ten and depend on the initial moisture content. **BUTLIN**'s paper suggests that higher drying rates lead to higher set. Moreover, samples with higher initial moisture content had higher final sets after drying and reconditioning.

Before applying the harsher drying regimes all **BUTLIN** samples were strained and held in the conditioned atmosphere for a five
minute period. After which time the applied strain was removed and the set was measured after 30s of recovery. If this set data is replotted against the initial moisture content, recalculated on a wet weight basis, the relationship between area set after five minutes relaxation and initial moisture is linear, with the set increasing with decreasing moisture content.

HOLMES and WARD found that the area set for biaxially strained samples was greater for dry heat set samples than for those which were steam heat set. They argue that during steam heat setting moisture transferred from the air into the leather while the sample of leather is under strain, and therefore the presence of water plasticises the recovery.

WHITTAKER states that the energy(U) put into viscoelastic material when it is strained to a value of applied strain can be related via equation 1.3 to the hysteresis(H), calculated from the area between the load-elongation curve and the load-retraction curve.

\[ U = aH^b \] (1.3)

For chrome leather and poromerics the constant of proportionality a and the exponent b are 1.5 and 0.88 in the first strain cycle and 1.8 and 0.86 in second cycle. WHITTAKER concluded that leather and its substitutes have similar viscoelastic responses to applied strain. WHITTAKER also found that set and stress softening, defined as the difference between the energy put into a material in the first strain cycle and the energy put into a material in a second strain cycle, correlated for both leather and poromerics. Moreover, WHITTAKER found that leather shows a greater degree of strain softening and hence a larger amount of set.

1.3.2.3 DEFINITION OF RELAXATION MODULUS AND REDUCED STRESS

In polymeric material the relaxation modulus \( G(t) \) is defined (equation 1.4) as the stress \( \sigma(t) \) at a time \( t \) after the
application of an applied strain divided by that applied strain \( e \), [WARD].

\[
G(t) = \frac{\sigma(t)}{e} 
\]  

(1.4)

\( G(t) \) is used to compare relaxation in materials that do not deviate greatly from linearity.

The reduced stress \( R(t) \) is defined as the stress \( \sigma(t) \) at time \( t \) divided by the stress at the start of relaxation \( \sigma(0) \) (equation 1.5).

\[
R(t) = \frac{\sigma(t)}{\sigma(0)} = \frac{F(t)}{F(0)}
\]  

(1.5)

Since the reduced stress can be alternatively written as the load after time \( t \), \( F(t) \) divided by the initial load \( F(0) \) (assuming the area of cross-section remains constant during relaxation). Many workers prefer this definition to the relaxation modulus when comparing relaxations for biomaterials with non uniform specimen dimensions.

1.3.2.4 STRESS RELAXATION IN LEATHER

POPLEWELL and WARD found that the load in a dry linear sample strained to 25% strain decreased linearly with log(time) even after four days under strain.

SHESTAKOVA and KALININA looked at the stress relaxation of leather in an unusual way. A stress of 0.5 MPa was applied and produced a certain strain. This strain was then held and stress relaxation was recorded. In linear samples of calf skin leather, over a range of 20% to 50% moisture content their results show that reduced stress increased with decreasing moisture content. Despite applying a range of maximum stresses of 0.125 to 1 MPa to calf skin at a moisture content(20%), SHESTAKOVA and KALININA's results show that they obtained the same reduced stress \( R(3600)=0.65 \) after a fixed time. Over the whole range
of loads and moisture contents they related the reduced stress to time using equation 1.6 in terms of exponent m.

\[ R(t) = t^{-m} \quad \text{(1.6)} \]

According to GUY this equation should be modified to account for the fact that \( \sigma(t) - \sigma(0) \text{ as } t \to 0 \) and not \( \sigma(t) \to \infty \text{ as } t \to 0 \). Although, GUY claims to have fitted equation 1.7 to the stress relaxation of leather he neither quoted values for m nor reproduced the curves.

\[ R(t) = (1 + t)^{-m} \quad \text{(1.7)} \]

Both equations 1.6 and 1.7 need to be made dimensionally consistent by dividing t in these equations by a characteristic relaxation time \( \tau \). SHESTAKOVA and KALININA also found surprisingly good correlation between calf, goat and pig skin for the variation of reduced stress as a function of time, at a particular maximum load and moisture content (0.5 MPa, 20%). Using SHESTAKOVA and KALININA's unconventional loading procedure GOLAYA and EGORKIN investigated compressional relaxation in leather. They found that the compressional reduced stress at a fixed time after applying a pressure of 3 MPa was greater in dry chrome tanned leather \( R(3600) = 0.65 \) than in dry raw hide \( R(3600) = 0.6 \). Whilst, the long term compressional comparative set was higher in raw hide \( S_{\text{comp}}(1 \text{ day}) = 71.1\% \) than in leather \( S_{\text{comp}}(1 \text{ day}) = 56.2\% \). This observation was accounted for in terms of enhancement of the elastic behaviour of raw hide by supplementary bonds formed in the tanning process. All GOLAYA and EGORKIN's relaxation curves for leather under compression have a similar shape to those found for leather under tension by SHESTAKOVA and KALININA.
1.3.3 HIDE VARIABILITY

Skin has inhomogeneous and anisotropic tensile properties [FUNG]. Consequently, leather exhibits inhomogeneous and anisotropic tensile properties. Variation in tensile properties is associated with structural and compositional changes in the hide. ATTENBURROW cites the variation of angle of weave as the main factor influencing the topographical variation in the physical properties of leather. The thickness distribution of collagen fibres might also play a role. However, MENKART et al suggest that the variation in fibre properties around the hide are insignificant in comparison to inter-fibre interactions and fibre orientation. The uneven distribution of chemicals (e.g., fatliquor) [ALEXANDER et al(1993b)] must also be considered.

MAESER characterised the topographical variation of tensile strength, elongation to break, high load modulus and low load modulus of bovine leather. He measured these properties over a regular matrix of locations parallel, perpendicular and at a 45° angle to the backbone of the animal. He then represented these measurements by an ellipse. The length of a line drawn from the centre of the ellipse to its edge in any direction represented the magnitude of that property in that given direction. Both the tensile strength and high load modulus were found by MAESER to have similar positional and directional variation around a hide and show symmetry across the backbone of the animal. He states that the correlation found between low load modulus and elongation to break indicates that leather stretches the greatest amount in the direction which has the least resistance to early stretch. MAESER suggests that a greater degree of hide asymmetry is found for the low load modulus and elongation to break because a non-uniform slicking procedure has permanently deformed some areas of the leather. Re-examination of MAESER's results shows that the asymmetry was limited to flank, belly and neck regions which have greater anisotropy than the central regions of the hide.
Recently OSAKI et al have shown that the direction of a minimum in transmitted microwave (3.9 GHz) intensity corresponds to a preferred direction of fibre orientation (as determined by the analysis of electron micrographs) and to the direction of maximum tensile strength in a corium split. Unfortunately OSAKI et al did not locate the area from which their samples were taken with respect to the Official Sampling Position (I.U.P 2) and therefore their results cannot be compared with those of other workers.

For dry samples strained uniaxially to 9% strain parallel to the backbone MITTON and MILLAR made two contour maps of the residual stress one after 6 s and the other 24 hr relaxation. Correspondingly they recorded the comparative set after a day's recovery and after one week's recovery on contour maps. MITTON and MILLAR also produced similar maps for linear strips strained to 9% strain perpendicular to the backbone. Like POPPLEWELL and WARD, MITTON and MILLAR found the relaxation and recovery of leather to be highly variable with position although they did not speculate as to the reason for this variation.

By applying a distension of 5 mm on a lastomer, MITTON and MILLAR also produced contour maps of (a) the applied load (b) the load after 15 minutes relaxation and the resultant area set after one day's recovery. MITTON and MILLAR suggest that a better correlation could be found between the variation of the area stress relaxation parameters and the variation in comparative area set than between these parameters for the linear case. MILLAR et al had earlier used a modified lastomer to investigate the effect of positional variation and sample orientation on the stiffness of chrome tanned leather.

Recently LIN and HAYHURST (1993a) developed constitutive equations describing the nonlinear relationship between uniaxial stress and multi-axial strain in chrome tanned calf skin. Assuming an orthotropic symmetry they calculated the components
of the compliance tensor relating the stress to the strain at various locations around a side. In uniaxial tests on chrome tanned calf skin they found that the tensile component of the stiffness tensor $c_{11}$, in a direction parallel to the backbone, was higher than the component, $c_{22}$, in the direction perpendicular to the backbone. The relative difference between these quantities was smallest, i.e. the skin was least anisotropic, in the butt region. The greatest values of $c_{11}$ and $c_{22}$ were in the shoulder region of their skin. The smallest value of $c_{22}$ was for the belly region. LIN and HAYHURST (1993b) further showed that the components of the stiffness tensor derived from uniaxial test could be used to predict the results of biaxial tests. LIN et al also used the constitutive equations to predict the stresses involved in lasting.

1.3.4 SUMMARY
Leather is a nonlinear viscoelastic anisotropic inhomogeneous fibrous composite whose properties are influenced by the amount of water present. Although, finished leather has been well characterised comparatively few studies on partially processed leather have been undertaken.

1.4 THE STRUCTURAL HIERARCHY OF COLLAGEN-BASED BIOMATERIALS

Understanding of the mechanical properties of a composite material requires knowledge of its structure. Leather, derived from skin and other biological materials, has a complex hierarchy built up of structural units ranging from the molecular (-nm) level to the visible level. So to understand the rheology and the response to mechanical operations of these, an appreciation of structural influences is required.

1.4.1 THE TROPOCOLLAGEN MOLECULE
The primary structural unit for all collagen-based biomaterials
is the tropocollagen molecule. The collagen molecule consists of three polypeptide chains formed by amino acid residues. TYPE I collagen, the predominant fibre forming collagen, has two molecular chains designated \( \alpha_1 \) and \( \alpha_2 \). HEIDEMANN (1993) lists the amino acid sequence of a typical \( \alpha_1 \) chain, pointing out that every third amino acid group is the hydrophobic non-polar residue glycine. Thus the molecular chain is effectively a polytripeptide with the sequence Gly-X-Y repeating, (where X and Y are other amino acid groups). SILVER states that, with one exception, all amino acids found in connective tissue differ from each other only in respect of the side chain residue \( R \) attached to the alpha carbon atom. Figure 1.7a shows the generalised structural formula for such a amino acid residue. The important exception to this rule is proline with a ring structure incorporated into the main chain (figure 1.7b). Proline, not commonly found in other proteins, is responsible for the intrinsic stiffness of collagen [SILVER]. The rotation in the main chain motion of the polypeptide unit is unrestricted at a glycine residue but totally impeded at the proline or hydroxyproline residue [YANNUIS]. Conformational maps for the allowable dihedral angles, calculated from hard sphere models for the amino acid side groups including glycine, proline and hydroxyproline are reproduced by SILVER. The glycine residue may be regarded as a hinge and the proline and hydroxyproline groups make segments of the polypeptide chain rod-like. Such a hinge and rod model is the starting point for the statistical theories of rubber elasticity [WARD]. The rheological properties of hydrated cross-linked gelatin, an amorphous random assembly of such chains, conforms to this classical theory [FINCH and JOBLING].

However, in contrast to gelatin, collagen has another source of molecular stiffness, chain folding. In type I collagen two \( \alpha_1 \) helices and one \( \alpha_2 \) helix, all with a left-handed twist and approximately three residues per turn, fold together into a
Figure 1.7  
a) The generalised chemical structural formula of a polypeptide chain. b) the ring like chemical structure of proline. [SILVER]  

\[
\begin{align*}
\text{a)} & : H & - & \overset{\textabel}{\overset{\text{ROH}}{\text{R}}}_2 & H \\
 & \text{H-N} & - & C_\alpha & - & C-N & - & C_\alpha & - & C-OH \\
 & & & & & H \\
\end{align*}
\]

Figure 1.8  
Schematic diagram of the collagen triple helix consisting of three alpha polypeptide chains with a left handed twist which are coiled around each other in right handed twist. [FUNG]
right-handed superhelix (figure 1.8). This triple helix structure is held together by hydrogen bonding and its formation results in the reduction of energy. The coiled-coil superhelix state is energetically favoured over individual polypeptide chain state because it allows hydrophobic residues to pack at its centre and so reduce their contact with water [SILVER]. SILVER and HEIDEMANN have both reviewed the X-ray diffraction data on which this model is based. Recently, KING et al, using computer modelling techniques, calculated the free energy difference between the superhelix state and the polypeptide chain state to be \(-11 \text{ kJ mol}^{-1} \text{ residue}^{-1}\). KING et al's model of the superhelix fulfils stereochemical requirements and complies with experimental observations from X-ray diffraction and electron microscopy. FUNG states the pitch of the superhelix is 8.6 nm and that the amino acids within each chain are displaced by 0.291 nm with a relative twist of \(-110^\circ\) making the inter-glycine displacement 0.873 nm. The ends of tropocollagen molecule are non-helical and consists of 10-20 amino acid residues known as telopeptides. Natural cross linkages between superhelices involve these terminal ends [SILVER].

1.4.2 FIBRILS AND MICROFIBRILS

The next level of structural hierarchy is the fibril. All collagen composite systems are structurally similar at this level [BAER et al]. Although, some disagreement exists about how the molecules pack [SILVER].

Fibrils resemble smectic liquid crystals being highly ordered axially but disordered laterally [HULMES et al]. Figure 1.9 shows the distortion of hexagonal lateral packing into a pentagonal arrangement [HEIDEMANN (1993)]. However, with reference to equatorial X-ray diffraction patterns, internal energy considerations and evidence of electron microscopy HULMES et al
**Figure 1.9**
The distortion of the dense hexagonal lateral packing into a less dense five membered unit suggested by HEIDEMANN.

**Figure 1.10**
The accepted quarter stagger model of collagen molecules showing the gap and overlap regions in the so called smith microfibril [FUNG]
have recently reviewed the validity of more sophisticated multi
start spiral and concentric ring models for the lateral packing
of tropocollagen molecules. In these models, which are outside
the scope of this introduction, the tropocollagen rods are less
tightly packed than in a hexagonal lattice.

Longitudinally the tropocollagen molecules are staggered one
quarter the length of a molecule with respect to each other.
Evidence for the quarter stagger model came from transmission
electron micrographs of fibrils positively stained with heavy
metals that bind to the charged amino acid residues. SCHIMITT et
al found that the observed banding pattern repeated every 64 nm.
The repeat unit is commonly called the macro-period D and
correlates with a meridional reflection observed in small angle
X-ray diffraction patterns obtained from tendon. When ATP is
added to collagen solutions under acid conditions, tropocollagen
molecules aggregate to form segment long spacing
crystallites (SLS). The collagen molecules with these crystallites
align side by side, i.e. unstaggered. Staining showed these to
have a characteristic length of 300 nm. The model SCHIMITT et al
postulated did not account for a hole into which negative stain
accumulates, which was found by HODGE and PETRUSKA. The model
therefore had to be modified to account for this "Gap Zone". This
zone is 0.6 the length of the macro-period. Figure 1.10 shows the
lateral arrangement of the tropocollagen molecules in the
currently accepted model, the so-called Smith microfibril. KING
et al, again using computer modelling techniques, calculated the
free energy difference between the smith microfibril state and
the superhelix state to be -7.1 kJ mol⁻¹ residue⁻¹.

The existence and size of microfibrils, sub units smaller than
the fibril, is source of controversy. Acid swelling results in
subdivision of fibrils which is seen under the electron
microscope ALEXANDER et al (1993a). Moreover, SILVER states that
reflections from medium angle X-ray diffraction points towards
the existence a subunit containing 2, 4, 5 or 8 tropocollagen
units. Fibrils can range from 10-500 nm in diameter [PARRY and
CRAIG] and can be longer than 2000nm HEIDEMANN(1982).

1.4.3 FIBRES, FIBRE BUNDLES, AND THE STRUCTURE OF SKIN
Aggregation of fibrils is determined by soft tissue function
rather than energy minimisation. Tendon is assembled (figure
1.11) from the fibrils into fascicle and then into tendon. Figure
1.12 shows the schematic cross-section of bovine hide. In the
leather manufacturing process the hair and the epidermis layer
are removed along with the ground substance. In wet skin the
ground substance consists of hydrated proteoglycans which provide
a rubberlike matrix in which the collagen fibres are embedded
[SILVER].

Up to the fibre bundle level, skin fibres from the corium
layer resemble tendon in their structural hierarchy. Figure
1.13a [STANLEY] shows how the fibrils pack parallel to each other
to form a fibril bundle or fibre. Figure 1.13b [STANLEY] shows
fibril bundles/fibres pack in fibre bundles. The fibres in a
fibre bundle are twisted which HEIDEMANN(1982) suggests results
in a rope like coherence. He also suggests that individual fibres
in one bundle branch off and become incorporated into another
fibre bundle. This branching is analogous to the fringe micelle,
or switch board model used to describe the macromolecular
architecture of semicrystalline polymers [WARD] albeit at the
fibre level rather than the molecular level. This branching is
responsible for the inherent strength of the corium layer
[HEIDEMANN(1993)]. Across the grain-corium boundary there is a
progressive change from a coarse weave to a fine weave. In skin
this indistinct boundary layer also contains elastin fibres which
surround the hair follicles [HEIDEMANN(1993)]. The structural
elements that form the grain layer are about ten times
thinner(<10 μ in diameter [B.L.M.R.A] than the fibre bundles of
**Figure 1.11**
Annotated schematic diagram illustrating the structural hierarchy of tendon according to **BAER et al.**, and indicating at which level X-ray diffraction, electron microscopy EM, scanning electron microscopy SEM and optical microscopy are used to probe its structure.

**Figure 1.12**
A schematic diagram of the cross-section of Ox hide [SHARPHOUSE]
Figure 1.13
Scanning electron micrographs produced using a cryostage microscope showing the hierarchy of bovine wet blue [STANLEY]
a) fibril bundle constructed from many fibrils, b) the fibre bundle built up from many fibril bundles (fibres)
the corium (~100 μ [STANLEY]) in bovine hide. Moreover, structural elements forming the grain layer are of approximately the same diameter 5 μ as the fibre (or fibril bundles) [STANLEY] that intertwine to form the fibre bundles.

1.5 THE MECHANICAL PROPERTIES OF SINGLE FIBRES

It is interesting and helpful to compare leather with other biomaterials and also consider isolated leather fibres. Historically the material for studying collagen fibres has originated from two major sources; (i) tendon fibres and (ii) fibres teased from the corium regions of hide. The stress-strain curve for these fibres is “J” shaped. This curve has an initial low modulus and then turns up into a linear region of high modulus. MORGAN used equation 1.8 to describe the load elongation curves of tanned and untanned fibres. In equation 1.8, e is the strain, P is the load and a is a constant (~0.5). MORGAN found that the exponent n ranged from 0.62 to 0.90, depending on humidity, tannage, fibre length and fibre density.

\[ e = a P^n \]  

(1.8)

MORGAN found this equation was more applicable than the neo-Hookean equation (1.9) which had been derived for a uniaxial deformation of an affine rubber. In this equation, the force f required to produce the extension ratio, \( \lambda \), (1+e) where, e, is the applied strain) is related by the Young’s modulus, E,

\[ f = \frac{E}{3} (\lambda - \frac{1}{\lambda^3}) \]  

(1.9)
The classical theory Gaussian rubber must be modified to account for the continuous breaking and reforming of low energy cross links when rubber is strained. MORGAN (1960) states that equation (1.10), derived using a reaction rate modification and relates the strain, e, to the load P (a and b are constants), fits well to the deformation of textile fibres but does not apply to collagen fibres.

\[ e = a \tanh(bP) \]  

CONABERE and HALL fitted a Young’s modulus to the high strain portion of the stress-strain curve. Dry (conditioned to 70%RH) centimetre long chrome tanned fibres with an average diameter of 0.128 mm were found to have a modulus around 400 MPa and a breaking stress of 30 MPa. Similarly vegetable tanned fibres with an average diameter of 0.0937 mm had a higher modulus of 1.13 GPa and a breaking strength of 50 MPa. Chrome tanned fibres had higher elongation to break of 13.2% than vegetable tanned fibres with an elongation to break of 8.9%. CONABERE and HALL also investigated the hysteresis of fibres in load cycling experiments. They found that both chrome and vegetable tanned fibres retained 20% of the applied extension. Despite the range of extensions produced by a load of 40 g applied at a rate of 0.75 g s\(^{-1}\) (defined as the set) the percentage of extension permanently retained was directly proportional to the extension. Repeated extension to the same load produced no further increase in set. HALL (1951) later found that both creep and recovery in wet collagen fibres are rapid over the first 10 minutes but levels out after 100 minutes. After 200 minutes the permanent set in these fibres increased roughly linearly with increasing time under load.

RIGBY et al found that repeated straining of wet rat tail tendon to a strain below a “safe limit” of 4% produces an identical
linear stress strain curve if a recovery period of 10 minutes is allowed between each cycle. Progressive straining to increasing strains above the safe limit lowers the modulus of the linear portion of the stress strain curve and develops a "toe" region below 4% strain. However, if the strain remained below 20%, the tendon recovered its initial length even if strained above the "safe" limit. This yielding phenomenon which has been reported by other workers [BAER et al] is associated with a planar crimp of tendon which is visible under polarised light. Straining gradually removes the crimp pattern until above the safe limit the observed crimp changes irreversibly. Theoretical models relate tendon crimp to elastin fibres bridging the wavy course of the collagen fibres [SILVER]. No evidence has been reported for crimp in fibres teased from skin. Direct comparison of tendon and corium fibres is therefore questionable. Hence, tanned tendon is not the ideal material on which to model the properties of tanned leather despite the suggestion by ARUMUGAM et al (1995). Unfortunately teasing tanned fibres of the belly regions from hides may irreversibly change their properties.

ABRAHAMSON and WILLIAMS WYNN(1968b) reported a correlation of the bending modulus of leather fibres with their set. The bending modulus of vegetable tanned fibres ranged from 330 MPa for lightly tanned fibres to 540 MPa for heavily tanned fibres. The bending modulus of chrome tanned fibres was smaller and ranged from 170 to 230 MPa depending on the degree of tannage. Increasing the temperature from 3 to 55 C led to an increase in fibre stiffness while increasing humidity from 20 to 65 %RH caused a decrease in the stiffness of the fibres, as did increased lubrication with fatliquor. Chrome tanned fibres gave a higher degree of set than vegetable tanned fibres. Heavily tanned fibres gave lower set than lightly tanned ones. Increased lubrication by fatliquor reduced set whereas higher testing temperatures resulted in higher set. Moisture content over the range of humidities that they used did not affect the set.
ABRAHAMSON and WILLIAMS-WYNN (1968a) also measured the frictional coefficient, \( \mu \), of leather fibres over metal and leather mandrels but their results were contradictory. Against metal \( \mu \) decreased with increasing humidity and lubrication. However, over a leather mandrel \( \mu \) increased with increasing moisture and oil content. ABRAHAMSON and WILLIAMS-WYNN (1968a) attribute the latter to the softer fibres being able to bed deeper into the leather mandrel gripping it more firmly. They suggest that this bedding is less likely to occur in inter-fibre friction and so \( \mu \) for fibres should decrease with increased moisture and lubrication. Increasing temperature was found to decrease \( \mu \). Type and degree of tannage had little significant effect.

DILLON et al compared the properties of vegetable tanned and untanned hide fibres in the wet (immersed in water) and dry (condition at 65\%RH) state. Tanned fibres have lower failure tenacity (load/linear fibre density) and extensibility than untanned fibres. In the wet state tannage had negligible effect on the ultimate fibre properties, wet fibres being weaker and less extensible than dry. Tanning had no significant effect on tensile modulus. The untanned fibres had a toe region up to 3\% strain associated with the alignment of more primitive structural units. The tanned fibres had a linear tenacity-strain curve to about 20\% strain at which there was a pronounced yield before rupture. This yield was less pronounced in untanned fibres. Dry tanned fibres exhibited less hysteresis and set than dry untanned fibres. RAJARHAM et al attributed a lack of hysteresis in centimetre long fibres, cycled to 2\% strain, to the absence of any internal fibre friction. Increasing hysteresis with increasing fibre length was ascribed to an increase in the number of free fibril ends whose slippage resulted in frictional energy loss. Similarly , hysteresis in one centimetre long fibres above 3\% strain was attributed to molecular slippage at the fibril level. RAJARHAM et al postulated that the number of load bearing
fibrils decreases as the fibre length increases so the effective crosssection of the fibre decreases and so the breaking stress of the fibre decreases, a fact first observed experimentally by MORGAN and MITTON in raw fibres shorter than a centimetre. From this review it can concluded that leather fibres themselves have non-linear viscoelastic properties and that these properties are highly dependent on moisture content. Also, tannage and fatliquor influence the mechanical properties of individual leather fibres.

1.6 HYDRATION STATES OF WATER AND ITS EFFECT ON THE MOLECULAR RELAXATION OF COLLAGEN

As is the case for many biopolymers, water greatly influences the mechanical properties of leather and leather fibres. The following review discusses how the rheological properties of collagenous biomaterials, those closely related to leather, are influenced by the presence of water. The review also emphasises that changes at the molecular level cause macroscopic changes in the mechanical properties in biomaterials. The approach described by KOMANOWSKY(1992) is to infer similarity between the influence of water on the physical properties of collagenous biomaterials and the influence of water on the physical properties of leather. Unfortunately, the following three factors complicate direct comparison:

i. The influence of tannage;
ii. The presence of fatliquors;
iii. The absence of other substances, e.g. protoeglycan, from leather that are present in collagenous biomaterials such as skin;

In biomaterials there are three types of water; (i) free, (ii)bound, and (iii)structural water [SLADE et al]. A commonly
held view, [LANDMANN] is that free water can be physically squeezed out of macroscopically sized pores in the leather by the tanning process. Although, little scientific data is available to support this statement. Free water is lost in the initial stages of drying. KOMANOWSKY(1992) argues during the constant rate drying period capillary suction transfers water into the smaller interfibrillar spaces. Structural contraction occurs due to the removal of the water film covering fibres and fibre bundles. The driving force behind this shrinkage suggested by KOMANOWSKY(1992) is the reduction of surface area. KOMANOWSKY(1992) also suggests that shrinkage is limited by the structural rigidity of the material. The differential scanning calorimetric (DSC) results of HALY and SNAITH indicates that free water exists within collagenous rat tail tendon when the moisture content is greater than 50% on a wet weight basis. The distinction between bound and free water is not clearly defined. BIENKIEWICZ(1983) lists seven different experimental definitions. An operational definition is suggested by NOMURA et al in which bound water has measurably different properties from bulk water as determined by the same experimental technique.

Water can be bound by either chemical or physical constraints. For example, water can be physically confined by the capillary forces experienced in microscopically sized pores. A second slower rate of structural collapse on drying (during the first falling rate drying period) is associated by KOMANOWSKY(1992) with the removal of water inside fibres. KOMANOWSKY(1992) estimates hydrostatic pressure of capillary water in the inter-microfibrillar spaces to be 2 MPa. The capillary mechanism could be an explanation for the depression in the melting point of water observed in rat tail tendon by HALY and SNAITH below 50% moisture content. KOMANOWSKY(1992) associates the removal of water from the gap zone with the second falling rate drying period. KOMANOWSKY(1992) calculates a relative humidity, of 94%RH
that is in equilibrium with the hide material where all the water has been removed from the "Gap Zone". The "Gap Zone" can be regarded as a collapsable reservoir (like an old fashioned gasometer) supplying water to the intermolecular capillaries. KOMARSKY (1992) argues that as water is removed from the "Gap Zone" the telopeptides on the ends of the collagen molecule move to fill the void and eventually molecular movement and alignment occurs. Evidence of further structural collapse during drying was provided by worker using X-ray diffraction. ROQUÈ and BEAR found the D period (Macroperiod) and the intermolecular distance of rat tail tendon fell off below 35% moisture. HEIDEMANN and KELLAR discovered that for cow hide powder the intensity of the reflection corresponding to the intermolecular spacing has a maximum close to 33% moisture. They infer from this result that the structure of the microfibril is most ordered at 33% moisture. A critical moisture content of 35% is suggested by other experimental evidence which includes measurements of dielectric strength [SHINYASHIKI et al], sonic velocity [CUSACK and LEES] and Nuclear magnetic resonance signal [MRBEVILSHVILI and PRIVALOV].

Using dynamic mechanical thermal analysis (DMTA) NOMURA et al investigated interaction between collagen and water in human dura membrane. The relaxation spectra observed were similar to those for various types of tendon reported by BAER et al (human diaphragm tendon), CHIEN and CHANG (Rat Tail Tendon) and STIFANOU et al (steer tendon collagen). They measured both the logarithmic decrement of a torsional pendulum with a frequency around 1Hz and torsional rigidity.

