

THE MECHANICAL PROPERTIES OF LEATHER IN RELATION TO SOFTNESS

**A thesis submitted for the degree of
Doctor of Philosophy
University of Leicester**

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To my mother — Sun Xiu-Zhen

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ABSTRACT

The deformation behaviour of chrome tanned crust leather (with or without fatliquor) and finished leather has been measured in three-point bend, tensile and compression tests. Relations between the experimental results and the perceived softness of the leather were investigated. The instrumentally assessed softness of a set of leathers was represented by parameters obtained from these tests and compared with a quantified subjective assessment. Differential Scanning Calorimetry (DSC) was used to analyse the water status in crust leathers. The influence of water content prior to staking on its softening effect was investigated. An orthogonal experiment was applied to investigate the influence of various factors (e.g. amplitude and frequency) on the softening effect of mechanical action to obtain an optimum combination of these factors.

The bending force, F , increased in a linear way with increasing sample width, w , in accordance with the standard theory of beam bending. However the change in F with increasing sample thickness, t , departed (markedly in some cases) from the standard theory. The theory of laminated materials offered a quantitative description of the dependency provided that the grain and corium layers were regarded as the laminae. F was approximately proportional to the actual bending length, l , raised to a power between -2 and -3.

An empirical equation based on the results of the bend testing was developed. A parameter, S_e/t^n , can be used to rank the softness of leather, where S_e is equivalent to the bending stiffness in standard bending theory, and n is the approximate index in the power function describing the relationship of the bending force F to the sample thickness t ($F \propto t^n$) for a particular type of leather.

A model describing the compression behaviour of crust leather is proposed which involves four stages of compression: (i) hair-like fibres being bent flat onto the surface and buckling of vertical fibre bundles, (ii) closing up of voids between fibre bundles, (iii) closing up of voids between fibres, and (iv) compressing of solid fibres.

DSC results indicate that water has a stronger interaction with collagen molecules in an unfatliquored leather than in a fatliquored one. Fatliquor appears to function as a shield between water and collagen.

The influence of water content prior to staking on the resulting softening effect was clearly reflected in bending and tensile tests, but was not nearly so evident in a compression test. It is shown that a maximum softening effect can be obtained in the staking process when moisture content is about 30 ~ 40%.

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CHAPTER 1

INTRODUCTION

1. 1 Leather and Softness

Historically leather was a functional material selected as “fit for purpose”. However in recent times, both aesthetic and practical factors are involved in a consumer’s appraisal of leather materials as used for various applications. This development prompts the need for an understanding of this natural material taking account of both process procedures and the structure of leather. In addition, setting up some reasonable objective standards to harmonise the subjective appraisals of different consumer groups also plays very important role.

The concept of “soft” or “softness” must have arisen along with the emergence of leather making. An early goal was to use animal skins to make leather in order to keep the body warm and protected in a comfortable way. There is no doubt that like some other physical characteristics of leather such as strength and elongation to break, softness is a crucial factor which needs to be considered frequently when leather is being made. Softness is also important to consumers.

For many years, the most common parameters used to describe the mechanical properties of materials in general, such as breaking strength, extension to break and modulus, have been used to characterise leather. Some other parameters and concepts which are used to characterise the properties and structure of some specific groups of materials have also been transferred with little or no modification by leather technologists and researchers. Such parameters and concepts include tear strength and density. Also some measurements and parameters were particularly designed to meet the singularity of leather structure; for example, the resistance to the grain crack obtained from the lastometer test, fibre compactness, and angle of weave.

The softness of leather is very important in the characterisation of its quality and also plays an important role in quality control in leather making. However, unlike many other parameters used in the description of the physical properties of leather which have an unequivocal definition and can be accepted unanimously no matter where the tests are carried out, the concept of softness appears to be harder to define and quantify. The terms “soft” or “softness” have been used in many papers related to either leather research or techniques used in the tannery^[1 - 5]. However few systematic investigations aimed at understanding softness

from both macroscopic and microscopic points of view, have been undertaken. Even the description “softness of leather” still remains as an ambiguous term, and has yet to be adequately defined. These difficulties arise because leather softness is actually related to several properties, rather than a single property of leather.

There do, however, exist a number of methods which can give a judgement of the softness of leather, but these are either too subjective (i.e. the use of assessors) or involve the use of an *ad hoc* instrumental test. Often such tests subject leather to a complicated stress pattern and so understanding the deformation behaviour is very difficult. The aim of this research has therefore been to establish procedures to characterise the resistance of leather to simple modes of deformation such as tension, compression and bending, to further understand the deformation characteristics of leather in relation to its microstructure, to determine the influence of some key processes used in the tannery (i.e. staking and fatliquoring) on the deformation behaviour of leather, and to assess the implications of the results for leather softness as judged subjectively.

1. 2 Literature Review

Research into the properties of leather can be broadly divided into two categories. The first category looks at the chemical processes associated with leather-making including (a) chemical reactions related to the manufacturing processes such as the mechanisms of liming, and tanning, and (b) chemical reactions indirectly related to leather making such as the treatment of effluent for environmental protection and the recovery and re-use of tannery disposals. The second category focuses on the improvement, understanding and control of the mechanical properties of leathers. Such research aims to (i) optimise the use of mechanical actions involved in the tannery (e.g. setting, staking), (ii) establish various mechanical testing procedures and (iii) improve the quality of leather. These two areas of research are closely linked. The research described in this thesis appertains mainly to the second category although to some degree it has been necessary to discuss the results from a chemical standpoint.

1. 2. 1 Hierarchical Structure in Leather

1. 2. 1. 1 Structure Levels of Other Materials

For materials made of small molecules, there are typically two structure levels: the chemical structure and the arrangement of the structural elements. Both levels play important roles in contributing to the properties of that material. There are typically three levels for macromolecular structure: 1) short range structure including chemical composition, geometric shape and configuration; 2) long range structure of the molecular chain such as the size of molecules and their conformations; and 3) structure of the aggregated state, e.g. the way the molecules aggregate to form crystalline or amorphous phases. Variations at any level of structure will alter the properties of the material.