NOMURA et al deduced that within the 35-60% moisture region the water behaves as a filler from the following observations:

i. Above 35% moisture the relative rigidity decreased almost to zero as the temperature was raised from 90K to ambient;

ii. The rigidity, at any given temperature, falls linearly to
its minimum at around 35% moisture content as the moisture content is reduced from 60%;

Below 35% NOMURA et al's results show that the stiffness increases with decreasing moisture content to a maximum at 0% moisture for samples at 270K and at 20% moisture for samples tested at 150K. For samples at 150K once this peak is reached the rigidity again drops until all water is removed from the sample. PINERI et al suggest that similar changes in rigidity modulus over the range 20-35%, which they associated with a glass transition moisture, has two possible origins, (i) fixation of water in the "Gap Zone" region or (ii) the fixation of water molecules between microfibrils by one hydrogen bond.

The variation of relative rigidity with moisture content found by NOMURA et al for samples tested at 270K compares well with the torsional rigidity variation measured by MITTON for leather fibres tested at ambient temperatures (figure 1.14). There is no appreciable rigidity until the moisture content falls below 35% moisture on a wet weight basis and then there is an increasingly rapid rise in relative torsional rigidity reaching a maximum value approaching zero moisture.

NOMURA et al identified three structural relaxation peaks for collagen; one peak associated with freezable water only found in samples with high moisture content, and two other peaks that predominated at lower moisture contents which they labelled $\beta_1$ and $\beta_2$. Figure 1.15 compares the variation of the glass transition temperature $T_g$ with moisture content found for collagen by BATZER and KEBBICH using DSC, to the variation with moisture content of the relaxations $\beta_1$ and $\beta_2$. Within the range 20-35% moisture $T_g$ (curve a) and the $\beta_1$ transition temperature $T_{31}$ (curve b) are close. Hence, the $\beta_1$ transition dominates relaxation within this range. Above 35% moisture $T_{31}$ remains constant as the moisture content increases whilst $T_g$ continues to drop with increasing moisture content. Below 15% moisture $T_g$ rises more
**Figure 1.14**

Variation of torsional rigidity with moisture content found by MITTON for leather fibres.

![Graph showing the variation of torsional rigidity with moisture content.](image)

**Figure 1.15**

Comparison of variation with moisture content of a) the glass transition temperature found by BATZER and KREBICH using DSC to b) The Beta 1 and c) Beta 2 relaxations found by NOMURA et al.

![Graph showing the variation of temperature with moisture content.](image)
rapidly than \( T_p \), as the moisture content drops. The \( \beta_2 \) transition temperature \( T_{p_2} \) (curve c) is constant above 20% moisture and rises below 20% with decreasing moisture content with this rise being most rapid below 7% moisture. NOMURA et al state that the peak intensity of the \( \beta_2 \) relaxation is not moisture sensitive whereas, the peak intensity of the \( \beta_1 \) relaxation increases rapidly to its maximum value at 30% moisture content and diminishes at a slightly slower rate as the moisture content increases above 30%. Thermodynamically a glass transition manifests itself as a second order change in the heat capacity of a material, i.e. produces a change in the base line of the DSC thermogram. Such changes may be obscured by first order changes such as the melting and freezing of ice. Therefore BATZER et al may have observed a single relaxation made up from contributions from \( \beta_1 \) and \( \beta_2 \) relaxations observed by NOMURA et al.

Between 23% and 37% moisture HALY and SNITH found in rat tail tendon that although water froze its enthalpy and temperature of fusion were different to that found for bulk water. Below 23% moisture they found that there was no freezable water. PINERI et al suggest that below a critical moisture content of 20%, water associates more strongly with the collagen molecule involving itself in two or more hydrogen bonds.

BIENKIRWICZ(1990) suggests that the most tightly bound water is bound inside the triple helical structure of the tropocollagen molecule by three hydrogen bonds involving hydroxyl groups of hydroxyproline and is detectable by NMR. Removal of this water would destroy the triple helix resulting in denaturation of the collagen [KOMANOWSKY(1990)]. PINERI et al have calculated the fixation energy of this water to be greater than 7.5 kJ mol\(^{-1}\). This water contributes less than 1% of the total moisture content. The next most tightly bound water, 1-5%, is inter-peptide water and participates in a "water bridge" with two
hydrogen bonds. BIENKIEWICZ (1990) illustrates the possible structure of such bridges that may or may not involve hydroxyproline. PINERI et al found that removal of this water is only partially reversible since the energy of desorption is 7.5 kJ mol$^{-1}$ while the energy of sorption is only 7.1 kJ mol$^{-1}$. PINERI et al imply that water molecules are unable to re-occupy the energetic positions they occupied in the native collagen. HALY and SNAITH denote this type of water unfreezable.

In summary there are six experimental distinguishable hydration states for collagen:

i. At 50% moisture content and above the free water is present and acts as filler inside macroscopically sized pores. Increasing the moisture content above 50% has negligible effect on the modulus;

ii. In the range 50%-35% moisture content water is confined by the microstructure of the collagen composite but not bound to the molecular structure and acts as a lubricant between fibrils;

iii. In the range 35%-20% moisture content the water is loosely bound to the microfibrils by only one hydrogen bond but increases the conformational entropy of the collagen molecule. The plasticising effect of water reduces the glass transition temperature;

iv. In the range 20%-5% moisture content water participates in two hydrogen bonds in forming bridges between microfibrils and triple helices. In this range water still occupies the gap zone. Addition or removal of this water causes drastic changes in the modulus. Such changes are probably due to the structural collapse of the microfibril resulting in steric hindrance of tropocollagen molecules by each other and so reducing the conformational entropy of the molecule;

v. In the range 5%-1% moisture content, water is double hydrogen bonded within the triple helix.
vi. Below 1% moisture content the only water present is triple hydrogen bonded between the polypeptide units of the triple helix.

1.7 PROJECT OBJECTIVES

This project has the following three objectives:-

i. To characterise the rheological properties of partially processed leather and determine the dependence of these properties on important physical parameters;

ii. To interpret these observations in terms of the structure of leather;

iii. To use the understanding gained from the first two objectives to make recommendations to the leather industry as how to optimise mechanical operation in leather manufacture;

Since this project was primarily concerned with maximising area yield, the approach used to achieve the first objective has been to relate directly the strain recovery and plasticity of leather to its stress-relaxation and stress-strain behaviour. This is probably the first investigation ever to take this approach for leather and certainly the first to examine partially processed leather in this way.

The remainder of this thesis is subdivided into six chapters. A brief description the content of each chapter is given below. Chapter 2 details the experimental procedure used to characterise the material.

The following three parameters are considered because of their known importance in respect of the rheology of leather and other biomaterials:-

i. Moisture Content;

ii. Time under strain;

iii. Applied Strain;
Unlike many previous studies of mechanical operations in leather manufacture and lasting these three variables are considered independently.

In Chapter 3 the role of moisture content is considered. The experimental results are discussed in terms of the hydration states of collagen and their effect on the viscoelastic behaviour.

In Chapter 4 the effects of holding leather for various times under strain is reported. Two fixed moisture contents were used. The results are discussed in terms of the rheological models which have been used to describe the viscoelastic and plastic behaviour of polymers and biopolymers.

In Chapter 5 the effects of holding leather under various applied strains for a fixed length of time are documented for leathers of two fixed moisture contents. Experiments exploring relative rheological contribution of the grain and corium layers and the role played by elastin in recovery are also presented. The results are then discussed in relation to existing and modified versions of structural models used to describe nonlinear behaviour in leather.

In Chapter 6 the effects of drying leather under strain on the physical properties are reported and discussed in terms of fibre orientation.

Finally in chapter 7, recommendations are made together with suggestions for further studies.
2 METHODOLOGY

2.1 MATERIALS

2.1.1 STANDARD LEATHERS

The major source material for this project was 10 wet blue hides from the Garston's Tannery\(^2\) in Liverpool: all the material used was from the same batch. The process is outlined in Appendix I. Initially twenty raw hides of similar area and approximate weight (42+/-1 kg) were selected from a pack of wet salted Friesian hides supplied by a Lisbon abattoir. Controlling the hereditary and husbandry of the cattle to the extent suggested by LAIGHT et al was not practicable. However, the possibility of hide to hide differences due to process variation and selection of raw material was reduced. The hides were split in the limed condition. LAIGHT et al suggest that this results in a uniform hide thickness giving better penetration and an even distribution of tannage. Lime splitting also reduced the variation in sample to sample thickness variation in tensile tests.

Since the original aim was to investigate the effects of mechanical stresses that occur during mechanical operations involved in the manufacture of leather the number of mechanical operations was kept to a minimum. Although, the leather was sammed, it was neither set out nor staked during its production. The wet blue leather was wrapped in plastic and stored in a sammed condition (i.e. at a moisture content of 50%), rather than dry since drying is irreversible \([\text{KOMANOWSKY 1992}]\). Fatliquoring

\(^2\)The Garston Tanning Co Ltd. King Street, Garston, Liverpool, Mersey side. L19 8EF, UK
was carried out, in the B.S.L.T tannery, immediately before use according to the process detailed in Appendix I. Attempts to store fatliquored wet blue hides resulted in visible bacterial deterioration.  

2.1.2 LEATHERS WITH ELASTIN REMOVED

Pancreatic trypsin fails to remove all the elastin from a hide during bating [ALEXANDER et al(1991)]. However studying leather from which elastin had been removed was desirable. To achieve the total digestion of elastin the use of bacterial enzymes with elastase activity, such as Pyrase (Novo Nordisk), has proved effective [ALEXANDER et al(1991)]. Thus, to obtain partially processed leather with a range of elastin degradation the Garston process was modified and partially carried out in house. The starting materials were two limed hides from Garstons.  

Upon arrival at the B.S.L.T the limed hide was placed in a holding lime (4 g l⁻¹) for two days before being processed. The hides were sided and one side from each hide was the control. The remaining two sides were both cut into four labelled segments. Each side was placed in a separate drum and delimed to pH 8.8-9 at 35 C for 1 hr, according to Garston’s process but without the addition of bating enzyme. ALEXANDER et al(1991) report a maximum in the activity profile for Novo’s enzyme at pH 9 and 35 C. Whereas, a lower pH of 8.5 is more common when bating with pancreatic bates [SHARPHOUSE].  

After the hour in delime the pancreatic bate 1% of PBW¹ was

¹One hide was rejected for this reason.

¹Novo Nordisk Bioindustries UK Ltd. 4, St Georges Yard, Castle Street, Farnham, Surrey GU9 7LW

²Hodson Chemicals Ltd PO Box 7 Chantry lane, Beverley, North Humberside HU17 0NN
added to the deliming liquor containing the control sides and the standard bating process was allowed to run for an hour. Two different offers of 0.1% and 0.01% Pyrase were added to the two drums each containing a segmented side. Segments were removed from both these drums at intervals, Table 2.1. Once removed each segment was then plunged into a vat of cold water (10°C) to arrest the enzymatic activity and held in that vat until all segments were ready to enter the pickling stage. From the pickle stage onwards the process was identical to that used at Garstons (Appendix I). The material was stored in a dripping wet state wrapped in a polythene sheet.

Elastin degradation was assessed using optical microscopy in which orcein was used to stain the elastin selectively. APPENDIX II summarises the process. A major problem was the disintegration of leather embedded in wax when microtoming sections thinner than 100 μ. This problem was overcome by allowing the solvent dehydrated samples to sit in molten wax for two hours to allow the wax to penetrate deeper into the structural hierarchy of the leather. Table 2.1 shows the assessment made from photomicrographs of the elastase treated material.
2.1.3 ISOLATED GRAIN AND CORIUM LAYERS
Predominately grain and predominately corium layers were produced by splitting using band knife splitter\(^4\) in the region of grain-corium junction. The leather was split in the same condition because at high moisture contents small deformations (which occur during splitting) had no permanent effects on the tensile properties. The isolated grain layer had a mean thickness of 0.8 mm and the remaining corium layer a mean thickness around 1.6 mm.

2.2 SAMPLING
Two common assumptions were made regarding positional variability \textsc{Mandel and Kanagy}. Firstly, hide symmetry was assumed across the hide backbone (i.e. each sample has its mirror image across the

\(^4\)Located at BLC leather technology centre.
backbone with identical physical properties). Secondly, the mechanical properties of leather were assumed to vary smoothly, and consequently, if the sample size was small, adjacent samples were regarded as identical. Most, but not all mechanical test samples were cut from the official sampling position (IUP/2). Within this region the mechanical properties of the hide are most consistent. For the hides obtained from Garstons Tannery this region was an area of 40 cm² located 5 cm from the backbone and 80 cm from the butt on each side of the backbone. Rectangular samples, 20 cm by 1 cm, were cut using a press knife. A unique code was marked on each strip indicating from which hide and side the strip was taken from and its location on that side.

2.3 DRYING, CONDITIONING, and MAINTENANCE OF CONDITION

2.3.1 CONDITIONING

Samples which were usually cut from sammed material were conditioned to various moisture contents. Samples with 67% moisture were obtained by soaking sammed material in distilled water for a period exceeding 8 hrs. Samples with 53% moisture content were obtained by mechanically pressing soaked material between samming felt material (the samming felt material had previously been conditioned at 65%RH and 20°C for one week) using a pressure of 400 psi (2.758 MPa) for 10 seconds. Before tensile testing these samples were allowed to recover for one week from this compressional load. Specimens with a moisture content of 20% were obtained by leaving sammed samples for at least one week in a conditioned room (65%RH, 20°C) to achieve equilibrium with the atmosphere. GRASSMAN and ZESCHIT (1965) have shown that chrome leather, like other porous natural materials, can take in over

This and other moisture contents referred to are on a wet weight basis.

46
a hundred hours to equilibrate in a given atmosphere. Three other moisture contents (35%, 13%, 11.5%) were obtained by conditioning samples containing 20% moisture over saturated salt solutions: Table 2.2. A large desiccator was the humidifying vessel containing saturated salt solution. Samples with a moisture content of about 5% moisture content were produced in a desiccator containing silica gel.

Each sample was weighed before and after tensile testing. Eventually after a period of recovery the samples were dried to a constant weight for 16 hrs in an oven at 100 C. The drying period was longer than that recommended by (I.U.C./5) because whole, rather than ground, samples were used with consequently less exposed surface area. Drying for a period in excess of 16 hrs resulted in further weight loss probably because of the evolution of less volatile components of the fatliquor.

The dried weight allowed the determination of the moisture content prior to testing, and an estimate of moisture loss during testing. Figure 2.1 curve(a) summarises the moisture content of partially processed leather calculated on a wet weight basis as a function of relative humidity. This curve is similar to typical curves for drying leather [BUCK, BIENKIEWICZ (1983), HEIDEMANN (1993)].

Table 2.2 The effect of conditioning partially processed leather over salt solutions

<table>
<thead>
<tr>
<th>Saturated Salt Solution</th>
<th>Relative Humidity/% at 20°C</th>
<th>Moisture/ % (on wet weight basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Acetate</td>
<td>20</td>
<td>11.5</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>32.3</td>
<td>13</td>
</tr>
<tr>
<td>Potassium Sulphate</td>
<td>95</td>
<td>35</td>
</tr>
</tbody>
</table>

2.3.2 SOLVENT DEHYDRATION

The method used to solvent dehydrate leather in this
Figure 2.1
Variation of moisture content (wet weight basis) with relative humidity a) Conditioned b) After one hour under test

Figure 2.2
Concentric cylinder assembly used to limit moisture loss or gain.
investigation was based on that developed by HEIDEMANN and RIESS to acetone dehydrate skin. They reduced the moisture content of wet skin to below 5% (on a dry weight basis) by immersing skin successively in five baths of acetone. Each bath contained the same volume of acetone as the volume of the skin. The samples were left in each bath for 24 hrs. HEIDEMANN and RIESS used densities to determine the water uptake of the acetone bath. Their results show that an hour would have been sufficient time to reach the point where a bath would not take up any more water. In this investigation only two baths of acetone were used. However, the volume ratio of acetone to fully saturated leather was 20:1. After 24 hrs immersion the weight fraction of water in the first acetone bath was 0.158. Following a 24 hr immersion in the second bath the weight fraction of water was 0.0428 and the resultant leather contained about 3% moisture on a wet weight basis. Following solvent dehydration the leather was aired off at ambient temperature inside a fume cupboard.

2.3.3 MAINTENANCE OF CONDITION
Before the test, during the test, and during recovery the moisture content of each sample was maintained near to a fixed value. All physical tests carried out done in a room controlled at 65%RH and 20 C. Samples conditioned to 20% moisture were maintained by leaving them in the room. Samples with 67% and 53% moisture content were sealed in polythene bags until tested. Samples with 11.5%, 13% and 35% moisture content were also sealed in plastic bags. As a precaution, these bags were kept in the humidifying vessel until immediately prior to testing. The hermetic seal was only broken immediately before loading a sample on the tensile testing machine. Preventing exposure of samples to the atmosphere of the conditioned room while drawing bench marks on samples and while loading and unloading samples from the jaws of the tensile testing machine was impractical. However, the time for these operations was less than two minutes. While on the
machine the condition of the strips was stabilised by enclosing
them inside two concentric plastic cylinders attached to the jaws
by "Blu Tac": figure 2.2. The cylinders did not form a hermetic
seal because the cylinder attached to the upper jaw had to move
freely past the cylinder attached to the lower jaw. Any
frictional force could have affected the measured load. This
assembly did not affect the recorded load. The assembly
stabilised the boundary layer of air around the sample and so
reduced both the water vapour uptake of samples conditioned below
20% moisture and water vapour loss of samples conditioned above
20% moisture. The moisture content of samples conditioned to 11%
and 13% moisture increased by less than 1% over one hour while
the moisture content of samples conditioned to 35% and 53%
mobility decreased by less than 1.5% over the same interval.
Unfortunately, the moisture content of desiccated samples
increased from 5% to 10% in one hour. Curve b in figure 2.1
reports the final moisture content plotted against the original
humidity. Saturated material was kept wet by spraying distilled
water at regular intervals. This spraying had negligible effect
on the recorded load. After testing all samples were resealed in
plastic bags to preserve their moisture content.

2.4 INSTRUMENTATION

Tensile testing was carried out using the Instron 1122 testing
machine in a conditioned room. This apparatus is a screw driven
machine capable of cross head speeds of up to 1000 mm min⁻¹.

2.4.1 GRIPS

A problem encountered in early plain strain pilot tests using
wide samples (15 cm by 5 cm) involved the slippage of the samples
from the grip plates. So measurement and application of strain
were inaccurate for these plain strain pilot experiments.
Fortunately, no significant slippage was observed when narrow (1
cm x 10 cm) samples were used. Absence of slippage was confirmed:--
i. by comparing the applied extension with the extension measured using a travelling cathetometer;
ii. by marking the material held in the grips with a broad silver marker and observing if this material became visible between the grips when the sample was under strain.

2.4.2 LOAD CALIBRATION AND ACCURACY
For loads up to the breaking load of the leather under test, a 5 kN load cell was used. This load cell was electronically calibrated, although, the calibration was confirmed using calibration weights. This load cell should measure loads down to within 100 N range. However, on this lowest range, the measurement of load was inaccurate, as a consequence of fluctuations in the load cell amplifier. A 50 kg load cell was therefore employed to measure loads down to the 100 g (\(-10\) N) range. With this load cell the Instron testing machine could only be calibrated with weights. The testing machine had to remain switched on for at least one hour before calibration to allow the components of the load cell amplifier to stabilise thermally, so as to minimise drift in the load reading.

2.4.3 DATA ACQUISITION
Two ways were used to record the load from the testing machine:--
i. using the dedicated chart recorder;
ii. via a 10-volt (voltage proportional to load) output from the machine. This output was connected via a 16 bit A-D converter (Strawberry Tree ACPC16) to an IBM 386 PC.
Originally, it was planned that the icon driven software (Labtech Notebook\(^1\)) used to collect the data would process the acquired

\(^{1}\)Laboratory Technologies Corporation, 400 Research Drive
Wilmington MA 01887 British agents Adept Scientific
Micro Systems, 6 Business Centre West, Avenue
data into a semifinished form. However, the amount of real-time analysis was limited by the rate of data collection. Therefore, the data was transferred following collection in an ASCII format to a spreadsheet environment (Quattro Pro\textsuperscript{\textregistered}). The collection rate could be controlled. A rate of 10 readings per second recorded the initial buildup of the load during extension, the rapid decay of load during the initial stages of relaxation, and removal of load during retraction. A higher collection rate was unnecessary because the response time of the Instron load cell amplifier was about 100 ms. A slower rate of one reading every 50 seconds recorded the remainder of the stress relaxation curve. The use of a chart recorder allowed the load elongation curve to be monitored and was used to determine immediate set.

2.5 SAMPLE GEOMETRY, BENCH MARKING, BENCH MARK MEASUREMENT

Standard tensile tests on leather (i.e. IUP/6) generally use dumbbell shaped samples to concentrate the stress along the central axis of the test piece. In this study 20cm by 1cm strips were used to increase the gauge length of the sample held between the two grips to 10cm. The aim was to optimise the accuracy of the set measurement. Moreover, in the dumbbell shaped specimen the strain distribution is not uniform thus making the measurement of strain less accurate.

On each strip two pairs of bench marks were drawn. One pair was separated by 10 cm which was the jaw separation at the outset of the test. The other pair was separated by 8 cm. These marks were drawn with a steel stencil which provided enough weight to flatten any waviness in the sample. The separation of these bench marks was measured using a travelling microscope. The latter

One Letchworth Herts SG6 2HB.

\textsuperscript{\textregistered}Quattro-Pro is part of the Perfect Office suite of programs now licenced by Novell Inc.
could measure distances to an accuracy of 0.04 mm. A piece of glass weighing about 100 g was used to flatten the sample during this measurement. The accuracy of the measurement of separation was not limited by the precision of the travelling microscope but by sharpness of the edges of the bench marks. The travelling microscope method was no more accurate than using vernier callipers with a precision of 0.1 mm. Moreover, the bench mark separation could be measured more quickly using vernier callipers. Therefore, the method based on the travelling microscope for measuring the separation of bench marks was dropped in favour of using vernier callipers.

2.6 TENSILE TESTING

2.6.1 THICKNESS AND WIDTH MEASUREMENT
To calculate the engineering stress, i.e. the force divided by the original cross-sectional area, a measure of the initial thickness and width of the sample strips was needed. In accordance with IUP/4, a standard thickness gauge which exerts a pressure of 0.05 MPa was used to measure the thickness to an accuracy of 0.01 mm. A period of five seconds was allowed to elapse before a measurement was made to allow the leather to comply to the compressional load. Even along the length of a twenty centimetre strip the thickness varied by as much as 10%. The thicknesses of samples conditioned to moisture contents other than 20% and 67% were measured inside the plastic bags. The bags had an invariable thickness of 0.05 mm that was subtracted from the measured sample thickness. The width of specimens was measured using vernier callipers to an accuracy of 0.1 mm. The sample width varied less than 0.2 mm from the width imposed by the press knife. However, the width of every sample was measured to confirm that it complied to this imposed width.
2.6.2 SAMPLE LOADING

To ensure accurate measurement of strain, individual samples were loaded between the grips of the testing machine such that the 10 cm bench marks coincided with the edge of the grip plates, which at the outset of the test were separated by 10 cm. However, so that no unintended strain was applied to the sample whilst being loaded on to the Instron the following procedure was used. The top portion of the sample was loaded between the upper grip plates and the upper grip tightened. The lower portion was allowed to hang free between the lower grip plates. The load reading on the tensile testing machine was then zeroed to account for the sample weight. The sample was then pulled straight between the lower grip plates without applying a measurable load (as indicated by the load monitor display of the testing machine) and the bottom grip tightened. For the experiments investigating the effect of moisture content, this procedure was further complicated by the concentric cylinder arrangement previously described which was used to maintain the moisture content of each sample. After the sample had been loaded, the concentric cylinders had to be attached to the grips and consequently the loading reading had to be zeroed to account for the weight of the upper cylinder and the "Blue tac" attaching the upper cylinder to the upper grip.

2.6.3 TESTING TO BREAK

Since a strip geometry was used in the relaxation and recovery tests in this investigation strips (20 cm by 1 cm, gauge length of 10 cm) were also used to determine the deformation over the whole range of strains to failure. This choice of test sample was made to elucidate the shape of the full stress-strain curve to break for strip samples. The viscoelastic parameters in this investigation are related to the shape of the stress-strain curve throughout this study. Dumbbell samples were not used because determination of the failure properties was of secondary
importance. Moreover, the dumbbell shape concentrates the stress along the axis of the sample and as does not to produce uniform strain distribution. A strain rate of 100% min⁻¹ was used in straining to failure.

2.6.4 RELAXATION AND RECOVERY TEST

The principal method of examining viscoelastic behaviour was a sequential stress relaxation and recovery test. This test can be described in terms of four stages.

Stage 1 Extension
The sample was extended at a fixed rate of 100% min⁻¹ to the required strain. The load build up was monitored using the tensile testing machine.

Stage 2 Relaxation
The sample was held at the required strain for a defined length of time while the decay in the load was recorded. During this time, the condition of the sample was maintained as closely as possible to its initial moisture content.

Stage 3 Retraction
The strain was removed at a fixed rate and the drop in load was monitored via the tensile testing machine. The strain at which the load dropped to zero was recorded and defined as the immediate set.

In early experiments, the load was removed at a strain rate of 20% min⁻¹ to facilitate the recording of immediate set from the digital extension readout on the Instron. In later experiments, it proved more practical to read the immediate set from the chart recorder using a strain removal rate of 100% min⁻¹.

Stage 4 Recovery
The sample was allowed to recover without physical restraint. The separation of the bench marks was recorded at intervals of time to determine the delayed set as a function of recovery time.
2.7 ACOUSTIC EMISSION

Acoustic emission signals from samples under strain were monitored with a sensitive piezoelectric transducer (Model R15/C, resonating at 150 kHz) attached to 25mm wide strips using a spring clip. These strips had a gauge length of 10 cm between the Instron jaws. A reliable acoustic coupling was achieved at the interface between the sample and the transducer using petroleum jelly smeared over the flat surface of the microphone. Signals from the samples under a test were analysed by the LOCAN system (on loan from the Physical Acoustics Corporation). This system was controlled using a 486 PC. A graphical format displayed a number of important parameters: e.g. the number of hits recorded over a fixed time interval as a function. A measure of the relative energy of acoustic pulses was given by the LOCAN system which it calculated from the ring down method [MILLER and McIntire]. The computer simultaneously recorded a voltage proportional to load signal from the Instron. A gain of 35dB and a threshold of 35dB were the most suitable amplifier settings for monitoring acoustic emission from partially processed leather. Thresholds below 35dB resulted in the LOCAN system picking up background vibrations.

16Physical Acoustics Corporation, Cambridge, CB4 5QH, UK
3 MOISTURE

This chapter considers the stress-strain behaviour, stress relaxation, set and recovery of part-processed leather in relation to its moisture content.

3.1 EXPERIMENTS

The results emerge from two similar matched side experiments. The first experiment relates the deformation, relaxation and recovery of conventionally dried partially processed leather to its moisture content (in the range 10-70%). The second experiment compares the mechanical properties of air dried samples with those of solvent dried samples over the range 5-35% moisture.

In the first experiment thirty-six 20 cm by 1 cm strips were cut from the official sampling position (O.S.P) of one side of tanned leather. Eighteen were cut parallel and eighteen cut perpendicular to the backbone. Three strips for each orientation were conditioned (as described in section 2.3) to 67%, 53%, 35%, 20%, 13.5%, 11.5% moisture content, loaded in the grips of the Instron testing machine and strained to failure at a rate of 100% min⁻¹. Similarly from the O.S.P on the opposite side thirty-six samples (assumed identical in rheological properties to the first set), were conditioned and subjected to a stress relaxation and recovery test as outlined in section 2.6.4. Each sample was strained at a rate of 100% min⁻¹ to 20% strain and held at that strain for 1 hr after which the strain was released at a rate of 20% min⁻¹. After removal of the applied strain the delayed set was recorded at increasing intervals; i.e. 2 minutes, 10 minutes, 1 hour, 1 day and 1 week, after each test.

In the second experiment the left hand side of the remainder of
the official sampling area, a 20 cm by 40 cm rectangle with its long axis parallel to the backbone, was solvent dried in acetone using the method described in section 2.3.2. The remainder of the right hand side of the official sampling area was air dried as a control. Forty strips were cut from the acetone dried material, twenty in the parallel direction and twenty in the perpendicular direction. The “mirror” of each strip was cut from the control air-dried material. Five strips for each drying procedure and each orientation were conditioned to each of the moisture contents 5%, 13%, 20%, and 35%. Again each sample was strained at a rate of 100% min⁻¹ to 20% held at that strain for 1 hr after which the strain was released at a rate of 20% min⁻¹ and after removal of the sample the delayed set was recorded at increasing intervals (i.e. 2 minutes, 10 minutes, 1 hour, 24 hours and 1 week) in the standard relaxation and recovery test.

3.2 RESULTS OF EXPERIMENTS

3.2.1 STRESS-STRAIN CURVES
Six typical stress strain curves are shown in figure 3.1, one for each moisture content, for samples strained parallel to the backbone. At first glance the curves appear have a typical “J” shape, discussed in chapter 1 section 1.3.1, found for many biological materials [SILVER, WAINWRIGHT et al., FUNG] and for many types of finished leather [ATTENBURROW, HEIDEMANN(1993), BIENKIEWICZ(1983)]. That is to say at small strains there is little resistance to tensile deformation and the modulus of the material is low but around 15% strain the slope of the stress strain curve increases markedly and turns up into a region above 20% strain where the curve is almost linear, except close to break where modulus falls as the curve turns over slightly. Similarly figure 3.2 shows that for the six typical samples strained perpendicular to the backbone the modulus is low below
Figure 3.1
Stress-strain curves to break for samples of partially processed leather with the following moisture contents a) 67%, b) 53%, c) 35%, d) 20%, e) 13%, f) 11.5% tested parallel to the backbone.

Figure 3.2
Stress-strain curves to break for samples of partially processed leather with the following moisture contents a) 67%, b) 53%, c) 35%, d) 20%, e) 13%, f) 11.5% tested perpendicular to the backbone.
25% strain after which point the stress-strain curve again turns up into a high modulus region. Again above this turnup region the stress-strain curve is linear.

In section 1.1.3.1 chapter 1 the strain at which the stress-strain curve turns up from the low modulus region into a high modulus region was defined as the "turnup" strain. This definition will be used in this thesis.

3.2.1.1 THE LOW STRAIN REGION AND YIELD

The curves shown in figures 3.1 and 3.2 show that moisture content has a significant effect on the shape of the stress-strain curves at low strains. Figures 3.3 and 3.4 indicate that, as the samples become drier, the slope of the initial stress-strain curve (i.e. between 0 and 2%) increases considerably. This influence is more clearly seen by plotting figure 3.5 the modulus against moisture content. This initial modulus was obtained by performing a linear regression fit on the stress-strain data between 1% and 2% strain (using a spread sheet written for a PC). The secant modulus was calculated using equation 3.1,

$$E = \frac{\sigma_2 - \sigma_1}{\Delta \varepsilon}$$  \hspace{1cm} (3.1)

where $\sigma_1$ is the stress at the lower strain value $e_1$ and $\sigma_2$ is the value of stress at the upper value of strain $e_2$ and $\Delta \varepsilon$ is the strain difference. This calculation was found to be as accurate a way of determining the modulus as opposed to the more time consuming linear regression analysis.

An order of magnitude change was recorded for the low strain modulus (figure 3.5) between the wettest and the driest samples. The only statistically significant difference between the modulus of the samples strained parallel and perpendicular to the backbone was found for the samples conditioned to 11.5% and 13%
Figure 3.3
Low strain regions of stress-strain curves for samples of partially processed leather with the following moisture contents a) 67%, b) 53%, c) 35%, d) 20%, e) 13%, f) 11.5% tested parallel to the backbone.

Figure 3.4
Low strain regions of stress-strain curves for samples of partially processed leather with the following moisture contents a) 67%, b) 53%, c) 35%, d) 20%, e) 13%, f) 11.5% tested perpendicular to the backbone.
Figure 3.5
Variation of low strain modulus with moisture content for samples tested a) Parallel, b) Perpendicular to the backbone
moisture. Both parallel and perpendicular low strain moduli show an exponential decrease in modulus with increasing moisture content.

Curve e on figure 3.3 is annotated to illustrate the definition of a yield point (characterised by a yield strain, $\varepsilon_y$, and a yield stress $\sigma_y$) as the point of intersection of a tangent fitted to the curve between 1 and 2% strain and the tangent fitted to the stress-strain curve between 3 and 8% strain. Figure 3.6 shows the dependence of yield strain on moisture content. Below 20% moisture yield strain is higher in the direction perpendicular to the backbone but at 20% moisture the yield strain is the same for both orthogonal directions within the limits of experimental error. Figure 3.7 shows that the yield stress decreases linearly with increasing moisture content and the yield stress is slightly higher in the parallel direction. Extrapolation of the line fitted through the experimental points of figure 3.7 indicates that the yield stress falls to zero around 53% moisture.

3.2.1.2 INTERMEDIATE AND HIGH STRAIN REGIONS

The intermediate strain modulus is defined as the slope of the stress-strain curve in the region just beyond the yield strain, i.e. between 3% and 8%. Whilst the intermediate strain modulus falls with moisture content (figure 3.8) the decrease is considerably less than that observed for the low strain modulus (figure 3.5). At low moisture content the intermediate strain modulus is one tenth of the low strain modulus. The high strain modulus was defined (chapter 1 section 1.3.1) was the slope in the linear region above the turnup strain but below the breaking strain. For the curves in figures 3.1 and 3.2 the slope in the region between 40 and 60% strain was used. The dependence of high strain modulus on moisture content is shown in figure 3.9 The variation of high strain modulus for parallel and perpendicular orientations is qualitatively similar. At about
Figure 3.6
Variation of yield strain with moisture content for samples tested a) parallel and b) perpendicular to the backbone.

Figure 3.7
Variation of yield stress with moisture content for samples tested a) parallel and b) perpendicular to the backbone.
Figure 3.8
Variation of intermediate strain modulus with moisture content for samples tested a) parallel and b) perpendicular to the backbone

Figure 3.9
Variation of high strain modulus with moisture content a) parallel and b) perpendicular to the backbone
30% moisture the high strain modulus has a maximum of 54 MPa parallel to the backbone and 38 MPa perpendicular to the backbone. Either side of this maximum the modulus falls to levels of 42 MPa parallel and 27 MPa perpendicular. In contrast to the low strain moduli, the high strain moduli have the same order of magnitude across the range of moisture content.

3.2.2 FAILURE PROPERTIES AS A FUNCTION OF MOISTURE CONTENT

The strain to failure, figure 3.10, is a function of moisture content. The driest samples break at strains that are on average 10% higher than the wettest samples for both parallel and perpendicular orientations. For any particular moisture content the perpendicular sample (within the limits of experimental error) is 10% more extensible than the parallel sample. As the moisture content decreases the failure strain increases linearly. However, the points plotted for 20% moisture deviate from the straight lines drawn on figure 3.10 for both parallel and perpendicular orientations.

The stress at failure (figure 3.11) is also a function of moisture content. The samples tested parallel to the backbone have higher failure stresses than those strained perpendicular to the backbone. The shape of both parallel and perpendicular curves show similar tendencies. Samples with moisture contents greater than 50% moisture have the lowest tensile strength. As the moisture content decreases from 50% down to 35% moisture content, the tensile strength increases markedly to its maximum value at 35% moisture. Then from 35% down to 20% moisture the samples become weaker. As the moisture content decreases below 13.5% moisture, the tensile strength again rises.
**Figure 3.10**
Variation of failure strain with moisture content for samples test a) parallel and b) perpendicular to the backbone.

![Plot 1](image1)

**Figure 3.11**
Variation of breaking stress with moisture content for samples test a) parallel and b) perpendicular to the backbone.

![Plot 2](image2)
3.2.3 STRESS RELAXATION.

The decay of reduced stress $R(t)$ (defined earlier in section 1.3.2.3 of chapter 1 as the ratio of stress at any particular time to stress at the beginning of relaxation) is plotted on figures 3.12 and 3.13 as a function of log(time) for a range of moisture contents; figure 3.12 for parallel and figure 3.13 for perpendicular orientations. In common with many polymers [WARD], biomaterials [FUNG] and finished leather [POPLEWELL and WARD, SHESTAKOVA and KALINA] these plots are linear at least over the first 300 s. This feature is discussed more fully in chapter 4 with respect to rheological models and with reference to other biomaterials. After 300 s there appears to be some deviation from linearity which is particularly noticeable on the wetter samples. These samples were tested on the lowest range of the 5000 N load cell and the deviation from linearity is a result of periodic fluctuations in the signal from the load cell amplifier.

Each relaxation can be characterised either by its slope, as suggested by [GUY], or by the reduced stress after a certain interval. In this study the latter was chosen and Figure 3.14 shows how the reduced stress after one hour, $R(3600)$, varies with moisture content. This figure reports the relaxation data for both experiments discussed in this chapter (i.e. it includes data for both air dried and acetone dried leather). Over the moisture content range 0 to 35% the reduced stress is independent of either orientation or drying procedure and all experimental points lie on the portion of the curve labelled a in figure 3.14. At 35% moisture the curve divides into two, lines b and c. The value of $R(3600)$ for line b, drawn through points for samples cut parallel to the backbone, is higher than line c, drawn through points for samples cut perpendicular to the backbone. This difference, however, is only statistically significant at 67% moisture.
**Figure 3.12**
Variation of reduced stress $R(t)$ with time $t$ for the backbone sample following with the following moisture contents a) 67%, b) 53%, c) 35%, d) 20%, e) 13%, f) 11.5% samples tested parallel to the backbone.

**Figure 3.13**
Variation of reduced stress $R(t)$ with time $t$ for the backbone sample following with the following moisture contents a) 67%, b) 53%, c) 35%, d) 20%, e) 13%, f) 11.5% samples tested perpendicular to the backbone.
Figure 3.14
Dependence of the reduced stress after one hour (R(3600)) on moisture content showing a pair of lines a) going through all experimental points below 35% moisture and above 35% moisture line b) going through points for samples tested parallel from first experiment and line c) through points from for samples tested perpendicular from first experiment.

- parallel air dried first experiment
- perpendicular air dried first experiment
- parallel air dried second experiment
- perpendicular air dried second experiment
- parallel acetone dried second experiment
- perpendicular acetone dried second experiment
3.2.4 RECOVERY

The tension set is plotted against the log(time) for samples strained parallel to the backbone in figure 3.15 and perpendicular to the backbone in figure 3.16. All curves have similar shape showing an initial rapid decay in set over the first 1000s, followed by more a gradual fall off in the set. The continuous lines drawn through the experimental points were generated using a multi-exponential model (see chapter 4 section 4.3.3) which accounts for the two logarithmic rates of recovery. The fully water saturated samples which produced curves a appear to lose all set over the first 15 minutes of recovery.

Using figure 3.17 the variation of immediate set is related to moisture content. Over the range 11.5 to 20% moisture immediate set decreases with increasing moisture content and over this range within the limits of experimental error the immediate set for both orientations appears identical. A similar variation of immediate set was found in acetone-dried samples over the range 5 to 35% moisture. Over the moisture content range 20 to 53% the immediate set was moisture independent. However the immediate set in samples strained parallel to the backbone is higher than that found in samples strained perpendicular to the backbone. Above 53% the set decreases with increasing moisture content and samples strained parallel to the backbone have higher immediate set.

The variation of delayed set as a function of moisture content after ten minutes and one day is recorded in figure 3.18. Below 20% moisture the delayed set is independent of moisture content but at 20% moisture the set starts to decrease with increasing moisture content for samples strained in both orientations. However in samples tested parallel to the backbone delayed set is constant between 35 and 53% moisture but continues to fall
**Figure 3.15**
Recovery of set in samples with the following moisture contents a) 67%, b) 53%, c) 35%, d) 20%, e) 13%, f) 11.5% for samples tested parallel to the backbone.

**Figure 3.16**
Recovery of set in samples with the following moisture contents a) 67%, b) 53%, c) 35%, d) 20%, e) 13%, f) 11.5% for samples tested perpendicular to the backbone.
Figure 3.17
Variation of immediate set with moisture content for samples tested a) parallel and b) perpendicular to the backbone.

Figure 3.18
Variation of delayed set with moisture content for samples tested a) parallel and b) perpendicular to the backbone after 10 minutes recovery and c) parallel and d) perpendicular to the backbone after 1 day recovery.
over the same range for samples tested perpendicular to the backbone. Above 53% moisture the delayed set in samples tested parallel to the backbone falls faster than samples tested perpendicular to the backbone.

3.2.5 THE EFFECTS OF ACETONE DRYING

No significant difference was found between air and acetone dried material in their relaxation and recovery behaviour over the range 5 to 35% moisture. For the moisture contents 35%, 20% and 13.5% the relaxation and recovery behaviour were very similar to that already reported for air-dried samples with these moisture contents. Although, the delayed set in the acetone dried samples was higher, within significance levels of 1%, than air dried samples at 5% and 20% moisture and identical at 13% and 35% moisture. Both acetone and air dried samples conditioned to 5% moisture showed greater relaxation, (see figure 3.14 where R(3600) fell from around 0.53 to around 0.4 as the moisture content decreases from 13.5 to 5%) and had 1% higher immediate and day set than those condition to 13% moisture. However, samples originally conditioned at 5% moisture were at 10% moisture after a one hour relaxation and therefore the observed increases in relaxation and set probably resulted from dilation of the sample caused by moisture regain.

Some differences were observed between air and acetone dried samples in the low strain region of the stress-strain curves. The variation of the low strain modulus of air-dried samples is compared with that of acetone-dried samples in figure 3.19. The low strain moduli of acetone dried leathers are less than half those of air dried leathers over the moisture range 5 to 35%. There is little difference, within experimental error, between the low strain moduli of acetone dried samples strained parallel to the backbone in comparison to acetone dried samples strained in the perpendicular direction. For air-dried samples the relationship between yield stress and moisture content (figure
**Figure 3.19**
The variation of low strain modulus with moisture content, a comparison between acetone and air dried samples a) air dried parallel, b) air dried perpendicular, c) acetone dried parallel, d) acetone dried perpendicular.

**Figure 3.20**
The variation of yield stress with moisture content, a comparison between acetone and air dried samples a) air dried parallel, b) air dried perpendicular, c) acetone dried parallel, d) acetone dried perpendicular.
3.2.20 curves a and b) appears parabolic whilst for acetone dried samples (figure 3.20 curves c and d) that have lower yield stresses the relationship appears linear. However, error bars would also allow a parabola to be drawn through the set of points describing curve d in figure 3.20. Extrapolating curves a-d in figure 3.20 to zero yield stress it is again apparent that 50% moisture is critical. The yield strain values found for this second experiment were invariant with both moisture and orientation and had a higher value of around 4.6% in comparison to the value between 2 and 2.5% noted earlier for the group of samples in the first experiment. This observation may suggest that the yield strain is a positionally variable quantity since the samples for each experiment were taken from different, but adjacent regions of the same hide. The yield stresses for air dried samples for the respective orientations from the first experiment curves a and b in figure 3.7, are of similar magnitude to those for air dried samples in the second experiment, curves a and b, in figure 3.20. This observation indicates that the yield stress is less positionally variable than the yield strain.

3.2.6 CYCLING AROUND THE YIELD POINT

Figure 3.21 illustrates the effect of cycling a sample of dry leather (20% moisture) between zero strain and an applied strain of 20%. Upon first extension the stress-strain curve a shows a definite yield point around 2% strain. However after returning from this extension (down curve b) and straining a second time, (curve c) the yield is lost and the stress does not rise above zero again until a nominal strain of 6% is reached. Further strain cycling results in loading curves that effectively overlie curve c and unloading curves that effectively overlie curve b. This phenomena is similar to the Mullins stress softening effect [AKLONIS and MACKNIGHT] found in rubber.

The acoustic emission signal from a sample of unfatliquored
Figure 3.21
Stress-strain cycling up to 20% strain (sample cut parallel to the backbone and conditioned to 65 RH) a) first extension, b) first retraction and c) second extension
leather when strained to 20% strain is shown in figure 3.22. Without fatliquoring the yielding phenomenon was more pronounced than with fatliquored material. On first extension, Figure 3.22a there is an appreciable acoustic emission signal even below the yield strain and the number of hits increases dramatically after the yield strain is reached. Whilst upon the second extension, the sample is effectively free from acoustic emission up to 12% strain despite the stress in the sample increasing above the zero level at 6% strain. At or up to 12% strain there is a much reduced acoustic emission signal in comparison to that of the first extension. This is known as the "Kaiser Effect" [KAISER].

There is an acoustic emission signal after a sample has reached its applied strain although this signal decays very rapidly over the first few seconds of relaxation.

3.3 DISCUSSION

The most striking difference between the stress-strain curves of the partially processed leather is the appearance of a moisture dependent yield point. This feature appears in samples containing 35% moisture and below. However, yielding phenomena may also be observed in samples (figure 3.7) with between 35% and 50% moisture. The observation that the low strain modulus increases as the moisture content decreases is consistent with the reported variation in torsional rigidity by NOMURA et al and PINERI et al for collagen and MITTON for teased leather fibres. MEREDITH reports a similar moisture dependent yield in silk, wool, cellulose acetate, viscose rayon fibres and casein conditioned at 100% RH or below. In engineering materials yield phenomena are associated with slippage within a material's structure which leads to plastic deformation. In metals this slippage occurs by the formation and movement of dislocations and the movement of grain boundaries relative to each other [ASKELAND]. NORTHOLT and
Figure 3.22
The effect of repeated extension on (i) the stress-strain curve and (ii) the acoustic emission signal of unfatliquored dry crust material

a) First Extension

b) Second Extension
BALTUSSEN associate yield in polymer fibres below 5% strain with the onset of sequential plastic orientation of polymer chains.

In an early hypothesis used in this investigation moisture dependent yield was attributed to the rupture of structural elastin fibres at the grain-corium junction. This network of elastic fibres is not removed by the ordinary bating procedure [ALEXANDER et al (1991)]. Elastin is known to change from a rubbery solid to a brittle polymeric glass over the moisture regimes used in this investigation [LILLE and GOSLINE]. As moisture content is reduced the \( T_g \) of elastin measured by BATZER and KREIBICH (curve b figure 3.23) first rises above ambient temperature at around 35% moisture, the point where the low strain modulus starts to increase dramatically with decreasing moisture content (figure 3.5). However, the \( T_g \) of collagen (curve a figure 3.5) does not rise above ambient temperature until the moisture content falls below 20%. It could thus be argued that as elastin enters the glassy state (below 35% moisture) it becomes brittle and so gives rise to the yielding phenomenon. At high moisture contents the presence of hydrated elastin fibres offered a plausible explanation for the total recovery observed for 70% moisture content samples. In skin [DALY] as in other soft tissue [SILVER] recovery at low strains is attributed to the network of elastin fibres [LANIR] since hydrated elastin is linearly elastic with a modulus of 0.6 MPa up to strains of 60% [FUNG]. If rupture of a natural elastomer such as elastin were responsible for the yield then not only should the yield stress be moisture dependent but also the yield strain since the failure strain of elastomers depends on their closeness to the glass transition [SMITH and STEDRY].

Although the above arguments seemed plausible, later experimental work (discussed in chapter 5) ruled out elastin fibres as responsible for strain recovery and by inference the yield
phenomena. A related model where grain fibres rather than elastin fibres "bridge" a network formed by the fibre bundles in the corium is developed in chapter 5. In this model the elastic and plastic unbending of fibres is used to explain yield, set, and recovery. Such fibre bridging may also explain why the low strain and high strain moduli at low moisture content are similar since both may be associated with the tensile deformation of fibres. In essence the model postulates that below 50% moisture the formation and breaking of adhesions within the structural hierarchy controls the elasticity and plasticity of the fibre feltwork of leather.

One possible cause of adhesion formation on drying is the presence of residual proteoglycan material [KRONICK and THAYER] on the surface of leather fibres. This residue will become a glassy solid as the leather dries and act as a glue within the fibre structure. ALEXANDER states that even after an 18 hour lime, i.e. one of similar length to that used by Garstons (appendix I) to produce the leather used in this investigation, only half the proteoglycan dermatan sulphate is removed.

An alternative source of adhesions suggested by KOMANOWSKY (1992) is that as the leather dries portions of the collagen molecules come close enough together for hydrogen bonding, van der Waals attraction, and even ion-ion interaction and covalent bonds to form across the gaps between them. If residual proteoglycan is present, it may prove difficult to discern whether it or collagen is responsible for the observed changes in mechanical properties with moisture content. Figure 3.23 compares the moisture dependence of the glass transition temperature for hyaluronic acid, one of the proteoglycans found in soft tissues such as skin [YOSHIDA et al], curve c with that for collagen, curve a [BATZER and KREIBICH]. Within the limits of BATZER and KREIBICH's experimental error the curves for collagen and the proteoglycan
Figure 3.23
Comparison of the variation of glass transition of a) collagen (BATZER and KREIBICH) with b) elastin (BATZER and KREIBICH) c) Hyaluronic acid (YOSHIDA et al) with moisture content determined by differential scanning calorimetry.

Figure 3.24
Comparison of the variation of differential set D(t) with moisture content, in samples strained a) parallel and b) perpendicular to the backbone, to the variation of R(t) with moisture content in samples tested c) parallel and d) perpendicular to the backbone.
almost coincide. The population of adhesions involving proteoglycan, if present, may show the same variation with moisture content as that for adhesions formed by bonding between side groups on the collagen molecule.

The moisture dependence of the low strain yield stress might be explained in terms of the occupancy of water and its effect on lubrication, physical separation at the molecular level and hydrogen bonding. Following the discussion in chapter 1 the following qualitative model is proposed.

i. Between 53% and 67% moisture content, ample water is present not only to occupy all the molecular sites for hydrogen bonding but also to lubricate completely the structure of the material preventing intimate contact between fibres. Over this range any frictional force is hydrodynamic in origin and results from a viscous resistance to flow and consequently the low strain modulus is small.

ii. Between 53% and 35% moisture content, sufficient water is present to populate all the available hydrogen binding sites and so the collagen molecules are fully plasticised. However, there is insufficient water to form complete lubricating films over the entire internal surface area of the material. Since such films would be held to the fibres by capillary forces, they will be progressively lost from structural elements deeper down the hierarchy of the material. Without these films friction can arise from the geometrical interlocking of asperities on the surface of fibres. The coefficient of fibre friction is probably low because it only requires weak hydrogen bonds to be broken. Therefore an increase in low strain modulus is found as the moisture content is reduced between 53% and 35% moisture, albeit a small one.
iii. Below 35% moisture content no free water is present to lubricate the structure and an increasing number of stronger bridges are formed between collagen molecules. Such bridges will involve hydrogen bonds that may or may not incorporate chromium. Removal of water at this stage not only increases the glass transition temperature, but also increases the strength of adhesion points at any level within the structural hierarchy. Over this regime rupturing of adhesions contributes to static friction between fibres whilst the breaking and reformation of hydrogen bonds provides a mechanism of dynamic friction.

This model does not isolate any level of the hierarchy as having the dominant influence on the observed yield.

In dry partially processed leather, as in rubbers [HARWOOD et al], poromericis [PAYNE and POPPLEWELL] and finished leather [WHITTAKER, MANSER, MARRIOT, VACULIC], considerable strain softening occurs in the first strain cycle. This strain softening is associated with the yield figure 3.21. Likewise, the observation of KRONICK and WALKER that strain softening correlates in partially processed leather with the "Kaiser Effect" [KAISER], found in other composite materials, is confirmed by figure 3.22. Close analysis of the first extension curves of WHITTAKER, MANSER and VACULIC shows that these first extension curves are J-shaped rather than showing a definite yield. MARRIOT'S curves for polymer impregnated leather do show a definite yield that becomes more prominent with increasing polymer content. WHITTAKER has shown that strain softening correlates to set in leather as well as in poromericis. For leather WHITTAKER attributes the major contribution to strain softening to slippage at fibre junctions and the breakage of individual fibres rather than the crystallisation of polymer
chains and the breakage of weak cross-linkages that contribute to hysteresis in rubber. It has been shown in this investigation and that of KRONICK and MALEEF that the yield phenomenon is associated with considerable amounts of acoustic emission. KRONICK and MALEEF associate the low energy emission observed at low strains with the rupturing of adhesions rather than the fibre breakage that they associated with high energy events, occurring at strains between the turnup strain and the failure strain. It is however difficult to perceive why the low energy events at low strains cannot be associated with the failure of smaller fibrous elements that may require lower forces to break them.

The presence of a moisture dependent yield point that disappears after one strain cycle implies that the permanent set in any sample will also be moisture dependent. It is a reasonable assumption that the major contribution to the long term set after a prolonged period is plastic (i.e. permanent deformation occurs during stretching). Like the general trend for the low strain modulus, figure 3.5, the set after one day, figure 3.18, curves c, d decreases with moisture content. However, the low strain modulus exponentially increases with decreasing moisture content while the one day set changes at different linear rates between various moisture limits and levels out between others.

It is feasible that the magnitude of the low strain modulus depends on both the number of adhesions present and their stiffness whilst the plastic component of the set may depend only on adhesion population. Below 20% moisture the loss of the bound water, which PINERI et al suggest participates in two hydrogen bonds with collagen, may be expected to result in the formation strong intermolecular bonds between collagen molecules. However, the loss of this water may not necessarily mean an increase in the number of adhesions formed. The experimental observation that the one day set remains constant with decreasing moisture content, below 20% while both the yield stress, figure 3.7, and
the low strain modulus, figure 3.5, increases with decreasing moisture content could be a consequence of this molecular process.

In section 4.3.1 of chapter 4 it will be shown using the Maxwell model that the comparative value of immediate set $S_i(t)$ and the reduced stress $R(t)$ after being held under strain for a time $t$ are interrelated by equation 4.4.

$$S_i(t) = 1 - R(t)$$  \hspace{1cm} (4.4)

However, as moisture content varies little correlation is apparent between the variation of immediate set (Figure 3.17) and $R(3600)$ (figure 3.14). Equation 3.2 expresses the fact that there are two contributions to the comparative value of immediate set $S_i(t)$ produced when a sample is held under strain for a time, $t$. These two contributions are the plastic (time independent) component, $S_p$, and viscoelastic (time dependent) component, $S_v(t)$.

$$S_i(t) = S_p(t) + S_v$$  \hspace{1cm} (3.2)

From equations 3.2 and 4.4 it follows that the recoverable set is proportional to $[1-R(t)]$, equation 3.3.

$$S_v(t) = 1 - R(t)$$  \hspace{1cm} (3.3)

Equation 3.3 states that with increasing stress relaxation the greater is the recoverable set imparted to the leather.
A "differential" comparative set $D(t)$, can be defined as the difference between the immediate set and the set after a prolonged period, e.g., 1 week. If it is assumed that $S_t$ = set after 1 week then from equation 3.2 that $D(t) = S_t$ and so $S_t$ can also be replaced by $D(t)$ in equation 3.3. The quantities $D(t)$ and $R(t)$ are plotted against moisture content in figure 3.24. From this figure 3.24 it can be seen that the peak in $R(t)$ at 20% moisture corresponds to the trough in $D(t)$ at 20% moisture. Hence at least over the range 10 to 35% the proportionality shown in equation 3.3 may hold for partially processed leather and therefore mechanisms for recovery and stress relaxation must be related.

Once yielding has occurred the shape of the stress-strain curve may be described in terms of either the fibre recruitment model or the fibre orientation model (Chapter 1 section 1.3.1.1). The fibre recruitment model implies that between the yield region and the turnup region a major contribution to the modulus comes from the frictional forces. Which are experienced as fibres slide against each other as they are recruited into the direction of applied strain. Similarly, the fibre orientation model also implies a major frictional contribution within the intermediate strain region as the fibres rotate against each other into the direction of applied strain. Therefore, the variation of the intermediate strain modulus with moisture content may be a measure of the variation of dynamic friction between the fibres making up the feltwork. In chapter 6 a model is developed that suggests in the intermediate strain region the predominate mode of fibre deformation is the unbending rather stretching. This model also gives reasons why the modulus associated with bending may be less than that associated with stretching.

Orientation with respect to the backbone influences set since it determines the shape of the stress-strain curve. In chapter 5, reasons will be suggested why samples with a high turnup strain
such as those strained perpendicular to the backbone, figure 3.2, have less immediate and long term set than those strained parallel to the backbone, figure 3.1. with a lower turnup strain. Explanations are also put forward in chapter 5 which relate the anisotropy observed in the low strain modulus and yield stress to structural models.

A consequence of either the fibre recruitment model [KRONICK and BEUCKLER(1986)] or the fibre orientation model [MITTON], introduced in section 1.3.1 of chapter 1 as structural mechanisms which explain the "J"-shaped stress-strain curve of leather, is that the high strain modulus and failure stress are both greatly influenced by the properties of individual fibres. Both the high strain modulus and the breaking stress are less than a quarter of modulus reported by ARUMUGAM et al (1995) for chrome tanned rat tail tendon. Therefore even at high strains we can assume that orientation is incomplete and the spaces between fibres reduce load bearing cross-sectional area.

The increase in both high strain modulus and breaking strain when the moisture content is reduced from 53% to 35% may be explained by the removal of water from the hierarchy of individual fibres making them behave as more cohesive units through the formation of adhesions and increased fibre friction. Evidence for this premise is provided by ARUMUGAM et al (1992) who suggest that dry fibres have greater internal coherence than wet fibres because the fracture surfaces of dry collagen fibres (tested at 65 %RH and 25 C) are smooth whereas those of native collagen fibres are frayed. RAJARAM et al found an increase in modulus with increasing fibre length. They suggest that this increase resulted from in increase number of free fibril ends causing an increased contribution to the inter-fibril friction.