1. 2. 1. 2 Structural Levels of Leather

Leather is a product made from a natural material, animal skins. Nevertheless, even after many processing steps in the tannery, leather still retains a prominent feature of natural organic materials, that is a multi-leveled structure which is organised in a unique way.

Major raw materials for leather are cattle hides, pigskins, goatskins and sheepskins. Sometimes other sources such as fish skin and reptile skin are also used for making leather. The structures of mammalian skins, though, are rather similar.

Examination under optical microscope with a low power lens indicates that skin comprises three distinct layers, (i) the epidermis layer, (ii) the whole corium layer and, (iii) the flesh layer; *Figure 1.1*^[6].

Epidermis:

This layer is formed by keratin and is a relatively thin, outer layer of epithelial tissue. The layer has a protective function for animals. The thickness of the layer depends on the hair coat development and is about 1% of the total thickness of skin for a thickly hair coated animal and 5% for a sparsely hair coated animal. The epidermal layer is removed in the early stages of leather making.

The whole corium:

This layer forms the main part of the skin. The structure of the corium determines the characteristics of the finished leather. This layer can be subdivided into two layers, the grain

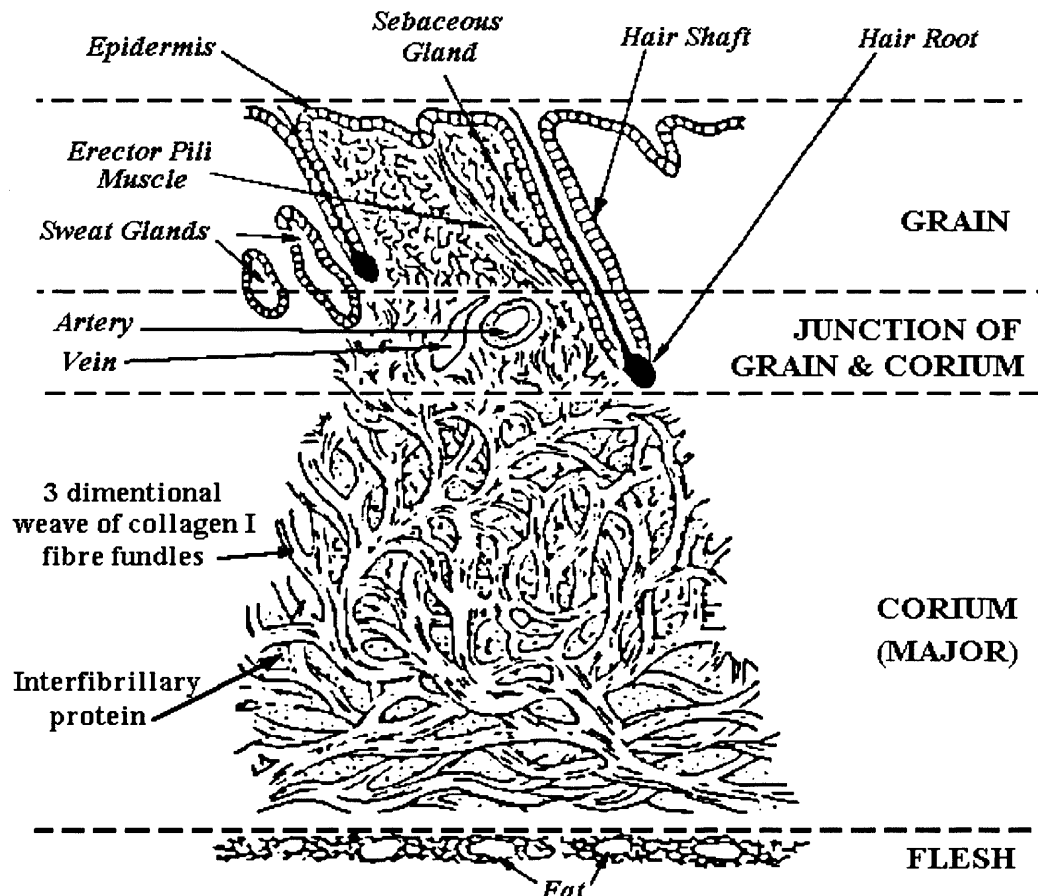


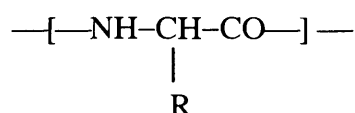
Figure 1.1 Cross section of the cattle hide^[6].

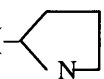
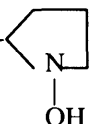
layer and the corium major layer — the latter is also simply called corium — as shown in Figure 1.1. The grain layer is thinner than the corium and contains the majority of the non-collagenous substances such as elastin fibres, fat cells, sebaceous glands, sweat glands, hair follicles and muscle tissue. These non-collagenous substances are either totally or partly destroyed in leather making. The result is a leather product which comprises mainly collagen I fibres and fibre bundles interwoven tightly in a form of network. The two sub-layers, grain and corium, visible under an optical microscope, differ in thickness, and in the way the collagen fibres are interwoven. The grain layer is thinner and more densely interwoven than the corium layer which is thicker with a lower density of interweaving of fibres^[7]. The thickness of the grain layer as a percentage of the total skin is generally about 25-35% in cattle hides, 40-65% in goatskins and 50-70% in sheepskins. The thickness also depends on the age of the animal and the process history. In pigskins no clear distinction exists between the two layers^[8]. For leather containing the two layers, the grain layer which consists of fine fibres interwoven and penetrated by hair follicles is somewhat weaker than the corium^[9], particularly with respect of tear strength. For tensile strength, recent research on these two

split layers shows that the grain layer is weaker only when the thickness is above a certain limit^[10].

The structural units of leather, the fibre and fibre bundles which branch and regroup to form a three dimensional network, have been observed and recognised for a long time. However a multiplicity of states of sub-division occurs in the “fibres”.