The decrease in the value of R(3600) as the moisture content is
increased from 20% to 67%, figure 3.14 may be caused by a reduction in friction between the more primitive elements inside the fibre bundles or grain layer since such a reduction in friction will increase the rate at which the more primitive elements rearrange to lower the energy. KOMNOWSKY et al also support this view and suggest it is why dry unfatliquored samples relax less than either wet or fatliquored material.

As the moisture content is decreased below 20%, greater adhesion through the formation of stronger intermolecular bridges as more strongly hydrogen bonded water is removed might be expected (see chapter 1 section 1.6). Expecting the high strain modulus, failure stress and $R(3600)$ all to continue to increase with decreasing moisture content is reasonable. However, it is observed that both the high strain modulus and the value of $R(3600)$ actually fall as the moisture content drops below 20%. Also the failure stress levels out as the moisture content drops below 35%. Both NOMURA et al and PINERY et al report that the torsional rigidity of collagen fibres continues to rise as the moisture content falls below 20%. MITTON also observed for leather fibres a continued rise in torsional rigidity as the moisture content decreased below 20%. The observations of all these authors suggests that any proposed mechanism of plastic deformation requires large shear strains along the axis of a fibre rather than the small shear strains in the directions orthogonal to the fibre axis such as those imposed during torsional measurements. Therefore there must be some additional mechanism associated with the sliding of elements inside the fibre bundle or grain layer making them behave in a less cohesive manner. An increased ability to slide will not only account for the fall in $R(3600)$ and high strain modulus below 20% moisture but also may account for the greater immediate set in samples conditioned to 11.5% and 13% moisture than in samples conditioned to 20% (Figure 3.17). The permanent rupture of intra-fibre adhesions
below 20% moisture offers a likely mechanism for an increased ability for elements within the hierarchy of a fibre to slide. More specifically the rupture of adhesions lower down the hierarchy of the bundle may permanently remove the rope-like twist of the fiber bundle suggested by HEIDEMANN (1982). Even small torsional shear strains may be sufficient to rupture inter-fibre and intra-fibre adhesions especially in rope-like structures. A possible mechanism for sliding at the fibril level which requires reasonably high tensile shear strains along the fibre axis could be the rupture of cross-linked teleopeptides within the overlap regions that tie the end of one tropocollagen molecule to the side of another. MOSLER et al suggest that these are stretched when the triple helices within the microfibril slide apart in response to strain applied to tendon fibres. These non-helical ends may become embrittled by the removal of water from the "Gap Zone". KOMNOWSKY (1992) argues that such moisture removal is significant below 15% moisture. However, a more significant fall in breaking stress, attributed to an increased number of molecules free to slide ends might be expected with this mechanism.
4 TIME DEPENDENCE

This chapter is concerned with the stress relaxation, set and recovery of part-processed leather in relation to the amount of time the leather was held under strain.

4.1 EXPERIMENTAL

The results arise from a matched side experiment comparing wet, 67% moisture, and dry, 20% moisture, partially processed leather. These moisture contents were chosen not only because they were the easiest to maintain but also because, as shown in the experiments discussed in chapter 3 they represented leathers with the largest differences in mechanical properties.

The material for this experiment was the top portion of the official sampling area, comprising two 20 cm by 40 cm rectangles either side of the backbone, of one hide of the standard leather. The left hand portion was dried and conditioned to 20% moisture and the right hand portion was soaked in distilled water and kept in a plastic bag. Twenty, 20 cm by 1 cm strips, were cut in the direction parallel to the backbone and twenty strips were cut in the direction perpendicular to the backbone from both the dry and wet material such that each dry strip had its corresponding wet strip with the same orientation cut in the opposing position across the backbone.
Each strip was extended to a fixed strain of 20% at a rate of 100% min\(^{-1}\) and held at that fixed strain for a fixed length of time (the duration of which was varied between strips). Following which the strain was removed at a rate of 100% min\(^{-1}\). Five different durations, or hold times, were chosen as follows, one hour, 10 minutes, 1 minute, 10 seconds and zero seconds. For each hold time there were at least three and more often four replicates, equally spaced within the sampling regions, from which a standard deviation could be calculated.

4.2 RESULTS

4.2.1 STRESS-STRAIN CURVES

Four stress-strain curves typifying those curves found in this experiment are shown in Figure 4.1. Curve a for a dry sample strained parallel to backbone indicates a yield point at around 3% strain and has a higher yield stress, 0.17 MPa, than curve b. The latter was obtained for a dry sample strained perpendicular to the backbone that has a yield stress of about 0.10 MPa with a yield point at the same value of strain. Curves c and d for wet samples strained parallel and perpendicular to the backbone respectively, show no yielding behaviour. Curves a and c (straining parallel to the backbone) gone beyond their turn up strain (15%) whereas it is clear that samples strained
Figure 4.1
Typical stress-strain curves up to 20\% strain for samples used in the investigation of the effect of hold time on recovery a) dry parallel b) dry perpendicular c) wet parallel d) wet perpendicular

Figure 4.2
Variation of $R(t)$ with time for the following orientations and conditions a) dry parallel b) dry perpendicular c) wet parallel d) wet perpendicular (lines are for representative samples, error bars calculated from three representative samples)
perpendicular to the backbone have not gone beyond this critical strain. The significance of this observation is explored in detail chapter 5. The observed anisotropy in the turn up strain is consistent with the results reported in chapter 3 for samples taken from the same region of the official sampling area but from a different hide.

4.2.2 STRESS RELAXATION

Figure 4.2 shows the variation of reduced stress, \( R(t) \), with the time, \( t \), held under strain. This plot demonstrates that the relaxation is very rapid over the first 500 s. This rapid rate of relaxation is followed by a slower rate of relaxation. All the relaxations found in this investigation have a similar behaviour to those observed in figure 4.2 but for reasons that are discussed below have been plotted using a logarithmic time scale throughout this thesis.

The mean value of \( R(3600) \), the reduced stress after an hour, for dry samples strained parallel to the backbone is 0.63±0.01. This is higher than the mean value of \( R(3600) \) for samples strained perpendicular to the backbone for which \( R(3600) \) is equal to 0.60±0.01. This pattern compares with the average value of 0.62±0.01, common to the two orthogonal orientations reported in chapter 3 for samples of the same moisture content that were subjected to the same applied strain.
R(3600), 0.58±0.02, for wet samples strained perpendicular to the backbone is larger than 0.54±0.01 for wet samples strained parallel to the backbone. Curves c and d comparing R(t) for wet samples in the two orientations are distinguishable but not distinct within the limits of experimental error. R(3600) reported in figure 3.14 for samples with 67% moisture were distinct for the two orientations with a slightly higher R(3600)=0.55±0.02 for samples strained parallel to the backbone compared with 0.50±0.01 for samples strained perpendicular to the backbone. The observation that R(3600) is higher for dry samples than for wet samples is consistent in the two experiments.

In figures 4.3, 4.4, 4.5, and 4.6 the lines a show the relaxations curves from figure 4.2 plotted on a log scale. The reduced stress for dry samples strained parallel to the backbone, fig 4.3 line a, and for dry samples strained perpendicular to the backbone, fig 4.4 line a, are linear with the log(time). However, the reduced stresses for wet samples strained parallel to the backbone, figure 4.5 a and figure 4.6 a deviate slightly from this linearity. A decaying exponential can be fitted to these curves with a greater residual than is illustrated by the linear fits.
**Figure 4.3**
Comparison of the variation of $R(t)$ and the variation of $1-S(t)$ with hold time $t$ for dry samples strained parallel to the backbone
a) $R(t)$ and $1-S(t)$ b) Immediately, c) 2 minutes, d) 1 hour, e) 1 day after release.

**Figure 4.4**
Comparison of the variation of $R(t)$ and the variation of $1-S(t)$ with hold time $t$ for dry samples strained perpendicular to the backbone
a) $R(t)$ and $1-S(t)$ b) Immediately, c) 2 minutes, d) 1 hour, e) 1 day after release.
**Figure 4.5**
Comparison of the variation of $R(t)$ and the variation of $1-S(t)$ with hold time $t$ for dry samples strained parallel to the backbone a) $R(t)$ and $1-S(t)$ b) Immediately, c) 2 minutes, d) 1 hour, e) 1 day after release.

**Figure 4.6**
Comparison of the variation of $R(t)$ and the variation of $1-S(t)$ with hold time $t$ for wet samples strained perpendicular to the backbone a) $R(t)$ and $1-S(t)$ b) Immediately, c) 2 minutes, d) 1 hour, e) 1 day after release.
4.2.3 SET AND RECOVERY

The shape of recovery curves reported in this chapter for a range of hold times is similar to those reported in chapter 3 for a range of moisture contents, i.e. a rapid initial rate of recovery over the first 100 s or so followed by a much slower rate of recovery thereafter.

The recovery of the set in the dry samples strained parallel to the backbone is shown in figure 4.7 where zero time is defined as 0.1 s before the immediate set was measured. Curve a in figure 4.7, is the recovery curve for dry samples of 20% moisture, after being held at 20% strain for 1 hr and closely resembles curve d reported in figure 3.15 for a sample tested under identical physical conditions and taken from a similar region of a different hide. In both cases the one day set is 5% and the immediate set is 13% (for samples held under 20% strain for 1 hour).

Curve a in figure 4.8, indicates slightly less set over one day, 4% compared with 5% reported in figure 3.16 curve d for samples containing 20% moisture tested perpendicular to the backbone. This difference is not significant since the error in the measurement of delayed set is around 1% for both curves. The immediate set reported for both curves is 12.5% and is identical within the limits of experimental error.
Figure 4.7
Recovery of set in dry samples strained parallel to the backbone after the following times held under strain a) 1 hour, b) 10 minutes, c) 1 minute, d) 10 seconds, and e) not held.

Note in figures 4.7-4.10 Points represent experimental data while lines represent fit to model.

Figure 4.8
Recovery of set in dry samples strained perpendicular to the backbone after the following times held under strain a) 1 hour, b) 10 minutes, c) 1 minute, d) 10 seconds, and e) not held.
Wet (67% moisture) samples strained parallel to the backbone for less than 10 minutes, curves c, d and e in figure 4.9, have lost all their set after 10 minutes recovery. In contrast wet samples strained parallel to the backbone for more than 10 minutes, curves a, b in figure 4.9 retain some set after 10 minutes recovery. However, after 1 week this set has reduced to almost zero within the limits of experimental error.

Wet samples strained perpendicular to the backbone, figure 4.10, showed no set after ten minutes recovery irrespective of the length of time for which the sample was held. Again, as expected curve a in figure 4.10 closely resembles curve a in figure 3.16.

The simple Maxwell model of linear viscoelasticity requires that the quantity \( l - S(t) \), where \( S(t) \) is the residual strain divided by the applied strain, is related to \( R(t) \) the reduced stress. In figures 4.3 to 4.6 curves b, c, d, and e the quantity \([1-S(t)]\) immediately, two minutes, an hour, and a day after release respectively, is plotted against the logarithm of hold time, \( t \).

For dry material tested in the direction parallel to the backbone within the limits of experimental error the immediate \([1-S(t)]\) decreases roughly linearly with log time, figure 4.3 curve b, i.e. the set in these samples increases linearly with log time. However, for other situations a parabola may fit the data. Curves b for the immediate \([1-S(t)]\) in figures 4.4-4.6 show considerable departure from a straight line. These results
**Figure 4.9**
Recovery of set in wet samples strained parallel to the backbone after the following times held under strain a) 1 hour, b) 10 minutes, c) 1 minute, d) 10 seconds, and e) not held.

![Graph showing set recovery over time for parallel strain](image)

**Figure 4.10**
Recovery of set in wet samples strained perpendicular to the backbone after the following times held under strain a) 1 hour, b) 10 minutes, c) 1 minute, d) 10 seconds, and e) not held.

![Graph showing set recovery over time for perpendicular strain](image)
are consistent with the observations reported by BUTLIN who found that for samples of finished leather both linear and area set increase linearly with hold time on a logarithmic scale ranging from $10^2$ to $10^6$ seconds. Since BUTLIN'S experimental design did not examine hold times shorter than about 30 s it is understandable why he did not observe the deviation from the linear dependence found here especially for the delayed set.

Holding samples under strain for various periods less than a minute appears to have much less effect on the rate at which long term set is imparted to the leather than holding samples under strain for periods more than 10 minutes. This is evident from the slopes of curves e, in figures 4.3 to 4.5, that represent $1-S(t)$ after a day. Over the first two decades of hold time [$1-S(t)$] after a day is constant, within the limits of experimental error. However, over the next two decades [$1-S(t)$] drops by 0.2 for dry material tested parallel and perpendicular backbone (figures 4.3, 4.4 curves e) and by 0.05 for wet material tested parallel to the backbone (figures 4.5 curves e).

4.3 DISCUSSION AND THE RELEVANCE OF RHEOLOGICAL MODELS

In the following section both the significance of the results and the applicability of rheological models are examined.
4.3.1 IMMEDIATE SET, STRESS RELAXATION AND THE MAXWELL MODEL

The simplest model for stress relaxation in polymers is the Maxwell model, figure 4.11a. This model uses a Hookean spring in series with a Newtonian dash-pot. Since these elements are in series, the total strain in the Maxwell element, \( e_n \), is the sum of the strain in the dashpot, \( e_d \), and the strain in the spring, \( e_s \), equation 4.1.

\[
e_n = e_s + e_d
\]  

(4.1)

When first applied the strain is all taken up by the spring and the stress is a maximum. During relaxation the strain is transferred from the spring to the dashpot as the stress in the element decays. The stress in the Maxwell element, \( \sigma_n \), decays exponentially, with time, \( t \), according to equation 4.2. Where the characteristic relaxation time, \( \tau \), is given by the viscosity, \( \eta_d \), of the dashpot divided by modulus of the spring \( E_s \) [WARD, FERRY, FUNG, AKLONIS AND MACKNIGHT].

\[
\sigma_n = \sigma_s e^{-t/\tau}
\]  

(4.2)
Figure 4.11
Two and three element rheological models:
a) Maxwell, b) Voigt, c) Zener model, d) Shestacova et al.
The immediate set is related to the strain in the dash pot, since a perfect Hookean spring immediately regains its original length when the applied strain is removed. The rate of straining in the dash pot is related to the stress in the Maxwell element by Newton's law of viscosity as indicated in equation 4.3.

\[
\frac{de_d}{dt} = \frac{\sigma_s}{\eta_d} \quad (4.3)
\]

If a strain, \( e_s \), is applied at time \( t=0 \) and removed at time \( t \) then equation 4.3 can be integrated between these limits by substituting equation 4.2 for \( \sigma_s \) to obtain equation 4.4 as shown below, where \( S(t) = e(t)/e_s \) is the comparative set divided by 100 and \( R(t) \) is the reduced stress \( \sigma_s/\sigma_d \).

\[
e(t) = \int_0^t \frac{\sigma_s}{\eta_d} \, dt = \left[ \frac{\sigma_s}{\eta_d} \right]_0^t (1 - e^{-\frac{t}{\eta}})
\]

\[
S(t) = 1 - R(t) \quad (4.4)
\]

This equation indicates that the immediate comparative set in the sample increases in proportion to the decrease in stress relaxation.

In figure 4.12 the immediate value of \([1 - S(t)]\) is plotted against \( R(t) \) for dry samples tested parallel, line \( a \), and perpendicular,
Figure 4.12
Reduced stress, R(t) plotted against 1 - S(t) where S(t) is the immediate residual strain divided by the applied strain for dry samples a) parallel, b) perpendicular c) model

Figure 4.13
Reduced stress, R(t) plotted against 1 - S(t) where S(t) is the immediate residual strain divided by the applied strain for wet samples a) parallel, b) perpendicular, and c) model
line b, to the backbone. The line c represents a material described by the model. Figure 4.13 shows a corresponding plot for wet samples. The properties \(1-S(t)\) and \(R(t)\) are linearly related since a regression line with a residual greater than 0.9 can be fitted to each set of points in figures 4.12 and 4.13. The immediate set in all four cases agrees with the prediction of a Maxwell model as the immediate set increases linearly with relaxation. However, the simple Maxwell model predicts that, to obtain set, relaxation must occur. Line b in figure 4.13, for wet samples strained perpendicular to the backbone, is the only case that complies with this prediction since the curve passes through the point \((1,1)\). In the other cases some mechanism of set is occurring that either does not cause relaxation or results from relaxations markedly shorter than the time taken to strain a sample. When \(R(t)=1, [1-S(t)]\) extrapolates to 0.8 for dry material tested in both orientations and to 0.7 for wet samples tested parallel to the backbone.

### 4.3.2 THE REQUIREMENT FOR THREE AND FOUR ELEMENT MODELS

One major limitation of the Maxwell model in describing stress relaxation in polymeric material is that in contrast to the model predictions the stress does not decay to zero even after very long times. Another limitation is that the model does not describe strain recovery. Like polymers and biomaterials, such as skin and tendon, partially processed leather maintains a finite
stress, even after very long periods of relaxation and also exhibits strain recovery on release.

The Voigt model, which is a spring and dashpot in parallel (see figure 4.11b), describes recovery but cannot describe stress relaxation. The simplest model that describes both phenomena is the three element Zener model (figure 4.11 c) when an extra spring is in parallel with a Maxwell element. For the Zener model the following relationship holds between stress and time (equation 4.5) [WARD].

\[ \sigma'_t = \sigma'_0 (e^{-t/t} + c) \]  

FINDLEY et al point out that with an appropriate choice of constants the Zener model is quantitatively the same as the three element model consisting of a spring in series with a Voigt element. Both models belong to a family of models known as the standard linear solid. SHESTAKOVA and KALINA replaced the elastic element used by MITTON in the fibre orientation model with this version of the standard linear solid to describe the relaxation of finished leather as a function of applied strain (such relaxation is the subject of chapter 5).

Standard linear solid models can be shown to describe recovery, following a period loading, by a single exponential decay to zero residual strain, i.e. these models describe viscoelasticity but not plasticity (for an example see WARD). The standard linear solid model is able to describe qualitatively not
only stress relaxation to a finite stress after a long period of relaxation in wet leather but also its observed total loss of set. Unfortunately, for dry leather the standard linear solid model only describes qualitatively stress relaxation and not strain recovery since there is appreciable long term set. In dry leather some plastic mechanism that may be associated with the observed yielding which occurs during straining. Such a mechanism may involve the rupture of adhesions. This rupture results in the irreversible slippage of fibres or structural elements within fibres.

In the approach used by FRISIN et al in modelling plastic phenomena in collagenous soft tissue a special type of non-reversible dash pot was introduced, termed a limited dry frictional element. This development is illustrated in figure 4.14 as a frictional block lying on a rough plane anchored by a loose string that cannot be extended when taut. If this extra element is introduced in series with a Zener element then this four-element model can describe qualitatively the observed relaxation and recovery behaviour found for the drier material. That is to say relaxation to a finite stress and recovery to a finite strain. With the dry frictional element, once a limiting strain is reached, the special dash pot makes no further contribution to relaxation or recovery. Mathematically this model is simpler than the Burgers model [FINDLEY et al] with an ordinary dash pot, because once the limiting strain is reached
**Figure 4.14**
Four element model including a frictional brake element

**Figure 4.15**
Triple exponential fit to representative stress relaxations a) dry parallel, b) dry perpendicular, c) wet parallel, d) wet perpendicular
the model reduces to the standard linear solid. The observation that set can be obtained without apparent relaxation is one justification for the use of this model.

4.3.3 THE EXTENSION TO MULTI ELEMENT MODELS

Another limitation of the simple Maxwell model is that a single exponential does not describe satisfactorily the relaxation of partially processed leather. Even in the simplest of polymers such as polypropylene the relaxation and recovery cannot be represented by a single exponential decay with one characteristic relaxation or recovery time. Partially processed leather in common with finished leather [SHESTAKOVA and KALINA, POPPLEWELL and WARD, GUY], soft tissues such as lung tissue [SAKI et al], skin [BARBENEL], other biocomposites such as wood [KUBAT and KLASON] and plant cell walls [HAUGHTON et al], many plastics [WARD] rubbers [SMITH], and even metals have a stress relaxation behaviour that is linear with the logarithm of time.

Figure 4.16a illustrates the extension of the generalised Maxwell model into a ladder of n Maxwell elements in parallel with a spring. Such a model is known as the Maxwell-Wiechert model [AKLONIS and MACKNIGHT]. Each Maxwell element i has a characteristic relaxation time constant \( \tau_i = \eta_i / E_i \). HAUGHTON et al used this approach to model the relaxation of plant cell walls.
**Figure 4.16**
Generalised multiple element models: a) multiple Maxwell (Maxwell-Wiechert model) b) Multiple Voigt Model

**Figure 4.17**
Plot illustrating how a curve which is linear with log time over many decade is formed by the successive summing of exponentials of equal weight with one time constant per decade.
The spring of modulus $E_{ur}$ is added to the end of the ladder to account for the unrelaxed component of the stress. The reduced stress for this model is given by equation 4.6.

$$R(t) = \frac{\sum E_i e^{-\frac{t}{\tau_i + E_{ur}}}}{\sum E_i + E_{ur}}$$

(4.6)

Recently, KOMANOWSKY et al achieved a satisfactory triple exponential fit to day long stress relaxations in leather. Figure 4.15 shows the fit of the triple exponential model to representative relaxations from the experimental data of the current investigation. The parameters are shown in table 4.1. Although $E_1$, $E_2$ and $E_3$ obtained here and by KOMANOWSKY et al are of the same order of magnitude the relaxation time constants do not compare. Calculations show that $\tau_1$ ranged from 3 to 10 minutes, $\tau_2$ ranged from 1 to 5 hours and that $\tau_3$ ranged from 50 to 500 hours. KOMANOWSKY et al's times $\tau_1$, $\tau_2$ and $\tau_3$ are around 100 times longer than the times quoted in table 4.1. The discrepancy is explained by the difference in the respective experimental time intervals. Whereas in the present investigation the first reading after the maximum stress at zero time occurred around half a second later KOMANOWSKY et al made the corresponding first
reading in their experiment a minute later. Also in the current investigation the relaxation was terminated after one hour rather than the twenty hours used by KOMANOWSKY et al. Fitting a triple exponential decay to relaxation appears to yield three time constants. The shortest is the same magnitude as the interval between the maximum stress reading and the first stress reading after relaxation has commenced. Whereas, the longest is about ten times the period of the experiment. FUNG points out that fitting a sum of exponentials to a relaxation is a non-unique process. Therefore, time constants should not be interpreted literally. Triple exponential fitting may provide a way of assigning parameters to relaxations but unless the time intervals over which stress decays are measured are the same any comparison is meaningless. However, the results for the time constants in table 4.1 support the conclusion of KOMANOWSKY et al that the initial rate of relaxation is faster in dry crust leather than moistened leather.

<table>
<thead>
<tr>
<th>Sample condition and orientation</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
<th>$\times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Parallel</td>
<td>0.84</td>
<td>0.72</td>
<td>4.07</td>
<td>2.2</td>
<td>71</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Dry Perpendicular</td>
<td>0.40</td>
<td>0.41</td>
<td>1.91</td>
<td>2.7</td>
<td>80</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Wet Parallel</td>
<td>0.79</td>
<td>0.79</td>
<td>2.42</td>
<td>3.9</td>
<td>63</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Wet Perpendicular</td>
<td>0.22</td>
<td>0.26</td>
<td>1.08</td>
<td>4.4</td>
<td>19</td>
<td>27</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 Parameters determined from triple exponential fit
Consider the following restrictions on the choice of parameters in equation 4.6:

i. The initial contribution, at time $t=0$, of each exponential term to the sum is the same, i.e. $E_i = E_1 + E_2 + \ldots + E_n$.

ii. $\tau_i$ is allowed to take discrete values so that there is at least one time constant for each decade. Equation 4.7 states this restriction algebraically, $m$ is an integer less than $n$ which determines the shortest time constant and $k$ is an integer greater than zero that determines the number of time constants per decade.

$$\tau_i = 10^{\frac{m-1}{k}} \quad (4.7)$$

If these restrictions are made then the $R(t)$ will decrease linearly with the logarithm of time over $n$ decades to a fixed value $R_{ur}$ related to the unrelaxed modulus $E_{ur}$. This is expressed qualitatively in equation 4.8.

$$E_{ur} = \frac{R_{ur} \sum E_i}{1 - R_{ur}} \quad (4.8)$$

Figure 4.17 illustrates how the successive summing of twelve such
equally weighted exponentials with a range of relaxation time constants from $10^{-5}$ to $10^6$ s (for the case where $n=12$, $m=-5$, $k=1$, and $E_{ur}=0$) produces a straight line on the log-linear plot over the same range of time.

The major limitation of multi exponential modelling, identified by Fung is the erroneous identification of the limiting value of $R_{ur}$ as the value of $R$ at the end of the relaxation experiment. Popplewell and Ward found that the stress in finished leather decays linearly with log time over a period of three days so choosing $R(3600)$ as the limiting value would be wrong since the calculation would yield a time constant of the same order of magnitude as the length of the observed relaxation i.e. 3600 s. Indeed extrapolation to $R(t)=0$ of the plots of $R(t)$ against log $t$ would suggest that the stress in samples drops to zero between, 6 months in a wet sample, and 10000 years (in a dry sample).

Saki et al, who have recently reviewed the mathematical framework used to describe lung tissue viscoelasticity, point out that multi exponential modelling may adequately fit empirical observations but provides little information as to the structural origins of viscoelasticity in soft tissues. Because of the limitations of multiexponential modelling it may be simpler and just as appropriate to ascribe a single parameter to stress-relaxations in order to compare them. Guy used the slope of the line in the plot of reduced stress against log time.
Throughout this investigation the reduced stress at the end of a fixed period of relaxation is used for comparison.

Unlike its stress relaxation the strain recovery of partially processed leather is a two-stage process on a logarithmic time scale. This has been found to be the case for the recovery of linearly strained samples over the whole range of test parameters used in this investigation. This observation is consistent with those observations made by WHITTAKER for full chrome tanned side leather taken to various strains and also by MARRIOTT for unfinished chrome tanned leather samples and leather samples with a range of finishes. There is less evidence for this two-stage process on the recovery plots given BUTLIN, which are linear with log time over periods extending from 10 minutes to two years in some cases. This linearity is probably a consequence of the fact that the earliest set measurement which BUTLIN made was 30 seconds after the removal of applied strain. In polymers such as polypropylene, strain recovery after creep (a process that itself is in two stages on a logarithmic time frame) is reported by TURNER to be a process with rates which are linear on a logarithmic time scale. In the polymer literature it is possible to find examples where recovery is rheologically modelled after periods of creep [WARD, FINDLEY et al]. Unfortunately, it has proved difficult to find an example of the application of a rheological model to recovery following a period of stress.
relaxation. Therefore, the following approach was developed and used to describe the recovery data in this investigation.

In the same way equation 4.6 relates the decay of stress to relaxation time, equation 4.9 relates the loss of set to recovery time. Figure 4.14b illustrates the equivalent rheological model, consisting of a number of Voigt elements all in series with a frictional element, to which this equation applies. Here \( S'(t) \) is defined as the set \( t \) seconds after recovery \( S(t) \) divided by the initial set \( S(0) \). \( S(0) \) has purposely been defined as the set 0.1 s after retraction so that the data can be plotted on a graph with a logarithmic time axis.

\[
S'(t) = \sum \frac{1}{E_i} \cdot S(0) \cdot e^{-\frac{t}{\tau_i}} + \frac{1}{E_{ur}} \sum \frac{1}{E_i} + \frac{1}{E_{ur}}
\]  

The frictional element to account for the permanent set is represented by the quantity \( S_{ur} \) in equation 4.10.

\[
\frac{1}{E_{ur}} = \frac{S_{ur} \sum \frac{1}{E_i}}{1 - S_{ur}}
\]

Like the stress relaxation the strain recovery is linear with the
logarithm of time but it has already been remarked that recovery appears to have two logarithmic rates of recovery. To model this experimental observation the following simplifying assumption was made. Compliances $1/E_i$ corresponding to retardation times longer than a critical retardation time $t_c$ were assumed to be a multiple $K$ of the compliances of elements which had retardation times shorter than $t_c$. Using this simplification equations 4.9 and 4.10 combine to become equation 4.11.

$$S(t) = \frac{c \sum_{i=0}^{n-1} e^{-\frac{t}{t_c+K\left(n-c\right))} \sum_{i=1}^{c} e^{-\frac{t}{1-t_c+K(n-c)S_{ur}}} \frac{c+K(n-c)S_{ur}}{1-S_{ur}}}{c+K(n-c)S_{ur}}$$

In this investigation equation 4.11 was manipulated using a mathematical software package (Maths cad 5.1+) using the following procedure.

An initial estimate $S_{ur}$ was defined from the residual set after one day divided by the immediate set. The time constant of $t_c$ was estimated from the intercept of the line drawn through the points for 10 minutes, 1 hour and 1 day set and the line drawn through the points for immediate set and two minutes set. Then $K$ was
varied in order to obtain the best curve through to the experimentally determined values of $S'(t)$. The estimates of $S_{ur}$ and $\tau_c$ were revised to obtain the best fit to the data. In figures 4.7 to 4.10 the value of $S'(t)$ for each hold time has been multiplied by the immediate set for that hold time and plotted as a continuous line through the experimental points.

The parameters required to give the best fit of equation 4.11 to the curves on figures 4.7 to 4.10 are given in table 4.2.

<table>
<thead>
<tr>
<th>Table 4.2 Recovery Model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Parallel</td>
</tr>
<tr>
<td>Figure 4.9</td>
</tr>
<tr>
<td>Hold Time/s</td>
</tr>
<tr>
<td>3600</td>
</tr>
<tr>
<td>600</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

| Hold Time/s | curve | $K$ | $S_{ur}$ | $\tau_c$/s | $K$ | $S_{ur}$ | $\tau_c$/s |
| 3600 | a | 0.25 | 0.36 | 50 | 0.25 | 0.28 | 50 |
| 600 | b | 0.23 | 0.33 | 50 | 0.2 | 0.24 | 50 |
| 60 | c | 0.2 | 0.25 | 50 | 0.14 | 0.22 | 50 |
| 10 | d | 0.2 | 0.25 | 50 | 0.14 | 0.15 | 50 |
| 1 | e | 0.17 | 0.25 | 50 | 0.13 | 0.19 | 50 |

Unfortunately, the accuracy of the fit is limited for the following three reasons:

i. There are no experimentally determined delayed sets for hold
times shorter than two minutes;

ii. The applied strain was removed at a fixed but finite rate so the starting point of recovery is uncertain therefore defining the time at which the immediate set was measured as 0.1 s after the removal of the applied strain is arbitrary.

iii. The range of retardation times used in the model was limited from $10^{-1}$ to $10^7$ s. As a consequence the predicted values of immediate set, plotted at $t=0.1$ s are lower than the experimental values since retardation times shorter than 0.1 s do not contribute to the summation in equation 4.11.

In the limit of an infinite number of Maxwell or Voigt elements the summations become integrals, eg equation 4.12

$$
\int_0^{\infty} E(\tau) e^{-\tau} d\tau 
$$

(4.12)

for a continuum of Maxwell elements where $E(\tau)$ is the distribution function of relaxation times, known as the relaxation spectrum. WARD suggests that although it is theoretically possible to determine the relaxation spectra by Fourier and Laplace Transform method these are much more readily determined from dynamic mechanical tests. In the literature much of the information on the relaxation spectra of collagen comes from torsional pendulum measurements where the relative rigidity
has been explored as a function of temperature and moisture content. The principle of time temperature equivalence states that long time scale events predominate at low temperatures while short time scale relaxations predominate at high temperatures. Hence some qualitative comparisons can be drawn of the observed relaxation or recovery behaviour of partially processed leather with these dynamic mechanical measurements.

Ignoring a peak in the relaxation spectrum due to the free water NOMURA et al found two water sensitive peaks in a plot of logarithmic decrement against temperature:

i. The peak labelled $\beta_2$ was of constant intensity and fixed temperature (150K) above 20% moisture.

ii. The labelled $\beta_1$ peak falls in temperature from 250K to 200K, (as its intensity increases), with increasing moisture content from 10 to 35% after which it remained constant at 200K. The intensity of this peak dropped with increasing moisture content above 35%.

If the principle of time-temperature superposition is applicable then in both the wet and dry cases of the observations reported in this chapter two contributions to the relaxation or recovery might expected. A long term contribution can be attributed to the $\beta_2$ process and a short term contribution can be attributed to the $\beta_1$ process. Changes in the relative contributions of these two processes to relaxation and recovery as moisture content changes might also be expected. However, the stress relaxation of both
wet and dry leather is fairly linear with log(time) which suggest that in fact there is no dominant process.

Bonds of various strength can be categorised in terms of their influence on relaxation times. GUPTA and RAMA RAO did this categorisation for wool fibres. Hydrogen bonds, van der Waals interactions and salt linkages are regarded as weak bonds and are associated with relaxation times of approximately one second. Strong covalent bonds are associated with relaxation times of over 600 s. Bonds with intermediate strength have relaxation times between these two extremes and occur between the fibrous a matrix component of the wool. A continuous distribution of relaxation times might be expected in a material such as tanned collagen fibres since bonds of varying strength from weak single hydrogen bonds to strong covalent bonds exist in this material.

KUBAT and KLASON showed stress relaxation behaviour of scots pine veneer, that decays linearly with log(time), may be explained by the theory of stress dependent thermal activation, whereby events constituting the macroscopic relaxation, occur cooperatively in clusters of varying size. With these types of clustering of events bursts of acoustic emission might be expected. These bursts becoming less frequent and less intense with increasing stress relaxation time. In pilot tests in this investigation few acoustic events were observed in samples during relaxation and none after a period of 3 s after the strain application. However,
it is probable that such events may have resulted in acoustic events which were below the 35 dB threshold of acoustic emission apparatus. KRONICK et al introduce the concept of craze formation to explain why acoustic emission occurs while straining dry unfatliquored leather to strains well below those required to break individual fibre bundles. The propagation of such cracks within fibre bundles is a possible mechanism for cooperatively clustered events within dry leather.

SAKI et al propose that a process of gradual disentanglement by curvilinear diffusion of collagen fibres from a tangled network, similar to reptation in polymer melts [FERRY] at the molecular level, may be a suitable mechanism for long term relaxation in soft tissue. However, complete disentanglement of a fibre from one configuration in a network of fibres and re-entanglement into a new energy minimum position, as they suggest may be an immeasurably slow process, since it may require a large number of molecular re-arrangements. In leather the bending of segments of fibres to new positions is a more likely process particularly in the corium layer of leather, where fibres can be over 10 cm in length and hence the number fibre ends is limited.

Consideration of how the fibre structure re-organises may answer the following puzzle which has arisen from this investigation. If relaxation is a single stage process on a logarithmic time scale then why is strain recovery a two stage
process on a logarithmic time scale? A possible explanation is that during relaxation the ends of the fibres under strain are constrained between the jaws of the tensile testing machine that hold the sample and hence relaxation by curvilinear diffusion is inhibited. However, when a linear test sample is allowed to recover the ends of the fibres are unconstrained and the fibres are free to curl up as they contract by curvilinear diffusion. In a sample of dry leather the number of fibre free ends will be limited by the presence of inter-fibre adhesions. Inter-fibre friction may also inhibit curvilinear diffusion. The removal of this mechanism may give rise to the long term set found in the drier samples of this investigation.

Figures 4.3 to 4.6 show that periods of relaxation exceeding 10 minutes resulted in greatly increased amounts of long term set. A possible explanation for this observation is that the driving force, the reduction of the internal energy of the fibres that causes a fibre to contract by curvilinear diffusion, is removed over a prolonged period of relaxation by intra-fibre structural re-arrangement.
5 THE INFLUENCE OF STRAIN

In this chapter the influence of strain on relaxation and recovery of partially processed leather is examined. Also, the stress-strain, relaxation and recovery behaviour of the grain and corium layers are compared to leather of standard thickness. The role played by elastin in the recovery of partially processed leather is also reported.

5.1 EXPERIMENTAL

The four similar experiments are described in chronological order.

i. A matched side experiment was carried out in which the effects of applied strain on the relaxation and recovery of wet partially processed leather were compared. Wet (67% moisture content) strips were cut from the right hand side of the lower portion of the official sampling position (O.S.P) and dry (20% moisture content) strips were cut from the left hand side of this region. The fatliquored leather used was the same piece from which samples were cut for the investigation of hold time reported in chapter 4. Both parallel and perpendicular orientations were considered in the design of this experiment. Test strips were cut and strained to a designated applied strain at a rate of 100%
min⁻¹ and held at the designated applied strain for 600 s. Applied strains of 2, 5, 10, 15, 20, 25, 30, 40, and 60% were used. Three representative samples were tested for each applied strain, at each moisture content and orientation.

ii. A map of the topographical variation (in both parallel and perpendicular orientations) of the shape of the stress-strain curves as characterised by the turnup strain, was achieved by straining strips of wet leather, to break at a rate of 100 % min⁻¹. The sample strips were spaced at 20 cm intervals in both parallel and perpendicular directions. The samples were tested with a moisture content of 67%. This map was used to find an area where the turnup strain was significantly higher than the 15-20% strain found for samples cut (in both parallel and perpendicular orientations) from the lower portion of the O.S.P. A new position (N.P.) was located where the turnup strain for samples strained perpendicular to backbone was between 35% and 40%. From this new position three representative wet samples were strained to each of the designated applied strains in an identical stress relaxation and recovery test.

iii. To investigate the role played by elastin in the recovery of partially processed leather, a matched side experiment was carried out. This compared the variation of the relaxation and recovery with applied strain of wet partially processed leather bated with 0.1% of a commercially
available enzyme with elastase activity for 2hrs to that of the control subjected to a standard bating procedure. (See Chapter 2 section 2.2.1). Staining with orcein showed that elastin fibres were present in the material produced by the standard pancreatic bating process and absent from that treated with the special enzyme. The material for this comparison came from the neck region of the hide.

iv. The dependence on applied strain of the relaxation and recovery behaviour of wet leather with a standard thickness of (-2.2 mm) was compared with that of isolated layers of grain, (-0.8 mm), and corium (-1.4 mm). Strips were tested in the direction parallel to the backbone. The standard thickness samples were cut from the right-hand side official sampling position as a control while the left hand side official sampling position was split into grain and corium layers. The applied strains used in this comparison were 5,10,15,20,25,30,35%. Higher strains were not used because the samples of corium material broke at around 40% strain. A similar comparison of the relaxation and recovery behaviour of dry (20% moisture content) leather was made. The material for this comparison was taken from a region the same distance from the backbone as the official sampling position but displaced 80 cm towards the neck from the point A (defined in IUP/2). The dry corium samples were found to break at an applied strain of 20%
5.2 THE EFFECTS OF STRAIN ON SAMPLES OF STANDARD THICKNESS

5.2.1 VARIATION OF SET WITH APPLIED STRAIN

The variation of set with applied strain for wet samples strained parallel to the backbone taken from the O.S.P is shown Figure 5.1. Curve a shows that the relationship between immediate set and applied strain is linear for this group of samples and that there is a threshold strain of about 4% below which no set at all is imparted. Curve c shows that the set remaining after one day is almost zero below 20% strain and increases linearly with applied strain above 20% strain. Within the limits of experimental error no difference in set was found between the set measured after a day and the set measured after a week. The set after one day is thus defined as the long term set in this chapter. Curve b shows the variation of the delayed 2 minute set with applied strain. Above 5% but below 15% applied strain the delayed set is small but finite. Around 20% applied strain the set increases rapidly and appears to vary linearly with applied strain between 25 and 40% applied strain. The intercept of the line drawn through the points for 5, 10 and 15% applied strain with the line drawn through the points for 25, 30, 40% applied strain again suggest a critical strain threshold of 20%. Above 40% applied strain, the set increases less rapidly with applied
Figure 5.1
Variation of set with applied strain in wet samples a) immediately, b) 2 minutes and c) 1 day after release.

Figure 5.2
Recovery of comparative set in wet samples strained to a) 10%, b) 15%, c) 20%, d) 25%, e) 30%, f) 40%, g) 60% applied strain, (model curves fitted through experimental data points).
strain. The delayed set after 10 minutes and one hour was measured. The shape of these curves is not recorded here but are similar to curve b and both lie between curves b and c.

Comparison is made in figure 5.2 of the shape of the recovery curves for the range of applied strain 10%-60% by plotting the comparative set against the logarithm of recovery time. These recovery curves have the same shape. That is they show a rapid logarithmic rate of recovery over the first 100 s followed by a less rapid rate of decay. After 100 s, samples strained above 20% strain appear to recover less rapidly than samples strained below 20%.

The relationship between applied strain and set in dry samples strained parallel to the backbone is shown in figure 5.3. Curve a shows that as for the wet samples the relationship between immediate set and applied strain is linear and the curve intercepts the applied strain axis around 4% strain. Curve c shows that, unlike the wet case, the one day set below 15% applied strain is finite and that the relationship between set and applied strain seems parabolic. Curve b for the delayed set after 2 minutes also fits this description. The intersection of the line drawn through the points for 5, 10 and 15% applied strain with the line drawn through the points for 25, 30, 40% applied

13For clarity these lines are not drawn on figure 5.3
Figure 5.3
Variation of set with applied strain in dry samples a) immediately, b) 2 minutes and c) 1 day after release.

Figure 5.4
Recovery of comparative set in wet samples strained to a) 5%, b) 10%, c) 15%, d) 20%, e) 25%, f) 30%, g) 40%, h) 60% applied strain, (model curves fitted through experimental data points).
strain suggests, as in the wet case, a critical strain threshold of 20%. Figure 5.4 shows the recovery of the set in the dry samples over time. The variation in one day set with applied strain for wet samples is distinguished from that for dry samples in figure 5.5. Only between 10% and 25% strain is there significant difference within the limits of experimental error between curve a for dry sample and curve b for wet samples.

5.2.2 DEPENDENCE OF STRESS AND RELAXATION ON APPLIED STRAIN

Figure 5.6 curve a shows the relationship between the stress at the start of relaxation as a function of applied strain for the dry samples. In similar experiments on biomaterials [SILVER] this curve is known as "elastic stress-strain curve". Curve b in figure 5.6 shows the stress at the end of relaxation as a function of applied strain which is called in the biomaterials literature [SILVER] the "viscous stress-strain curve". Curves c and d are the viscous and elastic stress-strain curves for the wet samples. The equation for a parabola can be fitted to all these curves. In chapter 1 section 1.3.1 the turnup strain was defined as the intersection of the tangent fitted to the low strain region of the curve and the tangent fitted to the high strain region of the curve. For the elastic stress-strain curves the turnup strain is around 20% strain while the turnup strain for the viscous stress-strain curves is nearer 25% strain.
**Figure 5.5**
Comparison of one day set between a) dry and b) wet samples strained parallel to the backbone.

**Figure 5.6**
Elastic and viscous stress-strain curves for samples strained parallel to the backbone; a) elastic dry b) viscous dry, c) elastic wet d) viscous wet.
The variation of reduced stress with applied strain is shown in Figure 5.7. Curve a shows that, for dry samples, as the applied strain is increased from 0% the reduced stress falls from an initial value of 0.75 to a minimum value of 0.65, between 15 and 20% applied strain, then rises again reaching the initial value again near 40% applied strain. For wet samples, curve b, as the applied strain is increased from zero the reduced stress falls from an initial value of 0.7 and levels out to a value of 0.55 at around 20% strain.

The threshold strain (20%), above which there is a significant amount of long term set (see figures 5.1 and 5.3) in wet leather is effectively the same as both the critical strain at which the reduced stress is a minimum or levels out (figure 5.7) and also the turnup strain on the elastic stress-strain curve (figure 5.6).

Samples strained perpendicular to the backbone from this portion of the official sampling position had the same turnup strain for the stress-strain curves as did parallel samples. Perpendicular samples also had identical recovery behaviour within the limits of experimental error (i.e. the perpendicular results were identical to those shown in figures 5.2 and 5.3). The perpendicular samples showed a variation of R(600) with applied strain very similar to that shown in figure 5.7 for parallel
Figure 5.7
Variation of reduced stress $R(600)$ with applied strain for a) dry and b) wet samples strained parallel to the backbone.

Figure 5.8
Variation of relaxation modulus $G(600)$ with applied strain for a) dry and b) wet samples strained parallel to the backbone.
samples. (i.e. the same critical strain for minimum $R(600)$ could be assigned). This observation further supports the contention that turnup strain in the stress-strain curve relates to the onset of more permanent set for wet material.

One way of assessing the linearity of a viscoelastic material is to determine if the relaxation modulus $G(t)$ (the stress at time $t$ divided by the applied strain) is invariant with applied strain. The relaxation modulus $G(600)$ of dry material, figure 5.8 curve a, above 25% strain increases with applied strain. However, between zero and 15% applied strain $G(600)$ for dry leather decreases with applied strain. Only within the region 15-25% is $G(600)$ for dry samples approximately constant. A parabola can be fitted to curve b on figure 5.8. For wet leather the relaxation modulus $G(600)$, curve b on figure 5.8, appears to increase linearly with applied strain and there is no region where the quantity $G(600)$ is strain independent.

5.2.3 TOPOGRAPHICAL VARIATION OF THE SHAPE OF THE STRESS-STRAIN CURVE

In the previous sections it has been suggested that permanent set in wet leather is associated with the turnup in the stress-strain curve. However, to confirm this view it was essential to find a region from which a set of samples with a significantly different
turnup strain could be taken. Therefore, the turnup strain was mapped together with the failure stress and strain around a side.

A map of the variation of turnup strain as a function of position around the hide for wet samples is illustrated in figure 5.9 for, (a) parallel (b) perpendicular orientations. The point 0,0 has the same meaning as the point "A" in the definition of the official sampling position, that is the point which is one third the length of the backbone (in the x-direction) from the butt and 5 cm out from the backbone (in the y direction). In the belly region of the hide in the perpendicular direction the turn up strain is above 40%. This appears to correlate with the high elongation to break (> 100%) which was found in samples strained from this region (see figure 5.10 part a ) The turnup strain has its lowest value of around 15% for both orientations in the region just behind the neck. This may correlate to the rather low elongation to break (-60%) found for samples from this region. In the parallel direction, over the region defined by the rectangle x=-50 to 50 and y=0 to 60, the turnup strain is in the range 20-30% (see figure 5.9 part a ). The elongation to break within this region is more variable and ranges from 60 to 100%, is highest (80-100%) within the official sampling area.

Tensile strength is mapped for parallel and perpendicular orientations in figure 5.11. Within the official sampling area
**Figure 5.9**

Variation of turnup strain with position around the hide a) parallel to the backbone b) perpendicular to the backbone.
Figure 5.10  (a)
Variation of elongation to break with position around the hide a) parallel to the backbone b) perpendicular to the backbone
Figure 5.11

Variation of failure stress with position around the hide a) parallel to the backbone b) perpendicular to the backbone
the tensile strength in the parallel direction, (see part a of figure 5.11), is consistently high and between 17 and 20 MPa. The lowest tensile strength, 8 MPa was found for samples tested in the perpendicular direction, (see part b of figure 5.11 ) cut from the belly region. Samples taken from the region just behind the neck in both parallel and perpendicular direction also had high tensile strengths, of between 17 and 20 MPa. From the topographical study the region "NP" marked on figure 5.9 was chosen as a region within which the turnup strain was significantly different from that found for material taken from the official sampling position. Within the region NP, from which samples were cut, the turnup strain did not vary significantly.

5.2.4 THE VARIATION OF STRESS, RELAXATION AND SET WITH APPLIED STRAIN USING MATERIAL FROM ALTERNATIVE SAMPLING POSITION (NP).

Figure 5.12 compares the elastic stress-strain curve a for the original group of wet samples taken from the official sampling position (strained parallel to the backbone) with curve b for wet samples taken from the alternative sampling area (NP) (strained perpendicular to the backbone). Samples taken from the alternative sampling area have a much higher turn-up strain of 37% in comparison to the value of 20% found for the samples taken from the official sampling position.
Figure 5.12
The stress-strain curves for wet samples a) from O.S.P strained parallel to the backbone b) from N.P strained perpendicular to the backbone.

Figure 5.13
Variation of set with applied strain in wet samples a) immediately, b) 2 minutes and c) 1 day after release for samples taken from area N.P.
A threshold strain of 5% below which there is no immediate set is again seen for curve a in figure 5.13. This curve shows a linear relationship between applied strain and immediate set for samples from this alternative region. Curve c in figure 5.13 shows that the variation of one day set with applied strain is "J shaped" and pinpoints a critical strain threshold of 40% strain above which the rate of increase of set with applied strain increases dramatically. This threshold value is close to the turnup strain identified in figure 5.12.

In figure 5.14 a comparison is made of the variation of reduced stress, $R(600)$ as a function of applied strain for the group of samples from the alternative area NP, curve b with that for samples taken from the official sampling position, curve a. The value of $R(600)$ from area NP is 0.05 higher than that of the original group over the whole range of applied strain. The critical applied strain at which $R(600)$ levels out appears somewhat higher (~27%) from area NP compared with the official sampling position sample group (~17%). The critical strain for the NP samples derived from figure 5.14 is not as high as either the turnup strain (figure 5.12) or the critical strain threshold indicated in figure 5.13 for the set data. This was not the case for the material taken from the O.S.P where all three critical strains were similar.
Figure 5.14
Comparison of the variation of $R(600)$ between stress-strain curves for wet samples a) from O.S.P strained parallel to the backbone and b) from N.P strained perpendicular to the backbone.

Figure 5.15
Comparison of wet stress-strain curve for a) control (pancreatic bate) samples to that for b) enzyme (elastase) treated samples.
5.2.5 THE EFFECTS OF ELASTIN FIBRE REMOVAL

In the discussion of chapter 3 it was suggested that a network of elastin fibres could be responsible for recovery. This section discusses the effect on recovery of elastin removal.

Comparison of stress-strain curves is made on figure 5.15 for material treated with the special elastase enzyme, curve b with curve a for control material treated with the standard pancreatic bate. The stress at any particular applied strain for the samples treated with the special enzyme is approximately one tenth of its control. If the stress at any applied strain is normalised with respect to the stress at 40% strain then within the limits of experimental error the shapes of the two curves are the same and have a turnup strain of 15%.

The immediate set for the enzyme treated material, curve a on figure 5.16, shows the same variation with applied strain as its control, figure 5.17, curve a. In other words a linear variation with applied strain above a low threshold strain of 5%. The set after one day for both the enzyme treated material (figure 5.16 curve c) and its control, (figure 5.17 curve c), show considerable similarity. That is, as reported for other samples, low amounts of one day set below a certain strain threshold (here 20% strain) are observed.
**Figure 5.16**
Variation of set with applied strain in enzyme treated wet samples a) immediately, b) 2 minutes and c) 1 day after.

**Figure 5.17**
Variation of set with applied strain in wet control (pancreatic bate) samples a) immediately, b) 2 minutes and c) 1 day after release.
The variation of reduced stress with applied strain for special enzyme treated samples and control samples is similar. This variation, reported on figure 5.18, levels out between 15 and 20% applied strain. $R(600)$ in the level region is higher for the control samples, (at 0.65), than for enzymatically treated samples, (0.57).

5.3 THE EFFECT OF STRAIN ON PARTIALLY PROCESSED LEATHER OF STANDARD THICKNESS IN COMPARISON WITH ITS EFFECT ON ISOLATED LAYERS OF GRAIN AND CORIUM

To identify if grain layer and corium layer have different influences on the mechanical properties of partially processed leather the rheology of individual layers was studied experimentally. The observations on isolated layers in comparison to standard thickness material are now presented.

5.3.1 STRESS-STRAIN BEHAVIOUR

Below 20%, strain the stress-strain curve of a wet sample of standard thickness (control) leather curve a in figure 5.19, overlies curve c for the wet corium sample. However, curve a in figure 5.19 is distinct from curve b for a wet grain sample. The turnup strain for the wet grain sample is 30%, but it is nearer 10% for the corium and control samples. Curve d is derived from
Figure 5.18
Comparison of variation of $R(600)$ for wet a) control (pancreatic bate) samples to that for b) enzyme treated samples.
Figure 5.19
Comparison of the stress-strain curves for isolated layers, standard thickness and laminate model samples: 
a) wet standard thickness, b) wet grain c) wet corium 
d) wet model e) dry standard thickness, f) dry grain, g) dry corium, f) dry model

Figure 5.20
The low strain regions of the stress-strain curves for dry samples of layers a) standard thickness, b) grain, c) corium, d) model
a very simple laminate model in which the stress at a particular applied strain in the sample of standard thickness is estimated from the sum of the load in the grain sample and the load in the corium sample divided by their combined cross sectional area. This model does not fit experimental observations since at no point along its course does curve a overlie curve d.

Curve a in figure 5.19 shows the stress-strain curve of a dry control sample of standard thickness leather. This curve is distinct from curve f for a dry grain sample and curve g for a dry corium sample. The same simple laminate model was used to generate curve g as was used to obtain curve d. At strains below 5% curve g does indeed overlie curve e. This agreement is shown more clearly in figure 5.20 where the region below 10% is magnified to emphasise the yielding phenomena that is absent in all the samples of wet leather but present in the dry samples around a yield strain of 3%. Yielding is more pronounced in the grain (yield stress of 1.3 MPa) compared with the corium (yield stress of 0.4 MPa).

The effect of cycling between 0 and 10% strain is shown in figure 5.21 for samples of grain and figure 5.22 for samples of corium. Both figures can be compared with that reported earlier in Chapter 3 (figure 3.21) for standard thickness samples. The yield region of the stress-strain curve for the first extension, curves
Figure 5.21
Cycling around the yield point of a dry grain sample
a) first extension b) second extension c) first retraction d) second retraction

Figure 5.22
Cycling around the yield point of a dry corium sample
a) first extension b) second extension c) first retraction d) second retraction
a, is absent from the second extension, curves b. The shape of the stress-strain curve for the second extension of the grain sample is linear while the second extension curve of the corium, figure 5.22 curve b is concave downwards towards the strain axis.

5.3.2 CHANGES IN LATERAL DIMENSIONS WITH APPLIED STRAIN

Application of strains above 10% produced lateral contractions and these were measured using vernier calipers. In both dry and wet samples of standard thickness, the lateral contraction in the front surface of the grain was greater than the contraction of the back surface of the corium. Consequently, at high strains these samples were noticeably concave with respect to the front of the sample. In isolated grain material a difference in lateral contraction between the front (i.e. the surface of the grain) and back, (i.e. the grain corium junction) was evident in wet samples but not apparent in dry samples. Similarly, in isolated corium material a difference in lateral contraction between the front surface, (i.e. the grain corium junction), and the back was again evident in wet samples but not measurably different in dry samples. Figure 5.23 shows the lateral strain as a function of applied strain for wet samples. Curve a for the front surface of the standard thickness control lies between curves c and d for the front and back surfaces of the grain samples respectively, while curve b for the back surface of the control lies between
**Figure 5.23**
Variation of lateral strain with applied strain in wet samples: standard thickness a) front b) back; grain c) front, d) back; corium e) front f) back

**Figure 5.24**
Variation of lateral strain with applied strain in dry samples: standard thickness a) front b) back; c) grain d) corium
curves e and f for the front and back surfaces of corium samples respectively. The lateral strain as a function of applied strain for the dry samples is shown in Figure 5.24. Curve b for the back of the control samples lies close to curves c for the grain sample and curve d for the corium sample, while curve a for the front of control is distinct.

When the applied strain was removed any lateral strain was eventually recovered by wet samples, even those strained to 35% strain, while dry standard thickness and grain samples strained above 15% the samples had residual lateral strain after a week.

5.3.3 RELAXATION

Reduced stress is plotted as a function of applied strain in figure 5.25 for wet samples. The variation for standard thickness samples, curve a is compared with that for samples of grain, curve b, and corium, curve c in this figure. As the applied strain is increased from 5 to 15%, R(600) drops; from 0.85 to 0.60 for the grain samples; from 0.75 to 0.475 for the corium samples and from 0.775 to 0.55 for the standard thickness control. Over this range the curve for the standard thickness lies between curve b for the grain and curve c the corium. Above 20% applied strain R(600) for the corium (curve c) is 0.45. As the applied strain is increased from 20 and 35%, curve b continues
Figure 5.25
Variation of reduced stress $R(600)$ with applied strain for wet samples of a) standard thickness, b) grain, c) corium

Figure 5.26
Variation of reduced stress $R(600)$ with applied strain for dry samples of a) standard thickness, b) grain, c) corium
to fall (albeit at a much slower rate than between 5 and 15% applied strain) to 0.55 while the reduced stress in the standard thickness sample rises again to 0.60.

Above 27% applied strain, the reduced stress in the standard thickness sample is higher than the reduced stress in the grain sample within the limits of experimental error.

The corresponding plot for dry material to figure 5.25 (for wet material) is figure 5.26. Here, as the applied strain is increased from 2 to 10%, the reduced stress also falls, from a common value of 0.8 at 2% strain to 0.77 for the standard thickness (curve a); to 0.67 for the grain (curve b) and 0.74 for the corium (curve c). As the applied strain increases above 10%, the reduced stress in all the samples rises. The reduced stress in the grain samples seems to level out to a value of 0.8 at 35% applied strain. By 35% strain the reduced stress in the standard thickness sample has reached a value of 0.84.

The decay of the relaxation modulus with log time for wet standard thickness samples is shown on figure 5.27 for each applied strain. All the curves a to g are linear with the logarithm of time and as the applied strain is increased the slope of this line increases. A similar set of relaxations, figure 5.28, for wet grain samples display the same tendencies. However, curves e, f, and g for applied strains of 25, 30 and 35% lie very close to each other. This proximity at high strains may
Figure 5.27
Variation of relaxation modulus $G(t)$ with $t$ for wet standard thickness: applied strain a) 5\%, b) 10\%, c) 15\%, d) 20\%, e) 25\%, f) 30\%, g) 35\%

![Graph showing variation of relaxation modulus $G(t)$ with $t$ for wet standard thickness.](image)

Figure 5.28
Variation of relaxation modulus $G(t)$ with $t$ for wet grain samples (see figure 5.27 for assignments)

![Graph showing variation of relaxation modulus $G(t)$ with $t$ for wet grain samples.](image)

Figure 5.29
Variation of relaxation modulus $G(t)$ with $t$ for wet corium samples (see figure 5.27 for assignments)

![Graph showing variation of relaxation modulus $G(t)$ with $t$ for wet corium samples.](image)
imply quasilinearity [FUNG]. The corresponding figure for the wet corium samples is figure 5.29.