Collagen is the fibrous biopolymer which comprise the major component of leather. It comprises amino acid residues with the following structure:



Here R stands for different substituents which determine the various types of amino acid residues. Different orders of amino acid residues lead to a variety of collagen types. At least 19 different types of collagen are known in vertebrates^[11, 12]. Type I collagen is the most prominent in leather but there are also traces of type III and V^[13]. Fietzek and Kühn^[14] propose that in skin type I collagen, each molecule contains more than 1000 amino acid residues. In collagen type I, the typical amino acid pattern is the repeating sequence Gly-X-Y, where X and Y are other amino acids arranged in a variable but *not* completely random way^[15, 16]. Another important feature is the high content of the imino acids proline (—) and hydroxyproline (—) in the X and Y positions, being about 12.2% for the proline and

9.4% for the hydroxyproline for type I collagen in cattle hide^[17]. The existence of these five membered rings, particularly due to their stereo volume and possibly their ability to form hydrogen bonds, is of great importance in terms of the three dimensional conformation of each peptide chain which has a helical rather than linear structure.

Three such collagen molecules twist together to form one strand of a right-handed triple helix, which is termed the tropocollagen molecule with an overall length of about 2800 Å, a diameter about 14 Å and a relative molecular mass of about 300,000^[18]. Such tropocollagen molecules pack together in a “quarter stagger” arrangement^[19]; i. e. a head-tail arrangement between the longitudinal molecules with a gap in between, and 75% overlap between the lateral molecules, resulting in a 640 Å periodicity seen in electron micrographs. The whole assembly of tropocollagen molecules forms a fibril with a diameter of 200 ~ 1000 Å, containing about 7000 collagen molecules. In fact, a further subdivision, the microfibril, can be observed occasionally under the electron microscope when fibrils are

swollen in acid ^[20]. There are possible two models for the constitution of microfibrils: one model involves 3 tropocollagen molecules and the other model 5 tropocollagen molecules. The latter model is more widely accepted, and is considered to be a “distorted penta-unit” (*Figure 1.2* ^[21]).

Fibrils within fibres can be easily observed by using an electron microscope (*Figure 1.3 (a)~(b)* ^[22]). Fibrils constitute the fibres and the fibres constitute the larger visible units called fibre bundles, which may be up to the order of 10^{-1} mm in diameter and of indefinite length.