Figures 5.30, 5.31 and 5.32 show the relaxation moduli of dry standard thickness, grain and corium samples respectively. Like the wet samples the moduli for dry material vary linearly with log time over the whole range of applied strains from 2 to 35%. Over the range of applied strains 5-35% the slope of these straight lines appears independent of the applied strain.

According to figures 5.30 and 5.31 the final relaxation moduli $G(600)$ have a similar variation with applied strain to that observed earlier (figure 5.8) for dry samples of standard thickness. An initial decrease occurs with increasing applied strain to a minimum around 10-15% strain following which $G(t)$ rises with increasing applied strain. Such a rise cannot be observed in corium samples which break before an applied strain of 20% is reached.

5.3.4 THE RECOVERY IN GRAIN AND CORIUM IN COMPARISON TO STANDARD THICKNESS MATERIAL

5.3.4.1 WET MATERIAL

The immediate set as a function of applied strain for wet samples is shown in figure 5.33. For the standard thickness control (curve
Figure 5.30
Variation of relaxation modulus $G(t)$ with $t$ for dry standard thickness samples: applied strains a) 2%, b) 5%, c) 10%, d) 15%, e) 20%, f) 25%, g) 30%, h) 35%

Figure 5.31
Variation of relaxation modulus $G(t)$ with $t$ for wet grain samples (see figure 5.30 for assignments)

Figure 5.32
Variation of relaxation modulus $G(t)$ with $t$ for dry corium samples a) 2%, b) 5%, c) 10%, d) 15%
**Figure 5.33**
Immediate set variation with applied strain for wet a) standard thickness b) grain and c) corium samples.

**Figure 5.34**
Two minute set variation with applied strain for wet a) standard thickness b) grain and c) corium samples.

**Figure 5.35**
One day set variation with applied strain for wet a) standard thickness b) grain and c) corium samples.
a) above a threshold of 5% applied strain immediate set increases nonlinearly with applied strain, since there is a toe region between 5 and 10% applied strain. This pattern is slightly different from earlier observations (figure 5.1) where complete linearity is observed. Within the limits of experimental error curve c for corium samples overlies curve a between 5 and 25% applied strain and deviates only slightly above curve a between 25 and 35% strain. Curve b for the grain samples is more strongly "J-shaped", with the toe region extending out to 20% applied strain. Above their toe regions curves a, b and c are linear and have similar slope.

Figure 5.34 compares the variation of the delayed, 2 minute set in the wet samples. Between 5 and 15% applied strain curve a for the control follows curve b for the grain. However, before 20% applied strain is reached curve a deflects towards curve c, for the corium, and joins curve c at around 30% applied strain.

Wet grain samples strained below 35% possessed no set after a day (figure 5.35 curve b). Whereas, the wet samples of standard thickness (curve a on figure 5.35) only had experimentally measurable amounts of one day set above 20% applied strain. However, wet corium samples had significant amounts of one day set above 15% strain (figure 5.35 curve c). At any applied strains above 15%, the one day set for corium samples was higher.
than the one day set in the standard thickness leather.

The recovery of the wet samples can be contrasted by considering the results summarised in figures 5.36, 5.37 and 5.38 in which the comparative set is plotted against log(t) for samples of standard thickness, grain and corium respectively. The set in the grain samples for all applied strains recovers rapidly, completely, and linearly with log(t) over the first $10^3$ s for all values of applied strain. Whereas, the set in the corium decays linearly with log(t) at a much slower rate over $10^4$ s. Above 15% applied strain, the recovery of the standard thickness samples appears to be a two-stage process, reported for all standard thickness samples throughout this study, with an initial rapid logarithmic rate of recovery followed by a slower logarithmic recovery rate.

5.3.4.2 DRY MATERIAL

A straight line can be drawn through all the experimental points on figure 5.39, the plot of immediate set against applied strain for dry grain corium and standard thickness leather. This line intercepts the applied strain axis at 5%. After two minutes recovery, (figure 5.40) this straight line has distorted into a "J-shaped" curve with a toe region between 5 and 10% applied strain. Above 20% applied strain, curve a for standard thickness samples becomes distinguishable from curve b for grain samples
**Figure 5.36**
The recovery of comparative set for wet standard thickness samples: applied strains of a) 10%, b) 15%, c) 20%, d) 25%, e) 30%, f) 35%

**Figure 5.37**
The recovery of comparative set for wet grain samples: applied strains of a) 10%, b) 15%, c) 20%, d) 25%, e) 30%, f) 35%

**Figure 5.38**
The recovery of comparative set for wet corium samples: applied strains of a) 10%, b) 15%, c) 20%, d) 25%, e) 30%, f) 35%
**Figure 5.39**
Variation of immediate set with applied strain for dry a) standard thickness b) grain and c) corium samples

**Figure 5.40**
Variation of two minute set with applied strain for dry a) standard thickness b) grain and c) corium samples

**Figure 5.41**
Variation of day set with applied strain for dry a) standard thickness b) grain and c) corium samples
whilst the lower set after 1 day (figure 5.41) shows a similar trend.

Recovery of the dry samples over time can be contrasted by considering the results shown in figures 5.42, 5.43 and 5.44 in which the comparative set is plotted against log time for samples of standard thickness, grain and corium respectively. All these recovery curves show a similar trend of a rapid logarithmic decay to a certain level over the first 1000 s of recovery followed by a much more gradual decay or levelling off.

5.4 DISCUSSION

Perhaps the most striking experimental observation in this chapter is that first noted in figure 5.1 for wet leather and subsequently in figure 5.3 for dry leather. Namely, there is a critical strain which has to be reached before significant amounts of long term set can be imparted to the leather. The apparent correlation between this critical strain and the turnup strain in the stress-strain curve may help explain why this critical strain threshold is seen. If it is assumed that to obtain permanent set following sample deformation, the fibres themselves have to come under strain, then a feasible explanation could be provided by considering the fibre recruitment model,
Figure 5.42
The recovery of comparative set for dry standard thickness samples: applied strains of a) 5%, b) 10%, c) 15%, d) 20%, e) 25%, f) 30%, g) 35%

Figure 5.43
The recovery of comparative set for dry grain samples: applied strains of a) 5%, b) 10%, c) 15%, d) 20%, e) 25%, f) 30%, g) 35%

Figure 5.44
The recovery of comparative set for wet corium samples: applied strains of a) 5%, b) 10%, c) 15%
used by KRONICK and BUCHLER (1986) to explain the shape of the stress-strain curve of leather (Chapter 1 section 1.3.1.2). The consequence of this assumption is that as the strain is increased not only are more fibres recruited to become load bearing, but also more fibres become plastically deformed. The recruitment model with this modifying assumption predicts that a sample with a higher distribution of slack fibres has a higher turnup strain and a higher critical strain threshold for long term set (as has been observed).

The permanent deformation of a fibre requires a permanent internal rearrangement of its structure. During relaxation it may be expected that the structural elements rearrange to reduce the stress within a fibre. It also seems reasonable to assume that the larger the relative amount of relaxation the greater the amount of structural rearrangement.

Experimental evidence for structural rearrangement on fibril level has been provided by RIEDL et al who have shown that increasing the applied strain in moist rat tail tendon from 0 to 10% results in a change in D period, associated in chapter 1 section 1.4.2 with the staggering of tropocollagen molecules, from 670 Å to 700 Å and that over a 1000 s relaxation in a tendon strained to 5%, the D period falls from 687 Å back to 675 Å in a manner that is linear with log time. In a more recent study,
FOLKARD et al showed that the stretching process is reversible at a molecular level up to 684 Å, corresponding to a strain of 9%.

It has been seen that for wet leather the reduced stress falls with increasing applied strain until a critical value of applied strain is reached when it starts to increase again, albeit at slower rate than at which it dropped (figure 5.14). The original fall may be explained by the recruitment model if two simplifying assumptions are made about the properties of the individual fibre:

i. If the strain in the fibre is below an elastic limit then that fibre is elastic and contributes a fraction of $1/N(\varepsilon)$ of the reduced stress of the test sample;

ii. Above an elastic limit the fibres are viscoelastic and contribute $k(t)/N(\varepsilon)$ to the reduced stress;

Where $N(\varepsilon)$ is the number fibres per unit volume under tension at an applied strain of $\varepsilon$.

At any applied strain within the test sample a total of $N(\varepsilon)$ fibres per unit volume will be under strain of which $N_b(\varepsilon)$ are below their elastic limit and therefore contribute $N_b(\varepsilon)/N(\varepsilon)$ to the reduced stress. Conversely, $(N(\varepsilon)-N_b(\varepsilon))$ fibres will be beyond the hypothetical elastic limit and will contribute $k(t)(N(\varepsilon)-N_b(\varepsilon))/N(\varepsilon)$ to the reduced stress. Therefore, the reduced stress
after a given time of relaxation can be expressed by the following equation.

\[ R(\varepsilon) = \frac{N_{b}(\varepsilon)}{N(\varepsilon)} (1 - k(t)) + k(t) \]  

(5.1)

Close to zero strain \( N_{b}(\varepsilon) = N(\varepsilon) \) and \( R(\varepsilon) = 1 \). Beyond a critical strain all the fibres under strain will be beyond their elastic limit i.e. \( N_{b}(\varepsilon) = 0 \) and \( R(\varepsilon) = k(t) \).

An estimate of \( k(600) \) equal to 0.5 \( R(600) \) at 30% strain obtained from figure 5.14 is approximately equal to that reported by RIGBY et al for reduced stress in rat tail tendon at the two strains (3.5%, 7.5%) after 600 s.

SILVER reports from incremental strain experiments, that the elastic fraction of skin (i.e. \( R \)) actually increases linearly from 0.5 at 10% to 0.7 at 100% strain. For aorta tested axially and circumferentially, the tendency reported by SILVER is more akin to that reported here for wet leather. That is the elastic fraction drops from 0.9 at 5% strain and levels out at 0.8 between 30% and 50% strain. SILVER categorises skin along with aorta as alignable collagen networks. Materials classified by SILVER as aligned collagen networks such as pericardium, psoas major tendon and dura mater have an elastic fraction between 0.7 and 0.8 that is independent of applied strain between 0 and 40%.
The fibre recruitment model of Kronick and Buechler (1986) is a one dimensional model in which the fibres do not interact with each other, and the unbending of the slack fibres does not contribute to the load required to deform the sample. These implicit assumptions may be applicable to soaking wet leather where water occupies spaces in the hierarchical structure and acts as a lubricant on a macroscopic level preventing inter-fibre friction and on a molecular level as a plasticiser making the material rubbery rather than glassy.

The permanent unbending of dry fibres as they are recruited, may account for the greater one day set in dry samples in comparison to that for wet samples observed between 5 and 25% strain, i.e. around the turnup strain, on figure 5.5. The mechanism for this plastic unbending is likely to involve the rupture of intra-fibre adhesions. At strains well above the turnup strain the plastic tensile deformation of fibres, may dominate over the plastic unbending of dry fibres as a mechanism for set. The insensitivity of the high strain moduli to moisture content reported in chapter 3, figure 3.11 suggests that the dominant mechanisms of tensile deformation in wet and dry fibres may be similar. Therefore, above the turnup strain a similar variation of long term set with applied strain in wet and dry samples might be expected.

The difference in the variation of R(600) with applied strain
between that observed for dry samples (curve a on figure 5.7) and that observed for wet samples (curve b on figure 5.7) may be explained qualitatively using the following semi-rheological model. In this model the description of the mechanical behaviour of the recruited fibre is modified from the elastic string of KRONICK and BUECHLER (1986) as follows:

i. At very low strains a slack dry fibre resembles a bent leaf spring and provides an elastic contribution to the reduced stress of the whole sample;

ii. The fibre unbends until it loses its spring-like character when it reaches a critical nominal yield strain. The fibre then contributes to the relaxation of reduced stress;

iii. At higher strains the fibre becomes straight and resembles a wire below its elastic limit and again makes an elastic contribution;

iv. The fibre reaches its tensile yield strain and again contributes to the relaxation;

v. The fibre breaks and makes no further contribution to the reduced stress.

Figure 5.45 illustrates these stages of deformation. Stage i, the elastic unbending, may occur in wet material. However, the absence of brittle intra-fibre adhesions within the structural hierarchy of wet fibres will lower the bending modulus and prevent stage ii from occurring in wet samples. Consideration of
Figure 5.45
The modified recruitment element
Stages (i) and (ii) therefore make clear why the reduced stress at 5% applied strain is initially higher in the dry case in comparison to the wet case (curve b in figure 5.7), and also why in the dry case R(600) falls less rapidly with increasing applied strain to the minimum level. Combination of stages (ii) and (iii) accounts for the much greater increase in the value of R(600) seen in figure 5.7 above 20% applied strain for dry material compared with wet (figure 5.7). Stage (iv) in the deformation of the element would suggest that R(600) should level out or even begin to drop at high applied strains. There is an indication that for dry material this indeed occurs above 40% strain (see curve a, figure 5.7).

A threshold strain below which no immediate set is seen was reported on figures 5.1 for wet leather and 5.3 for dry material. This suggests that the deformation is purely elastic below 5% strain. This simple assumption is somewhat contradicted by the fact that the reduced stress is still considerably below 1, the value for a perfectly elastic material, for both wet and dry samples at 5% strain (figure 5.7).

The fibre orientation model, introduced in chapter 1 section 1.3.1 has no component that provides the restoring force required for recovery. However, the representation of the collagen fibres by straight rigid rods in the orientation model is an over
simplification. A modification of the established model is proposed in figure 5.46a which allows for the possibility that collagen fibres between hinge points may need to unbend before the network can align in the direction of the applied strain. If the bending of the fibres is reversibly elastic, this model might explain the existence of the lower strain threshold of 5% below which there is no immediate set. However, it might be expected that a greater variation in the low strain threshold value should exist from one set of samples to another.

Plastic unbending, caused by the rupture of intra-fibre adhesions in dry leather, may be associated with the existence of a yield. The onset of the yield in dry material is around 2-3% in comparison to the 5% immediate set threshold. These observations may suggest that plastic unbending commences at around 2% applied strain and is complete at 5% where all the fibre elements between network junction points, (that may or may not be inter-fibre adhesions) are straight.

Breaking of fibres and inter-fibre adhesions at strains well below failure may free individual fibres. If this is the case the orientation model will degenerate into the recruitment model as illustrated in figure 5.46b. Acoustic emission data published by KRONICK and MALEEF provides evidence for the rupture of fibres before failure in dry leather. Figure 5.47 suggests that
Figure 5.46
Modification to the fibre orientation model a) at low strains showing that fibres between hinge points need to unbend before orientation occurs and b) at high strains where the orientation model degenerates into a recruitment model due to the rupture of fibres and interfibre adhesions.
Figure 5.47
The acoustic emission signal from a sample of wet leather a) The number of hits and b) The relative energy.
fibres also break well before the failure strain in wet leather. This figure also suggests that considerable acoustic emission only starts to occur once the turnup strain is reached. Fibre breakage is a possible mechanism for permanent set in leather above the turn up strain. Such a mechanism would of course be expected to weaken the leather.

A possible modification of the orientation model to explain recovery is to introduce a subnetwork of elastic elements that bridge the collagen fibres represented by the rigid rods and so provide a restoring force. (figure 5.48).

In chapter 3, reasons were put forward as to why in the early stages of this investigation, the presence of intact elastin was believed to explain recovery, at least at low strains, in partially processed leather. In this investigation orcein staining of partially processed wet blue leather which had been processed with a regular, pancreatic bate, showed that elastin fibres are still present at the grain-corium boundary. This is in accord with the findings of ALEXANDER et al (1991).

The results of this investigation show that the recovery behaviour (Figure 5.16) of material treated with the specialised enzyme to remove all the elastin is very similar to the recovery of the standard bated control material (Figure 5.17). This
Figure 5.48
Schematic diagram illustrating how a network of collagen fibres may be bridged by a sub-network of finer fibres a) which straighten as the network deforms b) and eventually yield and rupture.
observation suggests that elastin fibres have little if any effect on the recovery of set in partially processed leather. ALEXANDER et al (1991) found that removing elastin does increase area yield but associate this with changes in thickness caused by a collapse in the three-dimensional fibre weave rather than with any direct effect on the viscoelasticity.

The leather manufacturing process might downgrade the elastic properties of elastin such that it becomes much more viscoelastic. Possible mechanisms for this degradation maybe chain scission and cross-linking at a molecular level. However, there is no evidence in the literature that the beamhouse processes result in chain scission. Moreover, elastin is nonpolar and does not react with chromium(III) [HEIDEMANN 1993].

If elastin fibres are ruled out as responsible for recovery then the network of collagen fibres could be bridged by a subnetwork of smaller viscoelastic collagen fibres where the mechanism of recovery is the tendency of the smaller fibres to return to their initial bent configuration. VIIDIK highlights a similar controversy in the study of soft tissue. Most authors working on tendon, such as MINNS et al believe that resistance to uncrimping and subsequent recrimping during the recovery is due to presence of elastin fibres bridging the undulating collagen fibres. However, others such as BROOK, working on heart valve leaflet
tissue, attribute recovery to resistance to changes in internal stresses within the collagen fibres themselves.

Leather is typically a natural laminate comprising grain and corium layers. However, there is a gradual change from the coarse weave to the fine weave of the grain. The fibre bundles in the corium layer of the material used in this investigation were found, using scanning electron microscopy, to have a diameter between 50-100 μm. These bundles are much thicker than the fibres within the grain layer, which from the electron micrographs were measured to be 2-5 μm. The structural elements that form the grain layer have approximately the same diameter (5 μm) as the fibres (or fibril bundles) reported by STANLEY that intertwine to form the fibre bundles. The grain layer and a corium bundle may in general be considered as being at the same level of structural hierarchy. However, the uppermost layers of the grain may be lower down the hierarchy and are even made from a different type of collagen (collagen III) and may have a two-dimensional weave [HEIDEMANN 1993]. Regarding standard thickness leather as a bi-layer composite in which the fibres of the grain behave as a viscoelastic subnetwork effectively bridging the coarser network of corium fibres may be a simplification of a complex material. However, it does offer a conceptual framework that may explain some of the results of this investigation.
A consequence of the bilayer model would be that removing the grain layer should inhibit recovery of the remaining isolated layer of corium fibres and conversely the recovery of the isolated grain layer will be promoted by its separation from the corium layer. This consequence is indeed observed in figure 5.35 for wet samples where the grain (curve b) shows full recovery after a day, whilst the corium (curve c) has higher one day set than the standard thickness sample (curve a)

The higher value of reduced stress found for samples of wet grain in comparison to samples of wet corium (figure 5.25), implies that this layer has a greater elastic component compared with the corium over the range of applied strains examined. In accordance with the discussion of the Maxwell model, in chapter 4, there should be a greater amount of immediate set in the corium layer than in the grain layer, which is indeed observed (figure 5.35) for samples of wet leather. If there is a greater elastic contribution to the recovery, then by the simple Voigt model the recovery of the grain layer should be faster than the recovery of the corium layer. This is evident when figures 5.37 and 5.38 are compared. Figure 5.37 indicates a time scale less than 10^3 s for the recovery of wet grain samples, whereas figure 5.38 shows that the recovery is over an order of magnitude greater for wet corium samples. At low strains, between 5 and 15%, the set of the bilayer standard thickness wet leather is dominated by the grain.
but as the strain increases above, 20% strain, the corium layer appears to dominate the set. The grain layer's loss of dominance can only be partially explained by the loss of the elastic component associated with the drop in reduced stress between 5 and 15% applied strain. The strain above which the corium dominates the set is again 20%, the turnup strain. Above this strain, the set becomes more "permanent". This longer term set is due to the majority of corium fibres coming under strain. At the turnup strain the majority of the smaller grain fibres may become unbent and some may start to rupture. Another possibility is that the bi-layer composite delaminates by the rupture of interweaving fibres and inter-fibre adhesions at the grain corium boundary. Thus above the turnup strain, the major contribution to the set may be the tensile deformation of the fibre bundles in the corium layer.

It is evident from figure 5.41 that the ability of the wet grain layer to recover from significant amounts of applied strain is absent in the dry grain. The probable reason for this observation has already been put forward in the discussion of the modified recruitment model (figure 5.45) used to describe the behaviour of standard thickness material. That is, the formation of intra-fibre adhesions prevents the fibres comprising the grain layer from behaving like an elastic leaf spring and makes it behave more like a yielding plastic beam.
WARD AND BROOKS (1965) examined the effect of splitting dry, (~3mm thick) unfinished leather on the 0-10% region of the stress-strain curve (testing carried out at 30 C and 60RH). Three 1 mm thick layers were produced and labelled grain, middle and flesh splits. However, the term “flesh split” was a misnomer and the back of this layer was not the flesh side of full thickness leather. This layer actually corresponds to the centre of the corium layer in full thickness material. In figure 5.20 at 5% strain the stress in the dry grain is greater than the stress in the standard thickness material which itself is greater than that in the corium. WARD AND BROOKS (1965) original observations for crust leather at 5% strain show that there is more stress in the grain layer than in a standard thickness sample. Moreover, at 5% strain the stress in the middle and flesh layers was found by WARD AND BROOKS (1965) to be less than the stress in the standard thickness material. The findings shown in figure 5.20 are consistent with those of WARD AND BROOKS (1965).

Curve d on figure 5.20 shows the prediction of the two layer laminate model, that sums the relative contributions of the grain and corium layers to give the stress at a particular value of strain, for dry whole leather. Comparing this prediction with the stress-strain curve for dry standard thickness material there is good agreement below 5% strain. Likewise, WARD AND BROOKS (1965) compared the predictions of a laminate model that
summed up the relative contribution of the stress between 0 and 10% applied strain of up to as many as five layers to the observed behaviour of standard thickness material. They found that increasing the number of laminae decreased the stress at any particular value of strain and attributed this to the freeing of fibres that weave the layers together from frictional interaction as they move within the other layers. Below 5% strain in isolated layers of dry leather the movement of fibres may be freed by chopping fibres in delamination (i.e. they do not interact frictionally). However, inter-fibre adhesion within an isolated layer of dry material at low strains imposes far greater restriction on the movement of fibres. Beyond 5% strain some of the adhesions will have ruptured and this may explain why on figure 5.20 above 5% strain the stress predicted by the model is less than the stress in a standard thickness sample. In wet material inter-fibre adhesions are absent, thus freeing of fibres by delaminating may have a significant effect. Indeed, the stress at a particular value of strain predicted by the laminate model for wet samples (see curve d on figure 5.19) is considerably less than the experimentally measured stress in a wet standard thickness sample (curve a on figure 5.19).

The pronounced yield found for dry grain samples on figure 5.20 was not observed by WARD AND BROOKS (1965) in their initial investigation. However, later curves reported by WARD AND
BROOKS (1967) do show a definite yield. MARRIOT attributes the larger, low strain modulus (60-70 MPa) found by WARD and BROOKS (1967) in yielding grain layers in later work on commercial leathers to presence of impregnants. MARRIOT's thesis is that impregnants are a deliberate source of adhesions introduced by the leather manufacturer to produce firmer leathers.

Why is the yielding more pronounced in the grain layer than in the corium layer? A potential explanation is that the grain layer, having a tighter weave, has a greater number of fibre intersections than the corium layer and consequently there is a higher population of inter-fibre adhesions in the grain resulting in the more pronounced yield.
6 DRYING UNDER STRAIN

In this chapter the effects on the rheological characteristics of drying partially processed leather are explored. Moreover, the influence on the mechanical behaviour of drying isolated layers of grain and corium is compared with that of drying leather of standard thickness under an applied strain.

6.1 EXPERIMENTAL

6.1.1 DRYING STRIPS OF PARTIALLY PROCESSED LEATHER UNDER STRAIN

The sampling material for these experiments was obtained from the Official Sampling Position (O.S.P) of two wet unfatliquored hides.

From the O.S.P of one hide eight 25 X 300 mm strips were cut in the direction parallel to backbone. These samples were soaked in distilled water for more than 16 hours at 20 C. The surface of the samples was blotted and two bench marks with a spacing of 100 mm were drawn on the central portion of each sample. This spacing was verified by measuring the separation of the bench marks with vernier calipers. One strip was allowed to dry without constraint, the remainder were dried under various strains using
the SATRA linear plasticity apparatus [BUTLIN]. Each strip was strained, by hand turning the screw of the apparatus to achieve the required strain, which was confirmed by measuring the separation of the bench marks using vernier calipers. After the samples had been dried under strain for a week, the separation of the bench marks was remeasured and any change in lateral dimensions noted. The samples were released from the linear plasticity apparatus and any subsequent change in the bench mark separation and lateral dimension was monitored over the course of a day. The set in the samples after a day was defined as the dried in "Prestrain". Applied strains of 0, 5, 10, 15, 20, 25, and 30% resulted in prestrains of 0, 4, 9, 14.5, 19, 23 and 26.8%. The unconstrained sample had a prestrain of -5%.

In the next series of experiments, strips were cut in the direction perpendicular to the backbone from the right hand side of the O.S.P. of the second hide and then dried under strain. Applied strains of 0, 5, 10, 15, 20, 25, 30, 40% produced prestrains of 0, 5, 9.7, 15, 19.7, 25, 28.6, 35.5 % respectively and the unconstrained sample had a prestrain of -4.4%.

The O.S.P of the left hand side of the same hide was split into isolated grain and corium layers from which the 25 x 300 mm strips were cut and dried under strain. Applied strains of 0, 5, 10, 20, 30, and 40% resulted in prestrains of 0, 3.5, 10, 19.7, 24.6 and 35% in grain samples and in corium samples these
applied strains produced prestrains of 0, 5, 10, 19, 26.6, and 37%. Drying grain strips without constraint resulted in a prestrain of -6.2%, whilst drying corium strips without constraint resulted in a prestrain in corium samples of -4.5%.

6.1.2 CUTTING AND TESTING SAMPLES FROM STRIPS DRIED UNDER STRAIN

Each strip dried under strain was just long enough for two dumbbell shaped samples to be cut from either end and to leave behind a central portion, approximately 150 mm in length. From this remaining portion a narrow, 10 mm, strip was cut. The axes of the dumbbell samples and the narrow strip was the strain axis of 25 mm wide strip.

One dumbbell shaped sample was strained to break at a rate of 100% min⁻¹ to define the effect of drying under strain on the shape of the stress-strain curve. The other dumbbell sample was cut from lower portion of the strip after it had been soaked in distilled water for over a week. This was also strained to break at a rate of 100% min⁻¹ to see if the effects of drying under strain on the shape of the stress strain curve could be countered by rewetting.

The 10 mm wide strip was subjected to the following test procedure:-
i. extended to 10% strain at a rate of 100% min⁻¹;  
ii. held at 10% strain for 600 s;  
iii. retracted at a rate of 100% min⁻¹;  
iv. allowed to recover for 2 minutes;  
v. re-extended to 10% strain at a rate of 100% min;  
vi. held at that strain for another 600 s;  
vii. retracted at a rate of 100% min⁻¹;  
viii. released from the jaws of the tensile testing machine;  
ix. allowed to recover.  

During the final recovery of the strip the set was monitored. The original purpose of this procedure was to discover if mechanical rupturing of adhesions would reverse the set imparted by drying under strain.

The width of each strip which had been dried under strain was just wide enough for two thin strips (~2 mm wide) to remain when the 10 mm wide strip was cut. Two bench marks with a separation of 100 mm were drawn on one of the thin strips. Once marked the strip was soaked in distilled water for over a week and the separation of the bench marks was remeasured. Subsequently, the marked strip was redried over a period of a week after which the bench mark separation was again remeasured. The intended purpose of this procedure was to discover whether recovery in samples dried under strain could be induced by rewetting.
6.2 RESULTS

6.2.1 THE SET RESULTING FROM DRYING UNDER STRAIN

The resulting day set, defined as the prestrain, is plotted in figure 6.1 (curve a) against the applied strain at which samples of standard thickness were allowed to dry. The material used in these experiments had a stress-strain curve which had a wet turnup strain of 20% (see curve a figure 6.6). Curve a figure 6.1 closely follows a line of slope=1 representing ideal set, i.e. the set is equal to the applied strain. Even when the samples were rewetted, curve b,(figure 6.1) the data points for residual strain describing samples initially dried under 0 to 15% strain did not deviate significantly from the line of perfect set. However, when such samples are subsequently redried the departure from the line of perfect set is noticeable. This deviation is particularly obvious above 15% applied strain.