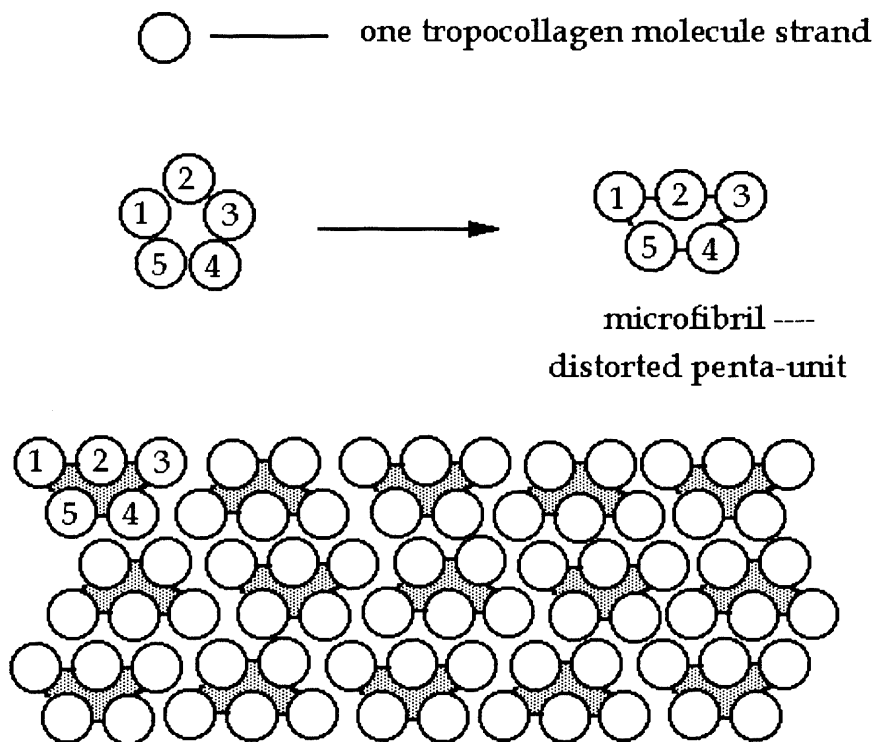
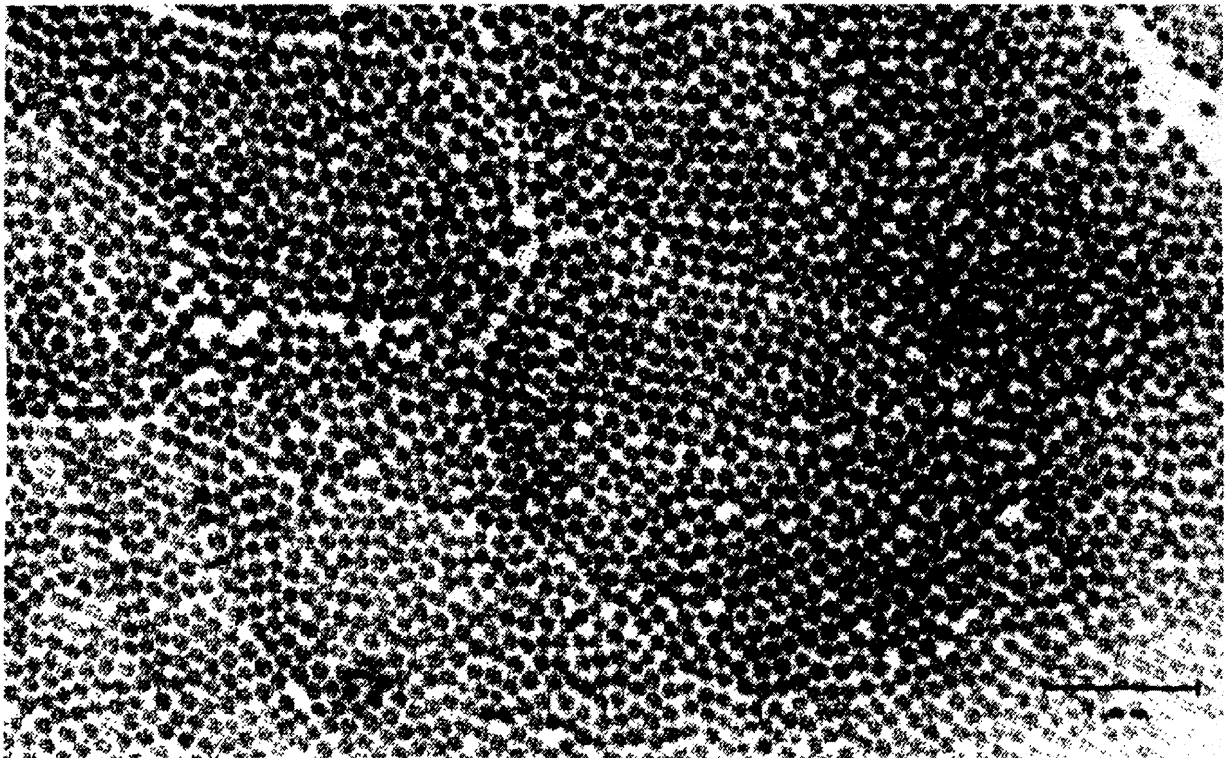
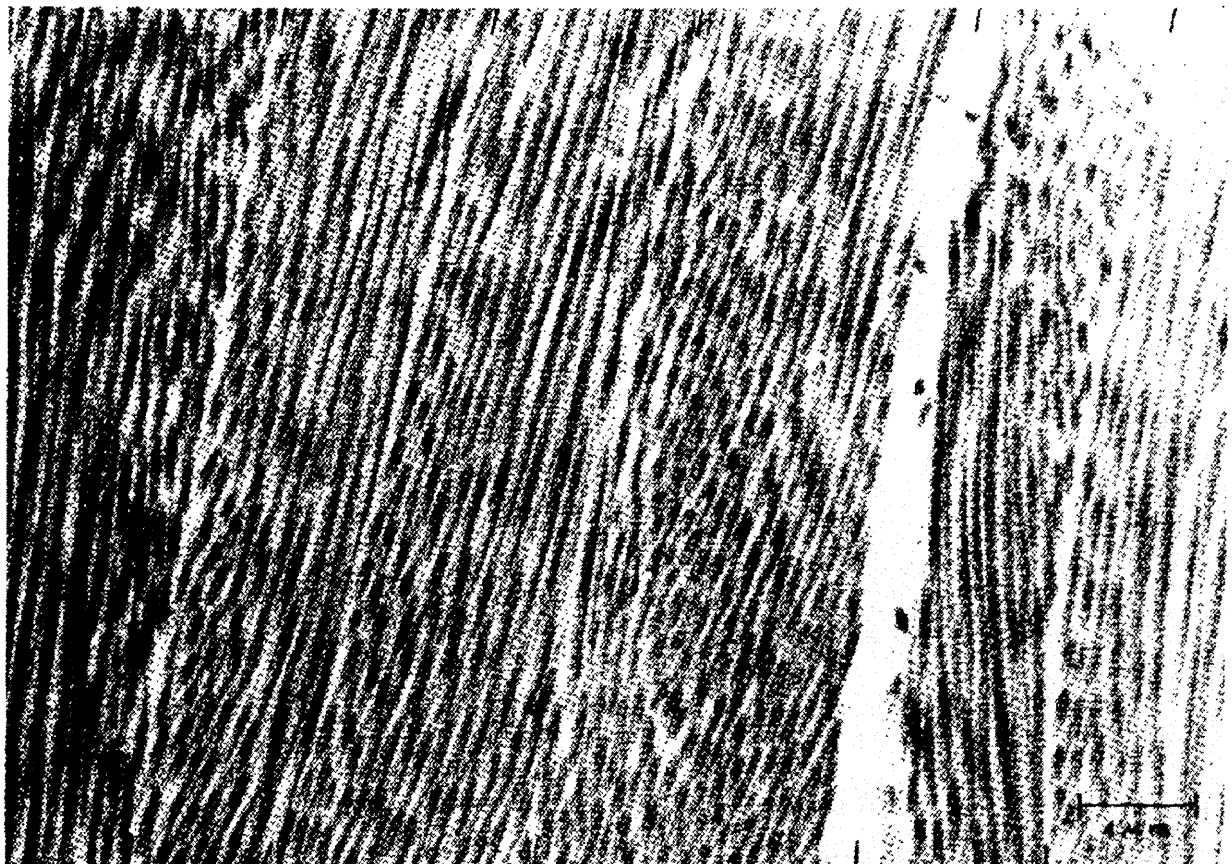


Figure 1. 2 The proposed distorted penta-unit for microfibrils.(based on reference 21)

The complete microstructural hierarchy of skin and leather is illustrated in *Figure 1.4*.



(a)



(b)

Figure 1.3 Fibril under transmission electron microscope^[22]. (a) cross section; (b) parallel.