Similar behaviour was found (figure 6.2) for the effect of drying under strain on the set of samples of standard thickness, which had a turnup strain of 30% for the wet stress strain curve. figure 6.2. The results shown in figure 6.3 (isolated grain) and figure 6.4 (isolated corium), show a similar variation of set with applied strain; cf. figure 6.2 for standard thickness material. After soaking and redrying, the set for grain samples
Figure 6.1
The variation of set with the applied strain under which standard thickness samples were dried: a) long term set (prestrain) b) after rewetting, c) after redrying (samples taken from a region with a low turnup strain of 20%)
Figure 6.3
The variation of set with the applied strain under which grain samples were dried: a) long term set (prestrain) b) after rewetting, c) after redrying (samples taken from a region with a high turnup strain of 30%)

Figure 6.4
The variation of set with the applied strain under which corium samples were dried: a) long term set (prestrain) b) after rewetting, c) after redrying (samples taken from a region with a high turnup strain of 30%)
appears to deviate most from the ideal pattern, while the corium samples deviate least.

Drying under strain fixed both the axial strain and the lateral changes in dimension. Samples dried under strain were permanently curved in the plane perpendicular to the direction of the applied strain. The permanent curvature is plotted in figure 6.5 as a function of prestrain for standard thickness, grain and corium material. This curvature was concave with respect to (a) grain surface for the grain and control samples, or (b) the grain corium boundary for the corium samples.

6.2.2 THE EFFECT OF DRYING UNDER STRAIN ON THE STRESS STRAIN CURVE

The stress-strain curves are shown in figure 6.6 curve a, for a wet standard thickness sample (turnup strain of 20%), and curves b through to i for samples from the same region which had been dried under increasing applied strains. As the prestrain is increased the yield becomes more pronounced and the curves lose their "J" shape. Indeed, curve f in figure 6.6 for 15% prestrain is almost linear. Above 15% strain "r" shaped rather than "J" shaped is a better description of the stress-strain curves.

The stress-strain curve ,a, in figure 6.7 describes wet standard thickness material from another region (turnup strain 30%). The "S" shape is gradually lost with increasing prestrain; curves b
Figure 6.5
Dried in curvature of samples dried under strain
a) standard thickness,
b) grain and
c) corium

Figure 6.6
Stress-strain curves of a) wet sample with a turn up strain of 20% and samples cut from the same area b) dried without constraint (~5% prestrain) and dried under c) 0%, d) 5%, e) 10%, f) 15%, g) 20%, h) 25%, i) 30% strain
through to h. Curve f in this figure for 20% applied strain is almost linear.

Stress-strain curves for prestrained grain samples are shown in figure 6.8. The stress-curves shown in figure 6.7 are for standard thickness samples, the control for the group of grain samples. Curve a (figure 6.8) for the wet grain sample as for the control shows a turnup strain of 30%. However, the yield, at around 3% strain is more pronounced in the grain (curves b to h figure 6.8) than the corresponding curves on figure 6.7 for the control samples of standard thickness. The stress-strain curves for grain samples with more than 20% strain do not display "J" shapes.

The stress-strain curve for a wet corium sample (figure 6.9 curve a), also indicates a turnup strain of 30%. In figure 6.9, curves b to h are much closer to linear than the corresponding curves in figures 6.7 and 6.8. Only in samples with less than 5% prestrain is there indication of a "J" shape. A definite yield is only observed in samples with more than 20% prestrain.

The effect of drying under strain on the low strain, 1-2% secant modulus is illustrated in figure 6.10. Curve a for samples of standard thickness material (from the region with the wet turnup strain of 30%) is displaced slightly above curve e for the corium samples but well below curve b for the samples of the grain.
**Figure 6.7**
 Stress-strain curves for standard thickness samples: a) wet sample with a turn up strain of 30% and samples cut from the same area dried to prestrains of b) -6.2% (unconstrained) c) 0%, d) 5%, e) 10%, f) 20%, g) 26.1%, h) 37.1%.

**Figure 6.8**
 Stress-strain curves for grain: a) wet sample with a turnup strain of 30% and samples cut from the same area dried to prestrains of b) -6.2% (unconstrained) c) 0%, d) 5%, e) 10%, f) 20%, g) 26.1%, h) 37.1%.

**Figure 6.9**
 Stress-strain curves for corium: a) wet sample with a turn up strain of 30% and samples cut from the same area dried to prestrains of b) -4.5% (unconstrained) c) 0%, d) 5%, e) 10%, f) 20%, g) 26%, h) 37%. 
Figure 6.10
The variation of low strain modulus with prestrain for a) standard thickness, b) grain and c) corium samples with a wet turnup strain of 40%.

Figure 6.11
The variation of modulus with prestrain for standard thickness material of a) low strain modulus b) high strain modulus (low turnup region) c) low strain modulus b) high strain modulus (high turnup strain region).
The gradients of curves a, b and c increase gradually as the prestrain increases from -5 to 10% and then at an increasingly rapid rate as the prestrain increases further to 35%. For the group of samples associated with the earlier turnup strain of 20% in the wet stress-strain curve, (curve a, figure 6.11) the departure from linearity at 10% prestrain is more rapid than the departure of standard thickness samples associated with a turnup strain of 30% (curve b, figure 6.11).

Figure 6.11 compares the variation with prestrain of the secant moduli at low strain (between 1 and 2%) and high strain, (subjectively defined as the linear region well above any turnup or yield) of the two standard thickness sample groups with high, 30% and low, 20% wet turnup strains. Below 10% prestrain the high strain modulus exceeds the low strain modulus. However, the low strain modulus increases more rapidly with increasing prestrain than does the high strain modulus and rises above the low strain modulus at 10% strain.

6.2.3 THE EFFECT OF SOAKING BACK ON THE STRESS STRAIN CURVE

Rewetting results in the disappearance of the low strain yield and a reappearance of a toe region. This effect is evident from figures 6.12, 6.13 and 6.14, for standard thickness, grain and corium material respectively, which show the stress-strain curves
**Figure 6.12**
Stress-strain curves for standard thickness samples: a) wet sample with a turnup strain of 30% and samples cut from the same area dried to prestrains of b) -6.2% (unconstrained) c) 0%, d) 5%, e) 10%, f) 20%, g) 26.1%, h) 37.1% and subsequently rewetted.

**Figure 6.13**
Stress-strain curves for grain: a) wet sample with a turnup strain of 30% and samples cut from the same area dried to prestrains of b) -6.2% (unconstrained) c) 0%, d) 5%, e) 10%, f) 20%, g) 26.1%, h) 37.1% and subsequently rewetted.

**Figure 6.14**
Stress-strain curves for corium: a) wet sample with a turnup strain of 30% and samples cut from the same area dried to prestrains of b) -4.5% (unconstrained) c) 0%, d) 5%, e) 10%, f) 20%, g) 26%, h) 37% and subsequently rewetted.
of samples dried under strain and subsequently rewetted. Since, these figures compare the stress-strain curves for rewetted material to the stress-strain curves for original wet samples.

In this case material came from the region with a wet turnup strain of 30%. For standard thickness material (figure 6.12) the stress-strain curves for the samples dried without constraint (curve b) and with 0% prestrain (curve c) overlie the stress-strain curve for the original wet sample (curve a). This pattern is also observed for corium samples (figure 6.14). However, for grain samples, (figure 6.13) the stress-strain curves for the samples dried without constraint (curve b) and with 0% prestrain (curves c) are distinct from the stress-strain curve for the original wet sample (curve a) and lie close to the stress-strain curve for the sample with 5% prestrain (curve d).

The low strain moduli after rewetting (figure 6.15) show a similar variation with prestrain to those before rewetting (figure 6.10) but the moduli are ten times smaller.

Figures 6.16, 6.17 and 6.18 compare the high strain moduli before soaking back, (curves a) with those moduli obtained after soaking back, (curves b) for standard thickness, grain and corium samples respectively (from the region with a wet turnup strain of 30%). In grain and standard thickness samples with less than 15% prestrain, soaking back reduces the high strain modulus to that
Figure 6.15
The variation of low strain modulus with prestrain for rewetted samples of a) standard thickness, b) grain and c) corium.

Figure 6.16
The variation of high strain modulus with prestrain for samples of standard thickness (turnup strain 30%) a) dried under strain and b) subsequently rewetted.
Figure 6.17
The variation of high strain modulus with prestrain for samples of grain a) dried under strain and b) subsequently rewetted.

Figure 6.18
The variation of high strain modulus with prestrain for samples of corium a) dried under strain and b) subsequently rewetted.
of the original wet material, namely 35 MPa for samples of standard thickness and 40 MPa in grain samples. In grain and standard thickness samples with prestrains above 20%, soaking back reduces the high strain modulus, but not to its initial undried value. Rewetting does not reduce the high strain modulus of the corium samples.

6.2.4 RECOVERY OF SAMPLES DRIED UNDER STRAIN AFTER AN APPLICATION OF A FURTHER 10% STRAIN

The additional set imparted to samples dried under strain upon the application of a further 10% strain, is dependent on the prestrain. Figure 6.19, curve a shows that, for samples with a wet turnup strain of 20%, immediate set decreases parabolically with increasing prestrain. Between -5 and 10% prestrain the set after one day is at a level of 2% but drops to zero between 10 and 35% prestrain. The delayed set after 2 minutes (curve b) shows a similar relationship.

The immediate set, the set after 2 minutes and the set after a day are summarised in figures 6.20, 6.21 and 6.22: standard thickness material (curves a), grain, (curves b) and corium samples (curves c) respectively (samples were taken from the area with an original wet turnup strain of 30%). The set in the corium samples was independent of prestrain and decays from an immediate value of 4% to 1.5% after a day. The variation of set
Figure 6.19
Variation of a) immediate b) 2 minute c) day set with prestrain in samples dried under strain to which a further 10% strain was applied (samples from 20% turnup strain region)
**Figure 6.20**
Variation of immediate set with prestrain in samples of a) standard thickness, b) grain and c) corium dried under strain and to which a further 10% strain was applied (samples from 30% turnup strain region)

**Figure 6.21**
Variation of 2 minute set with prestrain in samples of a) standard thickness, b) grain and c) corium dried under strain and to which a further 10% strain was applied (samples from 30% turnup strain region)

**Figure 6.22**
Variation of day set with prestrain in samples of a) standard thickness, b) grain and c) corium dried under strain and to which a further 10% strain was applied (samples from 30% turnup strain region)
with prestrain in the samples of standard thickness material appears to fall from a level around a critical prestrain of 10% for the grain samples and 15% for standard thickness samples. For both grain and standard thickness samples this fall is linear with increasing prestrain.

6.2.5 STRESS RELAXATION OF SAMPLES DRIED UNDER STRAIN AFTER AN APPLICATION OF A FURTHER 10% STRAIN

The influence of drying under strain on the reduced stress after 10 minutes \(R(600)\) after subsequently straining samples to an applied strain of 10% is shown on figure 6.23. At prestrains below 10% \(R(600)\) for corium samples, (line c) is higher than \(R(600)\) for the standard thickness material (curve a) and for the grain, (curve b). However, \(R(600)\) for the corium samples increases less rapidly with prestrain compared with \(R(600)\) for the grain. Between 30 and 35% curve a bends towards curve c. This tendency is not shown by curve d for the standard thickness samples (which had the earlier turn up strain of 20% associated with the wet stress-strain curve).

The decay of the reduced stress as a function of the logarithm of time is shown in figure 6.24 (for samples of standard thickness, with a wet turnup strain of 20%). At first glance the curves point to a linear dependency of \(R(t)\) with \(\log(t)\). However, close inspection of curves d, e and f shows a downward deflection.
Figure 6.23
Variation of $R(600)$ with prestrain for samples of
a) standard thickness, b) grain and c) corium (from
the area with a turnup strain of 30%), d) standard
thickness (from area with a turnup strain of 20%)
Sample were dried under strain following which a
further 10% strain was then applied

Figure 6.24
Variation of $R(t)$ with time for with prestrains of
a)-5%, b) 0%, c) 5%, d)10%, e)15%, f)20%, g) 25%, h) 30%.standard thickness material with a turnup strain
of 20%
indicating a more rapid logarithmic rate of relaxation after 100 s. This deviation cannot be dismissed as a fluctuation in measured load characteristic of the load cell amplifier, since the curves correspond to high values of measured load which are of the same order as the maximum load of the load cell. No such down turn is evident in figure 6.25 which shows the R(t) results, for standard thickness samples with a wet turnup strain of 30%. Such a downturn is however evident in curve d of figure 6.26 which shows the R(t) results for samples of grain and is also evident in curves d, e and f on figure 6.27 for samples of corium.

6.3 DISCUSSION

One hypothesis underlying the investigations into the effect of drying leather under strain is that if the adhesive bonds formed at specific points in the hierarchical structure are strong enough to produce the observed yielding (chapter 3), then these adhesive bonds may have enough adhesive strength in fixing the structure to inhibit recovery. Indeed, samples dried under strain did show near ideal set. This is unsurprising since BUTLIN found a high degree of area set in air dried samples in his lasting simulations. This high degree of set might be explained by the network model in which the junction points between fibres start out as freely hinged but become rigid. This line of reasoning
**Figure 6.25**
Variation of $R(t)$ with time curves for standard thickness samples (with a turn up strain of 30%) with prestrains of a) -5% b) 0%, c) 5%, d) 10%, e) 15%, f) 20%, g) 25%, h) 30%, i) 35% when straining a subsequent 10%

**Figure 6.26**
Variation of $R(t)$ with time curves for grain samples (with a turnup strain of 30%) with prestrains of a) -6.2% b) 0%, c) 5%, d) 10%, e) 20%, f) 26.1% when straining a subsequent 10%

**Figure 6.27**
Variation of $R(t)$ with time curves for corium samples (with a turnup strain of 30%) with prestrains of a) -4.5% b) 0%, c) 5%, d) 10%, e) 20%, f) 26% when straining a subsequent 10%
would also mean that removal of adhesions by rewetting, or rupture of the adhesions by applying a cyclic strain higher than the yield strain, might release the structure thus enabling recovery. The driving force behind this recovery is the resultant changes in internal stress. This phenomenon, called supercontraction, is observed in keratin fibres [MERIDITH]. Soaking back samples dried under strain did result in some recovery but this was considerably smaller than expected (Figure 6.1). The fibre orientation model suggests that when samples cut from wet leather with a turnup strain of 20% are dried under less than 20% strain they might be expected to fully recover upon rehydrating.

The absence of a yield point in the stress-strain curves of rehydrated material implies a lack of strong inter-fibre adhesions. However, there remains the problem of understanding those interactions preventing the recovery of the prestrained samples. Possibly drying under strain not only affects the junction points, but also permanently rearranges the internal structure of the fibres. This change in structure may involve the formation of new permanent intermolecular bonds. The strength of these bonds may be affected by the presence of water but not nullified. These bonds could possibly be new chrome bridges. The effect on an individual fibre of drying under strain and rewetting may thus be to change permanently its initial bent
equilibrium shape into a new straighter equilibrium shape. Drying under strain may thus result in a permanent decrease in the angle of weave in the direction of the applied strain. Indeed, DEMPSEY observed that drying leather under tension lowers the angle of weave.

6.3.1 THE ROLE OF WEAVE ANGLE CHANGES

If drying under strain followed by rewetting caused only a permanent decrease in weave angle, the orientation model predicts that the resultant stress-strain curve should be described by a simple shift of the origin along the stress-strain curve (see figure 6.28). The horizontal shift away from the stress axis is the prestrain plus an extra amount to account for fibre shrinkage. Fibre shrinkage on drying was equated to sample shrinkage by SPIERS and PEARSON. If sample shrinkage is prevented, as in this investigation, an additional lowering of weave may occur. Such an additional lowering equates to extra shift along the strain axis. The shrinkage of the samples dried without constraint was used as an estimate of this shrinkage in order to fit the model to experimental data.

The degree to which this model is successful is illustrated in figure 6.29. The curves (taken from figure 6.12) for rewetted samples of standard thickness material, are compared (figure 6.29 a) to those calculated using the model. Here experimental curves for standard thickness samples dried to prestrains below 15%
Figure 6.28
Illustration of the hypothesis that drying under strain and rewetting only results in a shift in the origin of the stress-strain axis.

a) original stress-strain axis b) prediction of the stress-strain curve of originally dried under strain. The origin of the stress-strain axes is shifted such that the new zero strain = prestrain + shrinkage and the new zero stress is the stress at strain equal to prestrain + shrinkage.
Figure 6.29
Comparison of rewetted stress-strain curves (heavy lines) with predictions of the orientation model (thin lines)

a) Standard Thickness

b) Grain

c) Corium
strain are close but not in precise agreement with those calculated using this model. Further, there is little agreement at 15% prestrain and above. Similarly, the experimental stress-strain curves for rewetted grain samples (figure 6.13) are compared in figure 6.29 b with the pattern required by the model. For the whole range of prestrains the curves for the grain samples disagree with the curves predicted by the model. The experimental stress-strain curves for rewetted corium samples (figure 6.14) are compared with those predicted by the model in figure 6.29c. This figure shows that at and below 20% prestrain there is good agreement between the observed and predicted pattern, but there is deviation from the predictions of the model above 20% prestrain. The model fails for a reason now discussed. Straining a sample of partially processed leather above the turnup strain not only decreases the angle of weave as the orientation model predicts, but also increases the number of load bearing fibres per unit of true cross-sectional area (the fibre density) as the recruitment model predicts. Drying under strain and rewetting decreases the weave angle and also increases the fibre density. The fibre density has a major influence on the modulus at high strains. Since the wet grain layer has a greater lateral Poisson's ratio (-2 from the slope of curve c figure 5.23) than the corium (-1 from the slope of curve f figure 5.23), then the fibre density in grain increases more rapidly with strain than that in the corium. Therefore, the properties of the grain
samples depart most from those predicted by the model.

A remarkable feature of drying samples under strain is the effect on the low strain region of the stress-strain curve. This effect is most noticeable for samples of grain, figure 6.8 and 6.10, where the yield and low strain modulus become increasingly pronounced with increasing prestrain. In chapter 5 it was remarked that the inter-fibre adhesion population may be far greater in the grain than in the corium, because of the larger number of fibre intersections. Straining will compact the weave of a sample of wet leather increasing the number of fibre-fibre contacts. Hence drying under strain may increase the number of inter-fibre adhesions formed on drying.

6.3.2 PREDICTIONS OF A NODE FIBRIL MODEL

Recently, ALDERSON and EVANS have developed a modified version of the fibre orientation model, called the node fibril model. ALDERSON and EVANS using this model aimed to explain the properties of microporous polymers where fibrils of orientated polymer join nodes of isotropic material.

6.3.2.1 THE RE-ENTRANT NODE FIBRIL MODEL AND ITS APPLICABILITY TO LEATHER

A two-dimensional model with a re-entrant geometry figure 6.30a is used by ALDERSON and EVANS to describe auxetic materials (those with a negative Poisson's ratio). The nonlinear variation in
Figure 6.30
Node fibril models a) Re-entrant, b) Non re-entrant, c) infinitesimal node
moduli and Poisson's ratio are related to changes in unit cell dimensions \( X, Y \) given by equations 6.1 and 6.2 respectively for their re-entrant geometry; \( l \) is the length of the fibril, \( \alpha \) is the angle made by the fibril to the x-axis and parameters \( a \) and \( b \) are the dimension of the nodes in the \( X \) and \( Y \) directions respectively.

\[
X = 2(a + l \cos \alpha) \\
Y = 2(b - l \sin \alpha)
\]

LIN and HAYHURST (1993a) found that the thickness of finished, chrome tanned leather increases with applied strain, i.e. leather is auxetic through its thickness. MITTON attributed increases in thickness when finished, vegetable tanned leather is strained to the release of compressional set imposed by heavy rolling. Samples dried under large amounts of strain were thicker than samples dried without constraint. However, it may be imprudent to conclude that partially processed leather is auxetic, since the variation in thickness may have been caused by non-uniform splitting.

6.3.2.2 THE NON RE-ENTRANT NODE FIBRIL MODEL AND ITS APPLICABILITY TO LEATHER

A two dimensional node fibril model is shown in figure 6.30 b with a non re-entrant geometry describing a material with a positive Poisson's ratio. The unit cell dimension in the \( X \)
direction is given by equation 6.1. The unit cell dimension in the Y direction is given by equation 6.3.

\[ Y = 2(b + l \sin \alpha) \quad (6.3) \]

In chapter 5 it was observed that the application of a positive axial strain to partially processed leather produced a negative lateral strain. This observation is consistent with that reported by Lin and Hayhurst (1993a) for the variation of lateral strain with axial strain for finished leather. The non re-entrant model is therefore more suitable for describing the properties of leather in the plane parallel to the surface of the grain than the re-entrant model.

6.3.2.3 THE ZERO NODE SIMPLIFICATION

In partially processed leather the length of the fibres may be much larger than the overlap at fibre intersections. A simplification of the non re-entrant node fibril model shown in figure 6.30 c will be presently applied to account for the variation of initial modulus with prestrain. The nodes are much smaller than fibril length in this simplification. Therefore, in the limit (a=0) and (b=0) the unit cell dimensions are given by equations 6.4 and 6.5.

\[ X = 2(l \cos \alpha) \quad (6.4) \]
\[ Y = 2(l \sin \alpha) \quad (6.5) \]
6.3.2.4 MODES OF FIBRIL DEFORMATION

ALDERSON and EVANS related the moduli in the X and Y directions together with the Poisson’s ratios to both the dimensions of the unit cell and the angle α for three modes of fibril deformation; i) hinging, ii) flexing and iii) stretching. Since the experimental investigation discussed in this chapter is based on uniaxial tests and accurate Poisson’s ratios were not measured the following discussion is based around the effects of these types of deformation on the Young’s modulus in the X direction.

i. Hinging. (figure 6.31a): The fibrils are inflexible rods but can freely rotate. In this type of deformation the true modulus\(^\text{14}\) in the X direction was related to the unit cell dimensions by equation 6.6 where \(K_h\) is the hinging coefficient and \(Z\) is the depth of the unit cell.

\[
E_{xa} = K_h \left( \frac{X}{1^2 Y \sin^2 \alpha} \right)
\]  

(6.6)

ii. Flexure. (figure 6.31b): The fibrils are flexible but inextensible rods that do not deform by shearing. For flexure the true Young’s modulus in the X direction is related to the unit cell dimensions by equation 6.7.

\(\text{14}\) The true modulus is defined as the differential of the true stress with respect to strain.
Figure 6.31
Modes of fibril deformation proposed by ALDERSON and EVANS

a) Hinging

b) Flexure

c) Stretching
The theory of elastic beam bending shows that $K_f$, the flexing coefficient, is related by equation 6.8 to the fibril width $w$, thickness $t$, length $l$ and intrinsic fibril modulus $E_s$. Bending deformation was considered as an explanation of many of the observations reported in chapter 5.

$$K_f = E_s \frac{wL^3}{3l} \quad (6.8)$$

**Stretching** (figure 6.31c): The fibrils extend elastically but are unable to hinge or flex. The true modulus for stretching is related via equation 6.9 to the unit cell dimensions and the stretching coefficient $K_s$. The stretching coefficient $K_s$ is related to the fibril dimension and the intrinsic modulus of the fibril by equation 6.10.

$$E_s = K_s \frac{X}{ZY\cos^2\alpha} \quad (6.9)$$

$$K_s = E_s wt \quad (6.10)$$
6.3.2.5 RELATIONSHIP BETWEEN FIBRIL ANGLE AND STRAIN

ALDERSON and EVANS assume the unit cell dimensions change in the same ratio as the dimensions as the bulk material and therefore relate the applied strain in the x direction to the initial unit cell dimensions using equation 6.11.

\[
e^{x} = \ln\left(\frac{X}{X_0}\right) = \ln\left(\frac{s+1\cos\alpha}{s_0+1\cos\alpha_0}\right)
\]  
(6.11)

In the simplified non re-entrant model (\(\alpha = 0\)) equation 6.11 yields equation 6.12.

\[
e^{x} = \ln\left(\frac{1}{s\cos\alpha}\right)
\]  
(6.12)

For hinging, flexing and infinitesimal stretching 1 equals 1. Hence, equation 6.12 can be rearranged to yield equation 6.13 which relates the angle \(\alpha\) to the applied strain \(e\) and the initial angle \(\alpha_0\).

\[
\alpha(e, \alpha_0) = \arccos\left(e^x \cos\alpha_0\right)
\]  
(6.13)

6.3.2.6 PREDICTIONS OF ZERO DIMENSION NODE FIBRIL MODEL

With zero dimension node simplification equations 6.6 for hinging, 6.7 for flexing and equation 6.9 for stretching become equations 6.14, 6.15 and 6.16 respectively.

\[
\frac{E\alpha x}{\alpha x} = \frac{K_3 \cos\alpha}{L^2 \sin^2\alpha} = \frac{K}{L^2 \alpha}(\alpha)
\]  
(6.14)
Inspection of equations 6.15 and 6.16 shows that the angular distribution functions for flexing, $D^f(\alpha)$, and hinging, $D^h(\alpha)$, are identical. The angular distribution function for hinging and flexing is compared in figure 6.32 with that for stretching $D_{ss}(\alpha)$. Identical expressions to equations 6.14, 6.15 and 6.16 are obtained for the modulus in the $x$-direction, the special case of the ALDERSON and EVANS re-entrant model when $b=2\sin(\alpha)$ and $a=0$, (i.e. the case when a node becomes fibril). Consequently, the analysis applies to either of the following possible two-dimensional cases: - 

i. $\alpha$ is the angle of weave and the through thickness Poisson's ratio is negative; 

ii. $\alpha$ is the average angular separation of fibres in the plane of the grain surface and the Poisson's ratio is positive. 

6.3.2.7 COMPARISON OF THE PREDICTION OF THE NODE FIBRIL MODEL WITH EXPERIMENTAL OBSERVATIONS

When the fibril modulus is larger than that of the node, ALDERSON and EVANS suggest that the mechanism of deformation is
Figure 6.32
Comparison of angular distribution term for a) hinging or flexing with that for b) stretching
predominantly hinging. Bending or flexure dominates over hinging if the nodule has a modulus greater than or equal to that of the fibril. In wet partially processed leather if adhesions are absent from the fibre contact points, then hinging should predominate at low strains. According to Alderson and Evans, hinging describes the deformation of auxetic PTFE below 15\% strain where the modulus in the X direction is low. Stretching of fibres may occur in wet leather at high strains due to fibre entanglement opposing rotation. A change from hinging to a stretching mode of deformation is used to explain the appearance at 15\% strain of a linear high modulus region on the stress-strain curve of auxetic PTFE.

Flexure and stretching should be the predominant modes of deformation in dry partially processed leather due to the presence of inter-fibre adhesions.

By substituting for \(\alpha\) from 6.13 into equations 6.14, 6.15 and 6.16 the true moduli at strain \(\varepsilon_s\) can be related to initial angle \(\alpha_0\).

Unfortunately, any precise node-fibril model should consider the following factors and their structural distribution:

i. The initial value of \(\alpha_0\), and its distribution;
ii. The distances between fibre intersections (i.e. the length of the fibrils between nodes, 1);
iii. The intrinsic fibril moduli and hinging coefficients;
iv. The fibre diameters and their distribution.
Alderson and Evans found the determination of such factors is difficult even for auxetic polymers which have fewer levels of structural hierarchy than leather. Factors ii, iii and iv above can be eliminated by dividing the modulus at a particular strain by the initial modulus at zero strain, i.e., normalising with respect to the value at zero strain. For an arbitrary $\alpha_0$ of 45° a normalised true modulus is plotted in figure 6.33 as a function of applied strain for flexing or hinging (curve a) and for stretching (curve b).

The predictions of the non-re-entrant node fibril model are now used to compare the moduli of samples dried under strain to the moduli of those that have been rewetted. The following assumptions are made:

i. Straining wet leather merely changes the angle $\alpha$ in accordance with equation 6.13;

ii. Drying under strain fixes the angle $\alpha$ by introducing intra-fibre bonds that cannot be destroyed by rewetting;

iii. Drying introduces inter-fibre bonds that can be removed by rewetting.

The third assumption is reasonable considering the ease with which water disrupts such bonds.

According to the first assumption if a sample with a prestrain of 0 has a fibril to x-axis angle (figure 6.31) of $\alpha_0$ then a sample with a prestrain equal to $\varepsilon$ has a fibril to x-axis angle of $\alpha$. The initial value of engineering modulus (i.e., at strains
close to zero) approximates to the true modulus. In this investigation the experimental measure of the initial modulus is the low strain modulus. Hence, if the true modulus cannot be determined because the changes in lateral dimensions cannot be measured accurately (as in the studies discussed here) at least the initial modulus value can be determined. In figure 6.34 the low strain modulus as a function of prestrain is plotted normalised with respect to the low strain modulus at zero prestrain. These curves can be compared with the predictions of the simplified node fibril model for an arbitrarily chosen value of 45° for \( \alpha_0 \) (figure 6.33). The striking feature of figure 6.33 is that curve a for hinging and flexure turns from a low slope region to a high slope region earlier than curve b (figure 6.34) for stretching. For standard thickness material, the curve b for rewetted samples turns into a high slope region, whereas, curve a for material that has not been rewetted does not turn into a high slope region over the range of prestrains investigated. For grain material in both the rewetted case (curve d) and in the case when samples have not been rewetted (curve c) there is no turn into a high slope region for the range of prestrains investigated. For corium material the turn into the high slope region for rewetted samples curve f occurs at an earlier prestrain than for samples that have not been soaked back, curve e. From these observations some important conclusions can be drawn about the mode of fibre deformation in partially processed
Figure 6.33
Prediction of the normalised variation of true modulus with applied strain for an initial angle of 45 degrees a) flexing or hinging b) stretching

Figure 6.34
The variation of low strain modulus with prestrain normalised with respect to the value at zero prestrain for samples of standard thickness a) dried, b) rewetted grain c) dried, d) rewetted and corium e) dried, f) rewetted
leather at low strains. Firstly, there is a larger contribution to the modulus from the stretching mode in dry compared with the contribution in wet material. Secondly, in the grain layer stretching dominates over hinging or flexing, whereas, in the corium hinging or flexing is the predominant mode.