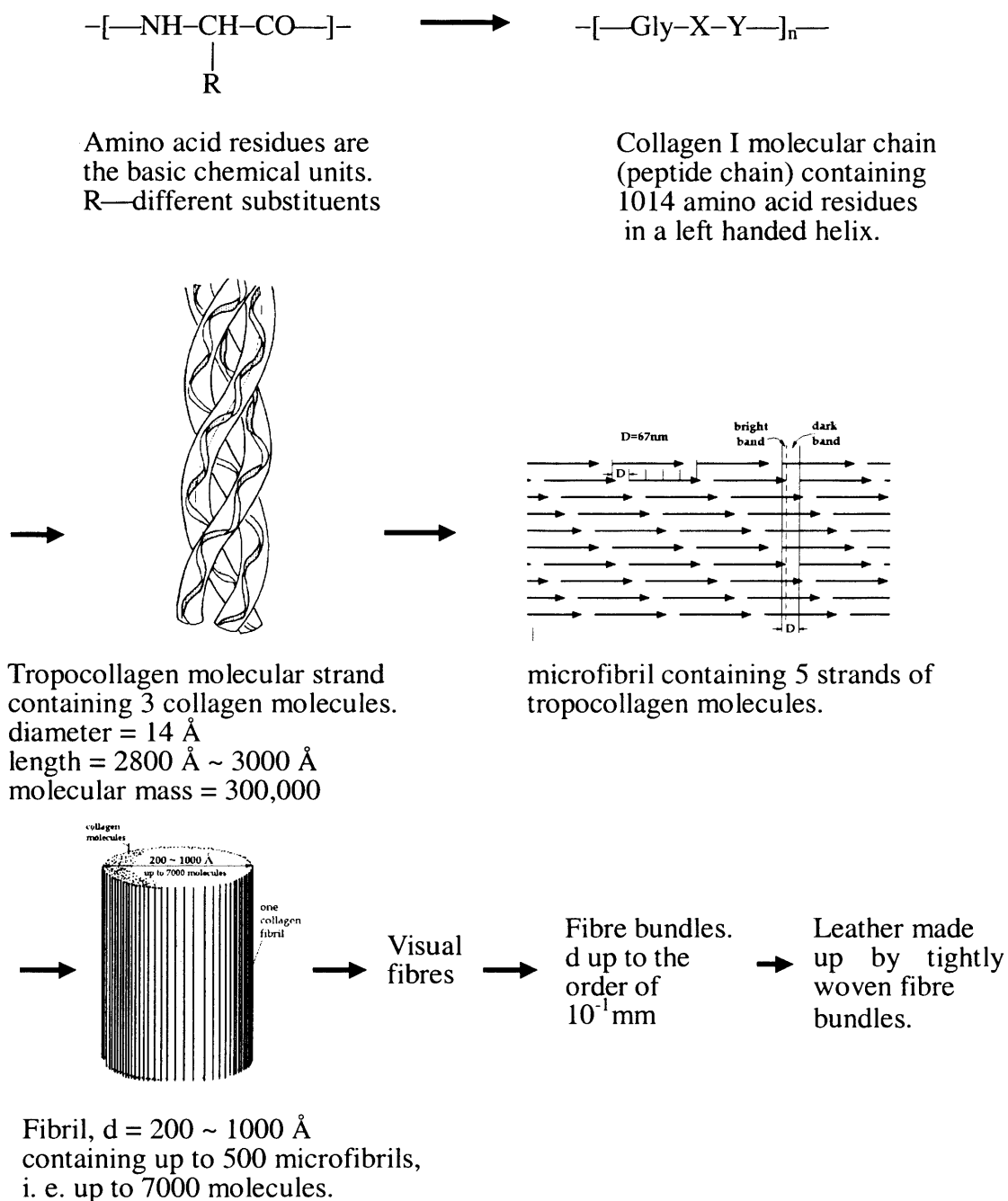


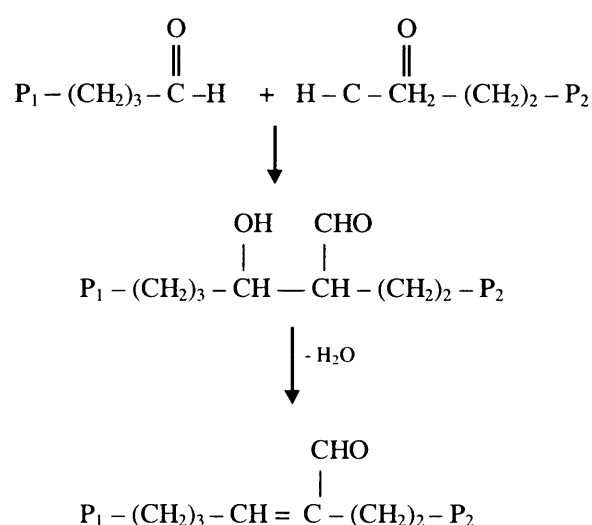
Figure 1. 4. Illustrative representation of the structure levels in leather ^[13].

1. 2. 1. 3 Crosslinks Inside Collagen and Their Influence

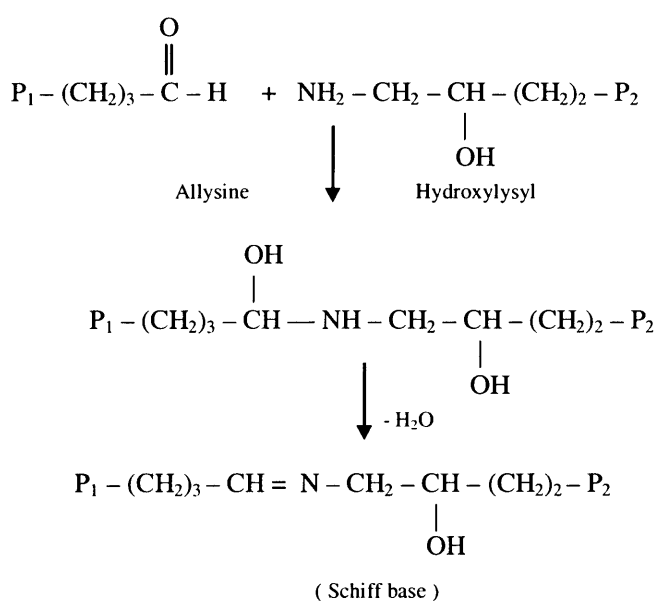
The character and properties of collagen are influenced by cross-link bonds, which are very important in tanning chemistry. There are several types of attractive forces between different sites on the collagen molecule which offer the possibility of forming cross-links between those sites. Such interactions may be Van der Waals, ionic or hydrogen bond. However the

most important are covalent bonds which form between functional groups of different α -chain molecules inside the tropocollagen molecules. α -chain denotes a collagen protein chain that is a *single* gene product.

The covalent cross-links in collagen can be divided into (1) intra-molecular and (2) inter-molecular cross-links. The former involve two α -chains within the same tropocollagen molecule. They are mainly aldol cross-links; i. e. aldol condensation of two allysine residues [23].



In leather, crosslinks are formed between two or more α -chains in different tropocollagen molecules through covalent bonds. These are mainly aldimine cross-links, forming a Schiff base; i. e. a condensation product of a hydroxylysyl residue and an allysine.



Within the group of inter-molecular cross-links, a further two types can be classified. One group is the cross-links in newly formed collagen which can be reduced by sodium borohydride, known as “reducible” cross-links. The other group is formed during maturation and is stable to high temperature and cannot be reduced by sodium borohydride; such cross-links are known as “mature”^[24].

These cross-links are important for the physical and chemical properties of collagen. Collagen becomes increasingly insoluble as more cross-links are formed. Its ability to swell in acid solution decreases, as does its susceptibility to enzyme attack, whereas its mechanical strength and hydrothermal stability increase^[25].

1. 2. 2 Mechanical Behaviour of Leather

1. 2. 2. 1 Mechanical Behaviour of Fibres from Leather

Individual leather fibres were studied in the nineteen twenties by Jovanovits and Alge^[26] who were soon followed by Ptschelin and Chemov *et al*^[27, 28]. Mitton^[29] made an extensive examination of the influence of moisture on the dimensions and torsional rigidity of fibre bundles. From tensile tests he concluded that:

- i) The tensile strength of fibres from vegetable-tanned leather was about 60~150 MPa. After correcting the possible error caused by reading of fibre diameter, he pointed out that this number would be 100~150 MPa.
- ii) Elongation at break was about 12%.
- iii) The stress – strain behaviour of fibres only approximately obeyed Hooke’s Law.

The load extension curve was accurately represented by the equation $E = a \cdot P^n$, where E — extension, P — load, a — 1.06 and n is slightly greater than 1.

According to Highberger^[30] the calculated tensile strength of collagen fibres based on the rupture energy of carbon-nitrogen bonds (the weakest in the chain at 203 kJ mole⁻¹) would be about 2900 MPa rather than the observed strength 120 MPa.

Hall^[31] did research on raw collagen fibres and tried to use the theory of rubber-like elasticity to analyse the stress strain curves. By suitable modification of Frenkels equation he obtained a good statistical fit of the data to the theoretical curve. However, the value of C , the initial length of a molecular chain became negative for a good fit! This is clearly impossible. In later work^[32] Hall recorded load as a function of temperature at constant length and, using the Wiegand-Snyder equation, calculated the internal energy and entropy contributions to the

retractive force. Entropies were too small to allow acceptance of a “rubber-like” theory and increased with increasing strain. This pattern was not to be expected but has apparently been noted with certain rubbers. The generation of “loose ends” by molecular rupture was not considered.

Crompton ^[33] tested fibres clamped between jaws rather than glued to hooks. Statistical analysis demonstrated that “jaw failures” did not increase experimental error. Tanning with an increased level of formaldehyde increased the shrinkage temperature but caused a decline in tensile strength. Chrome tanning also increased shrinkage temperature but did not reduce fibre strength.

In the 1960's Morgan ^[34, 35] studied in some detail the behaviour of collagen fibres. He showed that:

- i) Tanning reduced the strength of raw collagen fibre, together with a smaller reduction in breaking extension.
- ii) Variations in tannage produced no significant changes in either fibre strength or extensibility.
- iii) The reduction in fibre strength or in extension was nearly independent of the chrome content of the fibre.
- iv) Thinner fibres were stronger than thick ones.
- v) There was a low modulus region at low strain (below 1%) which was attributed to the straightening of molecular chains.

Rajaram et al ^[36] studied the mechanical properties of collagen fibres from another point of view and looked at the role of the fibre's length. They concluded that:

- i) As the length of fibres increased, the modulus increased and the breaking stress and breaking strain decreased. Break strength y , break strain x , and fibre length l were related in the form of following equation:

$$\ln y = - 4.11 + 2.04 \ln x + 0.73 \ln l$$

Attention needs to be paid to the fact that x is also a function of l .

- ii) Relaxation times increased as the length of the fibres increased.
- iii) The results observed above may be attributable to the existence of free fibril ends along the fibre and the friction associated with them.

Since the relaxation time is related to the length of the fibre, and the modulus is a function of time (or extension rate and relaxation time), allowance should be made for extension

rate when obtaining the comparable modulus from the fibres with different length. No such correction was made. The state of the fibres tested such as their degree of twisting, was not mentioned.

1. 2. 2. 2 The Fibre Network

The range of extension to break for fibre bundles is between 12% and 24%^[29, 35, 37] although in a tensile test, leather will generally extend to between 30% and 120% before rupture^[38]. Therefore a considerable network effect is present in which the spatial arrangement of fibres is altered by stress with presumably a degree of fibre alignment along the direction of stress. In the case of straining perpendicular to the backbone where larger elongation to break can be observed^[39]. Attenburrow^[10] suggested that deformation of the network accounts for at least 2/3 of the elongation to break. The typical strength of bulk leather ranges from 15 MPa to as high as 50 MPa^[40, 41], while the strength for a single fibre bundle ranges from 100 – 150 MPa^[29]. These discrepancies of strength and extension to break are due to 1) the presence of voids between fibres and 2) the imperfect alignment of fibre bundles at rupture.

In fact, the pattern of the fibre network inside leather can be influenced by processing and this pattern has a direct influence on service performance. Weave angle is defined as the average angle between the fibres and the outer surface of the leather and can provide a general description of how the fibre bundles are aligned in the leather. Generally, a low angle of weave is associated with a high modulus and a low extension to break whereas a high angle of weave provides a low modulus and a high extension to break. In addition, the average distance between junction points in the “mesh-like” construction, and the “loose ends” — unattached fibre ends generated when leather is split for the purpose of thickness control — also influences the mechanical properties of leather. These influences are particularly significant when the thickness of leather falls within certain limits. Some workers have argued that with sole leathers, these “loose ends” amount to a layer about 0.1 mm thick, while others have argued that in softer leather with greater fibre mobility, this is an underestimate^[42]. Attenburrow^[10] explained how a combination of average distances between junction points in the fibre network and the thickness of leather affects the tensile strength of leather. This model (*Figure 1.5*) demonstrates that at a certain split thickness there cease to be enough inter fibre connections to maintain a continuous network. This pattern accounts for the dramatic loss of strength as is observed for the corium when split thinly (*Figure 1.6*).