6.3.2.8 THE RELATIVE IMPORTANCE OF BENDING AND STRETCHING DEFORMATION MODES

If flexing and bending are the modes of deformation in dry leather the true modulus can be expressed using equation 6.17.

$$E_s(\varepsilon_s, \alpha) = \Omega(\varepsilon_s) K_{sD_s}(\alpha) + (1 - \Omega(\varepsilon_s)) \frac{K}{l^2} D_s(\alpha)$$

$$\Omega(\varepsilon_s) = \frac{N_s(\varepsilon_s)}{N(\varepsilon_s)}$$

$\Omega(\varepsilon_s)$ is the number of straight fibrils per unit volume, $N_s(\varepsilon_s)$, divided by the total number of fibrils per unit volume, $N(\varepsilon_s)$, at an applied strain of $\varepsilon_s$ (equation 6.18). The second term in equation 6.17 expression is cubically dependent on the fibril aspect ratio $t/l$ because $K/l^2$ is proportional to $t^3/l^3$ according to equation 6.8. Therefore, if the length of the fibrils is considerably longer than their thickness, the number of straight segments needs to be considerably smaller than the number of curved segments for flexing to make the major contribution to
the modulus.

**HARRIOT** suggests that the course of a curved fibre in leather consists of straight segments between fibre intersections (Figure 6.35a). The sharp decrease in modulus observed at the yield point in dry material in this investigation is explained by a change of the predominant deformation mode from stretching to bending. **HARRIOT** also suggests that, when strain is applied to leather, inter-fibre linkages break resulting in longer curved sections between the smaller number of remaining bonds (Figure 6.35b). This breakage increases the number of curved sections but also decreases the aspect ratio and the total number of node fibrils. Therefore, at low prestrains unbending alone may be a mechanism of deformation in which the yield is caused by the change in aspect ratio as inter-fibre adhesions rupture. The stretching term in equation 6.17 may dominate the initial modulus of samples with prestrains above the turnup strain because recruitment of straight fibres occurred prior to inter-fibre adhesion formation.

The relative number of straight segments per unit volume as a function of strain, $\Omega(\varepsilon)$, is described using an exponential term such as equation 6.19.

$$\Omega(\varepsilon) = 1 - e^{-\varepsilon/\varepsilon} \quad (6.19)$$

This expression for $\Omega(\varepsilon)$ is similar to one used by **VACULIC** to
Figure 6.35
Illustration of MARRIOTT's proposals a) that the course of a curved fibre is made up of straight segments between fibre intersections and b) that rupturing of bonds between fibres causes fibres to curl.

Figure 6.36
Numerical fit of node-fibril model to the normalised modulus as a function of prestrain for standard thickness samples from low turnup region (points represent experimental data)
describe the stress-strain curve of leather in terms of the recruitment of elastic elements. A more complex, expression relating the number of taut fibres to the initial distribution of slack fibres was used by KRONICK and BUECHLER (1986), who also only considered stretching as contributing to the modulus. The constant, $\varepsilon_o$, in equation 6.19 is related to such a distribution.

The prediction for $E_x(\varepsilon_n,\alpha_n)/E_x(0,\alpha_n)$ in equation 6.17 is fitted to the normalised experimental data for standard thickness material from the low turnup region in figure 6.38. To achieve this fit the prestrain, as earlier, was equated to the strain in the X direction $\varepsilon_x$. In addition the following substitutions have been made:

i. Equation 6.19 was substituted for $\Omega(\varepsilon_n);$  
ii. Equation 6.13 is substituted for $\alpha$;

For this fit $\varepsilon_n=150\%$, $\alpha_n=47^\circ$, and the ratio $K_x/K_s/l^2$ is 10:1.

The stress-strains curves for samples dried under strain at prestrains above the turnup strain are "r-shaped" but those dried under strain at prestrains below the turnup strain are "J-shaped" (figures 6.6 to 6.9.). The observation may have the following explanation. As yield occurs in samples prestrained below the turnup strain there is a definite change from a stretching dominated to a bending dominated mechanism of deformation. Whereas, at yield, in samples with prestrains above

165
the turnup strain, stretching remains the dominant deformation mode but becomes less influential on the modulus.

6.3.3 MODELLING THE HIGH STRAIN MODULUS

The high strain moduli of samples dried under strain increase with prestrain. Moreover, this increase appears to correlate with the turnup strain. By straining fibres the tropocollagen molecules may orient within the fibrils in the direction of applied strain. It seems reasonable that drying under strain fixes this new molecular configuration.

Using transversely isotropic collagenous soft tissue (carotid wall) dried under strain, BIGI et al applied x-ray diffraction techniques to determine the angular distribution of tropocollagen molecules in relation to the sample axis along which strain was applied. That is they determined \( \langle \cos^8 \theta \rangle \), the average value of \( \cos^8 \theta \), where \( \theta \) is the angle made by a tropocollagen molecule to the strain axis. BIGI et al found that for their material the axial modulus \( E_g \) increases linearly with \( \langle \cos^8 \theta \rangle \).

Following this approach by BIGI et al, the individual fibres and fibre bundles will be treated as axially symmetric materials composed of more primitive structural elements. These primitive elements, which could be fibrils and tropocollagen molecules, become permanently aligned by drying under strain. To achieve the theoretical maximum axial modulus \( E_{\text{max}} \), a transversely isotropic
material requires total axial alignment of its structural components. i.e. $<\cos^4\theta> = 1$.

If it is assumed that all the structural elements in the imperfectly aligned material, with a modulus $E_{av}$, are at the average $\theta$, rather than distributed around the average angle to the axis then $<\cos^4\theta> = \cos^4\theta$. This assumption is made because although there is information about the angle made by primitive elements to the fibre axis, there is no readily available information about its distribution. Using this assumption and the experimental observation of BIGI et al then it is possible to estimate using equation 6.20 the fractional increase in modulus $((E_{max} - E_{av})/E_{max})$ caused by total axial alignment of components.

$$\frac{E_{max} - E_{av}}{E_{max}} = 1 - \cos^4\theta$$

(6.20)

BASELT et al using atomic force microscopy found substructures on the surface of fibrils. They found these substructures, which they termed "micro-fibrils", make an angle of approximately 5° to axis of a fibril. Even if drying under strain totally aligns all the micro-fibrils with a fibril then from equation 6.20 the axial modulus increases only by 2%. Therefore, even if all the fibres had become load bearing whilst drying under strain, the maximum increase in high strain modulus that could be expected is around 2%.

However, the high strain modulus for samples dried under strain
and those subsequently rewetted often (see table 6.1) more than
doubles over the range of prestrains examined.

If the samples of grain, corium and standard thickness leather
are treated as transversely isotropic materials consisting of
alignable structural elements, then using equation 6.21, it is
possible to estimate the alignment $\theta_0$ required to produce the
observed changes in modulus.

$$\theta_0 = \arccos \sqrt{1 - \frac{E_{max}}{E_{ss}}^2} \quad (6.21)$$

In this case the structural elements that are aligned by drying
under strain are assumed to be the fibres. Perfect alignment is
assumed at 35% prestrain i.e. $E_{max}$ in equation 6.21 is the high
strain modulus at 35% prestrain and $E_{ss}$ in equation 6.21 is the
high strain modulus at 0% prestrain. The estimate of the change
in orientation $\theta_0$ required to produce the observed change in
high strain modulus between 0 and 35% prestrain is recorded in
table 6.1. This estimate for all cases reported in table 6.1 is
more than 30°. Hence, most of the increase in high strain
modulus with prestrain is associated with weave change although
changes in molecular orientation inside the collagen fibril may
still have an effect.
### TABLE 6.1

<table>
<thead>
<tr>
<th>Group of Samples</th>
<th>Figure and curve</th>
<th>High strain modulus at 0% Prestrain /MPa</th>
<th>High strain modulus at 35% Prestrain /MPa</th>
<th>Orientation(θ), required for modulus change /°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dried understrain turnup strain 30%</td>
<td>6.16 a</td>
<td>30</td>
<td>80</td>
<td>38</td>
</tr>
<tr>
<td>Grain</td>
<td>6.17 a</td>
<td>40</td>
<td>200</td>
<td>48</td>
</tr>
<tr>
<td>Corium</td>
<td>6.18 a</td>
<td>15</td>
<td>50</td>
<td>42</td>
</tr>
<tr>
<td>Dried understrain turnup strain 20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard Thickness</td>
<td>6.11 b</td>
<td>50</td>
<td>200</td>
<td>45</td>
</tr>
<tr>
<td>Dried understrain turnup strain 30% and rewetted</td>
<td>6.16 b</td>
<td>30</td>
<td>70</td>
<td>36</td>
</tr>
<tr>
<td>Grain</td>
<td>6.17 b</td>
<td>40</td>
<td>85</td>
<td>34</td>
</tr>
<tr>
<td>Corium</td>
<td>6.18 b</td>
<td>15</td>
<td>50</td>
<td>42</td>
</tr>
</tbody>
</table>

### 6.3.4 EXPLANATION OF RELAXATION AND RECOVERY FOLLOWING APPLICATION OF A FURTHER 10% STRAIN

Alignment might result in a more densely packed fibril. Within such a fibril there will be more opportunity for inter-tropocollagen bonds to form when water is removed. A larger number of inter-tropocollagen bonds should increase the resistance to the shear forces between tropocollagen molecules. This increased resistance to shear will tend to make i. straight fibres which have been dried under strain more like
elastic rods than straight fibres which have not been dried under strain.
i. bent fibres more like elastic leaf springs which have been dried under strain than bent fibres which have not been dried under strain.

If the reduced stress is a measure of fibre elasticity this concept may explain why R(600), reported in figure 6.23 increases with prestrain for all the samples dried under strain and restrained. In chapter 4 it was suggested that such an increase in reduced stress would cause a drop in immediate set. This expectation is confirmed for standard thickness and grain samples, curves a and b in figures 6.20. However, no such decrease is observed on curve c figure 6.20 for samples of corium.

The modified recruitment element (figure 5.45) was considered in chapter 5 as having a critical nominal bending yield strain above which the bending mode of deformation is plastic. Some bent fibre segments between adhesions or entanglements have a near straight configuration. Such segments may not reach this critical bending yield strain before becoming straight when strain is applied to a sample. In the grain layer there may be a large number of such segments in dry material. The number of near straight segments will increase with prestrain. Some originally near straight
segments may have not reached their upper tensile yield strain (also suggested in chapter 5) when samples dried under strain were strained a further 10%. Hence, the immediate set as a function of prestrain for grain and standard thickness falls with prestrain. In the corium layer there are probably fewer near straight segments and their absence explains why set in the corium is independent of prestrain (see curve c on figures 6.20 to 6.22).
7 CONCLUSIONS

7.1 CONCLUSIONS

Partially processed leather is a nonlinear viscoelastic material whose rheological properties are greatly influenced by moisture content. Leather with a moisture content of 35% and below has a low strain (-2% strain) yield point. This yield point becomes increasingly pronounced with decreasing moisture content, because both the adhesion population and adhesion strength increase as the leather's structure collapses on drying. Dry, staked, finished leather does not have a yield point, because mechanical action has ruptured inter-fibre adhesions. It can be concluded that there is a larger number of inter-fibre adhesions in the grain than in the corium, because yield is more prominent in partially processed grain samples. The yield phenomenon is observed because the rupture of inter-fibre adhesions results in a change from a stretching mode to a bending mode of deformation for the constituent collagen fibres. Such a change of deformation mode can be accounted for by the modified ALDERSON and EVANS node fibril model.

The ALDERSON and EVANS node fibril model also implies that the
stress-strain curve of wet leather turns from a low modulus region to a high modulus region at a critical strain due to a change of fibre deformation mode from bending to stretching. Below this critical strain, insufficient tensile strain has been applied to the collagen fibres for them to become deformed permanently. Importantly, therefore, no long term set is imparted to wet material strained below the critical strain. Wet fibres have an elastic limit. Below this elastic limit they have a coherent internal structure and deform elastically. When strained above this elastic limit the coherence of the internal structure breaks down and the fibres become viscoelastic. At strains above the critical strain, all the wet fibres under strain are above their elastic limit. Therefore, the reduced stress as a function of applied strain levels out at its minimum at the critical strain. The straightness of fibres must be an inhomogeneous and anisotropic quantity, since the critical strain is a positionally and directionally dependent variable.

Significantly, wet leather strained to applied strains below the critical strain fully recovers after ten minutes. This rapid recovery is as a result of the collagen fibres that form the grain layer returning to their initial bent configuration. Surprisingly, the elasticity of the network of elastin fibres is not responsible for the recovery of wet leather. Even if this network is digested by enzymes, wet partially processed leather
still recovers.

The configuration of a collagen fibre is determined its internal structure. In dry collagen fibres, this structure is fixed by the intra-fibre adhesions formed on drying. Intra-fibre adhesions rupture by shearing as a dry fibre unbends. Intra-fibre friction opposes the tendency of dry fibres to return to their initial configuration. The loss of this tendency means that long term set is imparted to dry partially processed leather by the application of strains lower than the critical strain. However, this set is small in contrast to the long term comparative set in such material strained above the critical strain. Above the critical strain the mechanism of set is the stretching of fibres, whereas below the critical strain the mechanism of set is the plastic unbending of fibres. In dry leather the shearing of intra-fibre adhesions also introduces a mechanism of relaxation.

The occurrence of long term set in samples of partially processed leather, subjected to strains below the critical strain, is associated with the appearance of a yield point. Although, in dry material the yield point is reached by 2% strain, an immediate set is not observed until a strain of 5% has been applied. Plastic unbending and stretching of fibres, responsible for long term set, involves the rupture of intra-fibre adhesions, whereas the rupturing of inter-fibre adhesions is responsible for the
yield point on the stress-strain curve.

When leather is strained uniaxially, the stress decays linearly with \( \log(\text{time}) \) over a wide range of applied strains and moisture contents. This decay can be modelled using the multiple Maxwell model. However, the time constants obtained from such a fit depend on the experimental relaxation time interval.

In both dry and wet leather, the immediate set and the stress at the end of a period of relaxation can be related directly by consideration of the predictions of the simple Maxwell model. Immediate set results from the internal rearrangement of structure which occurs during relaxation.

The recovery of set has two rates of recovery on a logarithmic time scale; they are a rapid and a gradual rate.

A modified multiple Voigt model, which incorporates a limited frictional brake element to account for the rupture of adhesions, successfully describes recovery in terms of three parameters:

i. a critical retardation time, \( \tau_c \), when the long term recovery processes supersede the short term recovery processes;

ii. the ratio of the long term to short term compliances, \( K \);

iii. the permanent (or irrecoverable) set \( S_r \).

In wet partially processed leather, the grain layer is
responsible for the initial rapid recovery and the corium layer is responsible for the slower rate of recovery.

The set in partially processed leather at any moisture content has two components:

i. the irrecoverable plastic set;
ii. the recoverable set.

The long term set and, by inference, the plastic set, fall as the initial moisture content is increased above 20%, because the population of intra-fibre adhesions decreases. The population of intra-fibre adhesions does not increase as the moisture content falls below 20% moisture. Therefore, below 20% moisture the long term set is invariant with decreasing moisture content. Recoverable set is related to the reduced stress at the end of a period of stress-relaxation. This implies that the structural rearrangement occurring during relaxation is reversed during recovery.

The structure of partially processed leather is fixed by drying due to the formation of:

i. non permanent intra-fibre adhesions;
ii. non permanent inter-fibre adhesions;
iii. permanent intra-fibre adhesions.

Non permanent adhesions can be eliminated by rewetting and are presumably composed of hydrogen bonds. Therefore, the pronounced yield found in samples dried under strain can be removed by
rewetting. Remarkably, the long term set imparted to unfatliquored partially processed leather by drying under strain cannot be removed by rewetting. Permanent inter-molecular bonds formed on drying must therefore fix the configuration of the fibres. These permanent bonds are covalent in nature and form on drying, as Komanowsky (1992) suggests, because side groups on adjacent collagen molecules come into intimate contact.

The firmness of leather is related to the population of straight fibres. Drying unfatliquored material under strain increases the number of straight fibres per unit volume. This is why toggle drying produces firmer leathers. Drying under strains greater than the critical strain removes all the bent fibres. For this reason the stress-strain curve of rewetted material dried under strains greater than the critical strain lacks a toe region. The modified Alderson and Evans model can be used to account for changes in the initial modulus, in terms of an increase in the number of straight fibres per unit volume.

Drying under strain also increases the high strain modulus of partially processed leather by fibre orientation and structural densification. These mechanisms have greatest influence on the grain layer. Drying under strain will therefore produce a stronger final material at the expense of thickness.
7.2 RECOMMENDATIONS

The following recommendations are suggested to the leather industry to increase area yield.

a. Dry rapidly after setting.

b. Replace setting with a process which applies strains, whilst the leather is kept saturated with water, for longer times.

c. Dry the grain as rapidly as possible.

d. Apply higher strains to looser regions of the hide.

Area can be gained when straining wet blue leather by:

i. applying high degrees of strain;

ii. Drying under strain;

iii. Applying intermediate amounts of strain for a prolonged time whilst wet, i.e. greater than 10 minutes, and drying rapidly, i.e. within minutes after straining, to a low moisture content, ~20% moisture on a wet weight basis.

Any area gained by setting out is achieved by applying high degrees of strain which stretches fibres. Unfortunately, some fibres will rupture under this tensile deformation. Consequently, the rupture of these fibres may weaken the final material. However, area yield is obtained using the third method by straightening bent fibres rather than by the stretching straight fibres. Toggle drying achieves area gain by drying under strain,
but stiffens the leather. A loss of softness may not occur if the third suggested novel method is used, because the leather’s structure is allowed to relax before it is fixed by drying. For the reasons discussed above, therefore, the third suggested method must be considered by tanners, as a way of achieving area yield without loss of softness or tensile strength.

Area will not be gained if:
i. too low a degree of strain is applied;

ii. intermediate amounts of strain are applied, but the material is not dried rapidly enough after the removal of the applied strain.

In this investigation, linear strains below 5% are considered as too low to gain any area, strains between 5% and the turnup strain are considered intermediate and strains above the turnup strain are considered high

Since the critical strain depends on orientation and position, then different regions of the hide require differing degrees of strain to optimise area gain. Drying belly regions under strain in the direction perpendicular to the backbone may make these loose regions firmer by reorientating the fibre structure.

At high moisture contents the grain layer was found to recover more rapidly than the corium layer. This result may provide a
novel way of improving the break of a loose leather comprised of
grain and corium layers; that is, to alter the relative tightness
of grain and corium layers by varying the recovery time in the
third stage of the following procedure:

i. apply an intermediate strain to the leather;

ii. allow the leather to relax at a fixed high moisture content
    , i.e. wet, for a prolonged period, i.e. in excess of 10
    minutes;

iii. remove the strain applied and allow the leather to recover
     whilst remaining wet;

iv. dry leather rapidly.

Short recovery times, i.e. less than 100 s (the recovery time of
wet grain), should result in tighter leathers. However,
intermediate recovery times, i.e. between 100 s and four hours
(the recovery time for wet corium) should be explored, to find
out the optimum time required to remove pipeness without a
detrimental effect on softness.

A minimal staking action applied to crust leather will soften the
leather, since merely by breaking inter-fibre adhesions the
initial tensile modulus of the crusted leather can be lowered.
Such a gentle action does not necessarily increase area yield.
From this investigation, a minimal action is one that applies
linear tensile strains of between 2 and 5%. 
An intermediate staking action will increase area yield by plastically deforming fibres through the rupturing of intra-fibre adhesions. An intermediate staking action is one that applies linear strains between 5% and the critical strain. Adhesions are probably weakest at 35% moisture and therefore there may be some advantage in staking at this moisture content, although staking is usually performed at lower moisture contents, -25% moisture. Staking at moisture contents much above 35% is pointless because adhesions will probably reform. A heavy staking action, especially below 20% moisture, is inadvisable because it may result in the rupture of bonds other than adhesions that can be reformed by rewetting and redrying. Over staking is known to cause looseness. A heavy staking action applies linear strains above the critical strain for a particular region of hide.

7.3 SUGGESTIONS FOR FURTHER STUDIES

A sophisticated model that predicts the mechanical properties of leather in terms of its structure is required. A finite element model based on the ALDERSON and EVANS node-fibril model may provide a starting point. For any model to be realistic the following information needs to be quantified:

i. the mechanical properties of individual fibres;
ii. the morphological configuration of fibres;
iii. the mechanical interaction between individual fibres;
iv. the role played by non collagenous material.
This quantification has not been achieved to any degree of satisfaction in the literature. Therefore, the following investigations are suggested to rectify this information gap:

i. an experimental study of the viscoelastic properties of isolated leather fibres in bending and tensile deformation in relation to their structural hierarchy, moisture content, degree and type of tannage and degree and type of fatliquoring;

ii. stratigraphic quantitative image analysis of the microstructure of leather, to confirm the accuracy of noninvasive measurement of weave such as the microwave method of OSAKI et al.;

iii. an experimental study of the effects of opening up and fatliquor type and droplet size on the yield phenomenon, stress relaxation and recovery of partially processed leather;

iv. a study of the effects on the mechanical properties of systematic removal of non-collagenous material with specific enzymes.

A study of the effects of opening up and fatliquoring could be based on the work of ALEXANDER et al (1993b) on softness. Such an investigation, coupled with acoustic emission analysis, should indicate which level of structural hierarchy is responsible for the yield in the stress strain curve. The fourth suggested study could be based on the work reviewed by ALEXANDER. Such a study
should incorporate optical and electron microscopy, with selective staining techniques to quantify the removal of non-collagenous material.

The next stage of this ongoing project is to study partially processed leather under biaxial strain, which realistically portrays the deformations experienced in practical mechanical operations. It is Attkenburrow’s hypothesis that in biaxial tests fibres come under strain at an earlier stage than in uniaxial tests. Biaxial tests were considered at the outset of this investigation. Several pilot experiments with a plain strain geometry were undertaken. However, two difficulties were encountered:

i. slippage of material from the jaws of the tensile testing machine made measurement and application of strain inaccurate;

ii. measurements of the strain field and area strain were impossible to determine accurately and rapidly with available equipment.

The slippage of material from the jaws can potentially be solved using hydraulic grips with textured grip plates. The cost of image analysis equipment and software required to determine accurately the strain field and area set has fallen. Both problems can now be solved with adequate capital investment. Ideally any future biaxial tests should include acoustic emission
analysis. In situ measurement of the change in the three dimensional weave and thickness should be made during straining of samples.
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APPENDIX I STANDARD PROCESS FOR WET BLUE LEATHERS

PELT-WET SALTED DOMESTIC OX

LIMING (Weight based on unflleshed wet salted weight)
DIRT SOAK 200% WATER @ 26 C RUN 60 MINUTES DRAIN
MAIN SOAK 170% WATER @ 26 C RUN 60 MINUTES DRAIN REPEAT
LIME 160% WATER @ 26 C 2.5% SODIUM SULPHIDE (60/62% FLAKE)
5% LIME RUN 90 MINUTES
THEN OVERNIGHT (12-15 HOURS) RUN 10 MINUTES STOP FOR 20 MINUTES
TEMPERATURE BETWEEN 24.5 and 26 C
DRAIN WASH OFF WATER @22 C
WHITE LIME 150% WATER @ 22 C 4% LIME
RUN 15 MINUTES
RUN 10 MINUTES FOR EVERY 2 HOURS FOR 20-24 HOURS
DRAIN WASH OFF WATER @ 22 C EMPTY DRUM
FLESH SPLIT 2.2-2.4mm BACKBONE 2.6-2.8mm BELLIES

CHROMING (Weight based on lime split pelt weight)
WASH 90% WATER @ 35 C RUN 10 MINUTES DRAIN
DELIME 70% WATER @ 35 C 3% AMMONIUM SULPHATE 0.4% SODIUM
METABISULPHITE 1% BATE(PBW) RUN 60 MINUTES DRAIN
pH 8.8-9.0 28-30 C clear crosssection to phenolphthalein
WASH 100% WATER @ 21 C RUN 10 MINUTES DRAIN

PICKLE 20% WATER @ 21 C 6% SALT 1% SODIUM FORMATE RUN 10
MINUTES>50°Bk
2.2% SULPHURIC ACID 77%(1:10) RUN 120 MINUTES
pH 2.9-3.4 yellow cross section to bromo cresol green

15 The Garston Tanning Co Ltd King Street, Garston, Liverpool, Merseyside. L19 8EF
197
8% CHROME POWDER 42% BASIC RUN 60 MINUTES

0.5% TANBASE RUN 10 HOURS  pH 3.6-3.8

DRAIN  WASH  EMPTY DRUM

FATLIQUORING ¹⁶(Weight based on Sammed Weight)

WASH  200% WATER @ 35 C RUN 10 MINUTES DRAIN REPEAT

NEUTRALISE 150% WATER @35 C 1% SODIUM BICARBONATE RUN 30 MINUTES

1% SODIUM BICARBONATE RUN 30 MINUTES

Subsequent additions of sodium bicarbonate added to achieve pH 5-5.5

DRAIN

WASH  200% WATER @60 C RUN 10 MINUTES DRAIN REPEAT

FATLIQUOR 150% WATER @60 C RUN 10 MINUTES

6% REMSYNOL ESI RUN 45 MINUTES

FIX  ADJUST pH TO 3.5 WITH FORMIC ACID

¹⁶ Process recommended by R.G. Graves Senior Lecturer
Leather Technology
APPENDIX II PREPARATION OF MICROSCOPE SLIDES STAINED FOR ELASTIN

i) Cut samples from the hide along the hair follicle direction.

ii) Remove all the water from samples by solvent dehydration. Using the following alcohol gradient:
   - 70% Alcohol 6 hours
   - 90% Alcohol 3 hours
   - Absolute Alcohol 3 hours
   - Absolute Alcohol 6 hours
   - Xylene 8 hour+
   to replace all the water in the sample with xylene

iii) Embed samples in paraffin wax
    The samples must remain in melted wax for over 2 hours to allow the paraffin to penetrate the hierarchical structure and replace the xylene

iv) Section to about 60μm with microtome (rocking)

v) Float sections onto slides with a constant temperature bath held at a temperature of about 50°C using Albumin (egg white) smeared over a clean slide clean slide.

vi) Dry slides in dust free environment (>16hrs)

vii) Dissolve wax by gently heating the slide over top of blue bunsen flame and immerse the slide in xylene.

viii) Take the slide down the alcohol gradient to 70% alcohol

ix) Stain in orcein (diluted 9:1 in acid alcohol\(^{1}\)) in overnight (ie >10 hrs)

x) Rinse in 70% alcohol and differentiate in acid alcohol

xi) Mount using (DPX mountant) and cover with glass cover slide

\(^{1}\) Method based on BLC Rawstock and Tanning Dept manual section 12 sheet 1 issue 1

\(^{1}\) 1ml of conc HCl to 99mls of 70% alcohol
APPENDIX III CONVERTING BETWEEN A WET WEIGHT AND DRY WEIGHT BASIS

If the mass of a conditioned sample before drying equals \( M \) and the dry mass of a sample equal \( M_0 \) then the mass of water lost on drying \( M_L \) equals \( M - M_0 \). The moisture content is expressed as a fraction of the wet mass (weight) \( C_{wet} \) is expressed in equation 1. Similarly the moisture content is expressed as a fraction of the dry mass (weight) \( C_{dry} \) is expressed in equation 2.

\[
C_{wet} = \frac{M_L}{M} = \frac{M - M_0}{M} \tag{1}
\]

\[
C_{dry} = \frac{M_0}{M_0} \tag{2}
\]

By substituting for \( M_0 / C_{dry} \) for \( M_0 \) from equation 2 into equation 1 and rearranging it can be shown that \( C_{wet} \) is related to \( C_{dry} \) by equation 3

\[
C_{wet} = \frac{C_{dry}}{1 + C_{dry}} \tag{3}
\]

Both sides of this equation need to be multiplied by 100 to express the moisture content on a wet weight basis as a percentage.

Figure AIII above has been plotted to assist the reader in performing the conversion from a moisture content on a dry weight basis (or g per g) to a the wet weight.