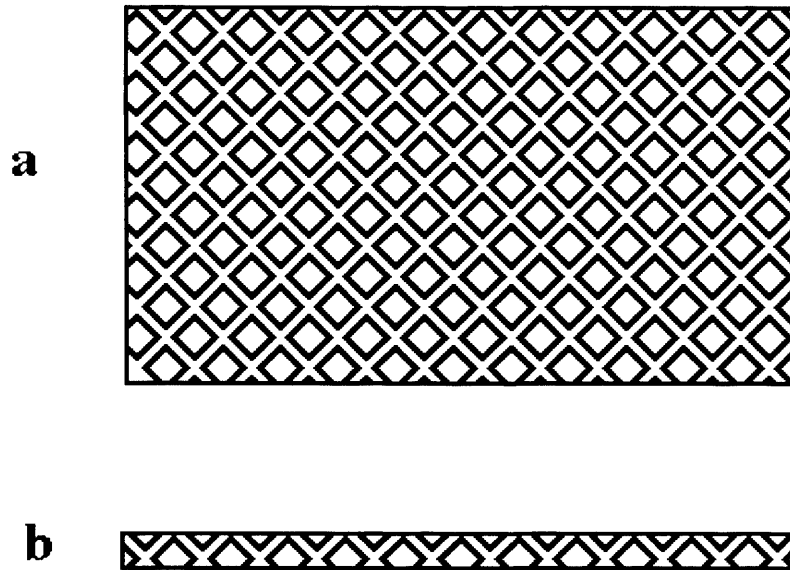


Figure 1.5 Schematic illustration of network units in corium layer^[10].

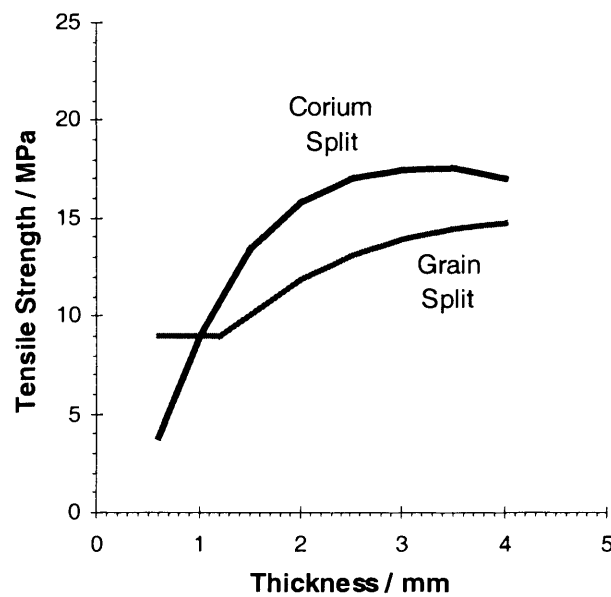


Figure 1.6 Tensile strength for corium and grain splits^[10].

The importance of fibre weave for strength is also clearly shown in studies of the physical properties of those hides which display vertical fibre defect^[43] and those hides made from kangaroo^[44]. The former (particularly from Hereford cattle) shows an unusually high angle of weave in the corium layer. Thus, during lateral stretching few of the fibres will be

involved in load bearing and so most of the load must be taken by the grain layer. Since, as shown in *Figure 1.6*, the grain layer has a lower tensile strength and tear strength compared to full bulk leather, leather from hides with vertical fibre defect is weaker. In the latter case, leather made from red kangaroo shows a very low angle of weave and so exhibits significantly higher tensile strength than the corresponding bovine leather.

In looking at the tensile testing of leather, Mitton^[29] also studied the influence of the inclination of the fibres inside the leather. He assumed the following:

- i) no lateral contraction in the test piece up to break.
- ii) a random distribution of angles of inclination of the fibres.
- iii) specimen rupture only occurred when the fibres had been aligned along the direction of stress and had reached their breaking extension.

Mitton calculated the tensile strength, P , of fibres using the following equation

$$P = 5 \cdot T \cdot \frac{A}{R}$$

where T is the tensile strength of the leather, and A and R are the apparent and real density of the leather respectively.

Although the calculated P in his studies was in tolerable agreement with that obtained from single fibre bundle measurements, the closeness of agreement is critically dependent on assumption (i) which just happens to be true for the leather used by Mitton. Assumption (i) is not usually valid.^[45]

Acoustic emission studies^[46, 47, 48] imply that assumption (iii) is not generally true, since normally an increasing failure rate (i. e. acoustic pulse rate, equivalent to the breaking event rate in the sample) was recorded as rupture was approached. In Kronick's study^[48, 49] of bovine hide, high energy acoustic pulses were noted at strains well before gross rupture. Since the magnitude of the pulse energy is related to the energy needed for that particular breaking event (or the average amount of energy for the breaking events in a selected interval of strain), the evidence of Kronick's work shows that fibres can break well before gross specimen rupture.

1. 2. 3 Measurement and Characterisation of Softness

It seems unlikely that the softness of leather can be completely represented by a single basic mechanical parameter (e.g. tensile modulus). Perceived softness is actually related to several, rather than one individual mechanical property of leather. A person forming a judgement on

softness tends to stretch, compress and bend the leather in question. However attempts have been made to quantify the softness of leather using a variety of instrumental methods, which may produce measures which correlate with subjective softness.

1. 2. 3. 1 Subjective Assessment

Hand grading by experienced tanners is a traditional method for determining leather softness. Softness is judged by the “feelings” of a tanner’s hand. Such a subjective approach allows leathers to be ranked for softness and it is sometimes argued that its subjectivity allows a skilled grader to take account of variations in softness between leathers^[5]. However this subjective response may be affected by factors which are not directly associated with the intrinsic softness of the leather. Firstly, the size of the sample, especially the thickness, will affect the judgement of the inherent softness of the leather, since it is unlikely that the assessor can compensate for sample size in the assessment. Secondly, the appearance of a sample, such as the smoothness of its surface, its colour and gloss etc., probably also affects the judgement. Thirdly, the variations in estimates of softness between individuals will always cause disagreement. Therefore, various instrumental methods and devices have been developed attempting to assign a numerical value to leather softness. Some of these approaches are reviewed below.

1. 2. 3. 2 Drooping Angle Measurement

Conabere^[50, 51, 52] studied the bending behaviour of leather using the Pierce flexometer, an instrument originally developed for textile fabrics. This approach was later taken up by Mitton and Duckworth^[53] who examined the variation of bending modulus with orientation and position on the hide. Considerable variability was observed with the highest and lowest values differing by more than an order of magnitude.

The features of the Flexometer are illustrated in *Figure 1.7*. Soft leather droops further (larger drooping angle θ) than firmer leather with the same overhang length L . The 41.5° cantilever bending resistance tester (Shirley Stiffness Tester) adopted the idea except that the drooping angle is set at 41.5° while the overhang length L is measured.

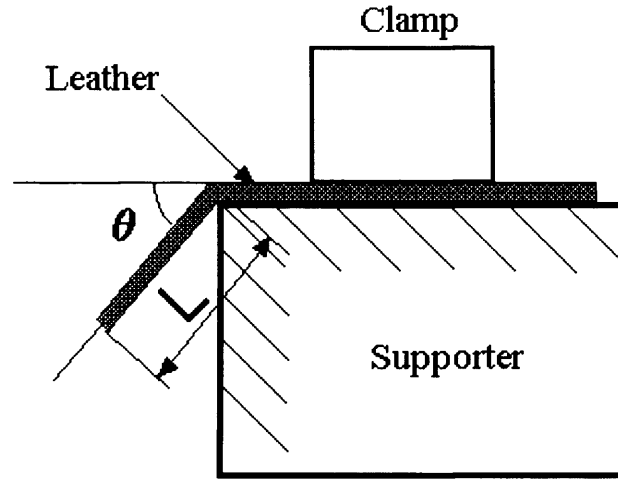


Figure 1.7 Principle of the Pierce Flexometer softness measurement.

The overhang length reflects the softness of leather according to the theory of bending modulus as reviewed by Walker^[54]. The fullness of a leather sample was determined using three equations. The first determines the “bending length”, C , of the sample. The “bending length” is a measure of the draping quality of a leather, and may be defined as length of leather which bends under its own weight, to a defined extent. For a rectangular specimen, C was given by

$$C = L \sqrt[3]{\frac{\cos \theta/2}{8 \tan \theta}} \quad (1 - 1)$$

where L is the overhanging length measured in centimetres.

θ is the angle of droop measured in degrees.

Thus the bending length C equals approximately half the overhang length L when the drooping angle is set to 41.5° .

The second calculation determines the “flexural rigidity” G of the sample:

$$G = WC^3 \quad (1 - 2)$$

where C is bending length.

W is weight per unit area of the sample (g cm^{-2}).

G is the force required to bend unit length through unit angle.

The third and last step calculates the bending modulus, q . For a homogeneous material, q is defined by the following equation:

$$q = \frac{12G}{d^3} \quad (1 - 3)$$

where G is the flexural rigidity.

d is the thickness of the sample expressed in mm.

The unit of the bending modulus is kg cm^{-2} . For the leather studied, G is proportional to a power of d nearer to 2.2 (rather than 3 as shown in equation (1 - 3)).

1. 2. 3. 3 Loop Test

In the vertical loop test ^[55], the force W required to depress a strip of leather clamped in the shape of a loop to a set distance is measured (*Figure 1.8*). The lower the value of W required, the softer is the leather.

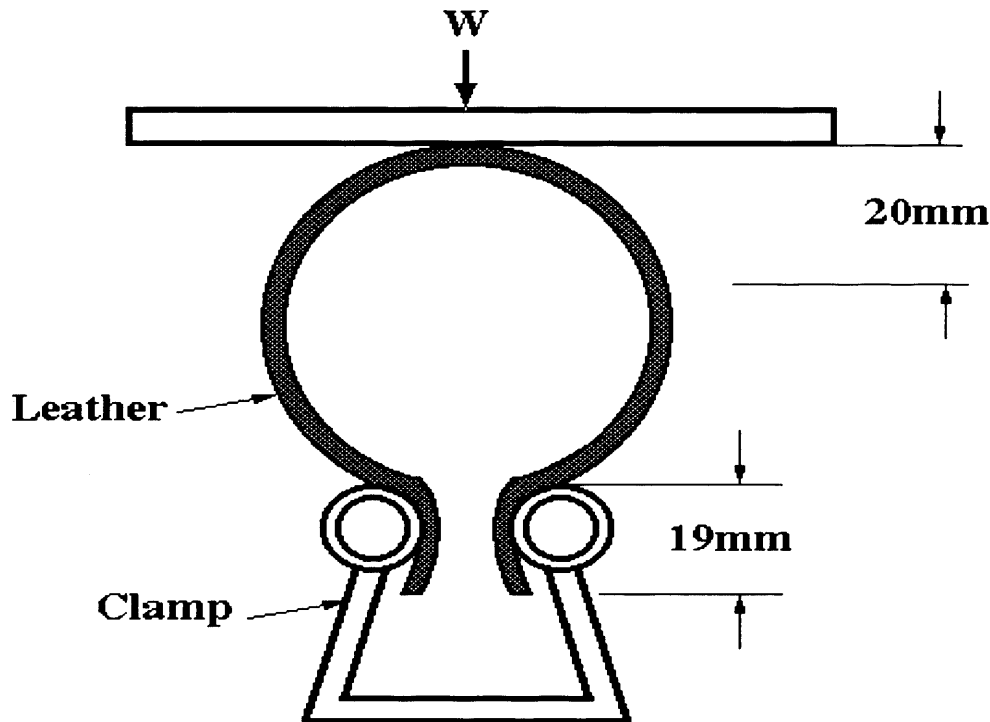


Figure 1.8 Loop Test illustration.

1. 2. 3. 4 BLC ST300 Softness Gauge

The ST300 softness gauge is a recent innovation developed by the BLC, the Leather Technology Centre^[56]. A disc shaped portion of the leather under test is clamped around its edge. A fixed load is applied to its centre and the amount of distension d , as shown in *Figure 1.9*, is measured. Two advantages are claimed for this instrument; (i) it is non-destructive (i.e. no samples need be cut) and (ii) the readings appear to correlate well with subjective

assessments of softness.

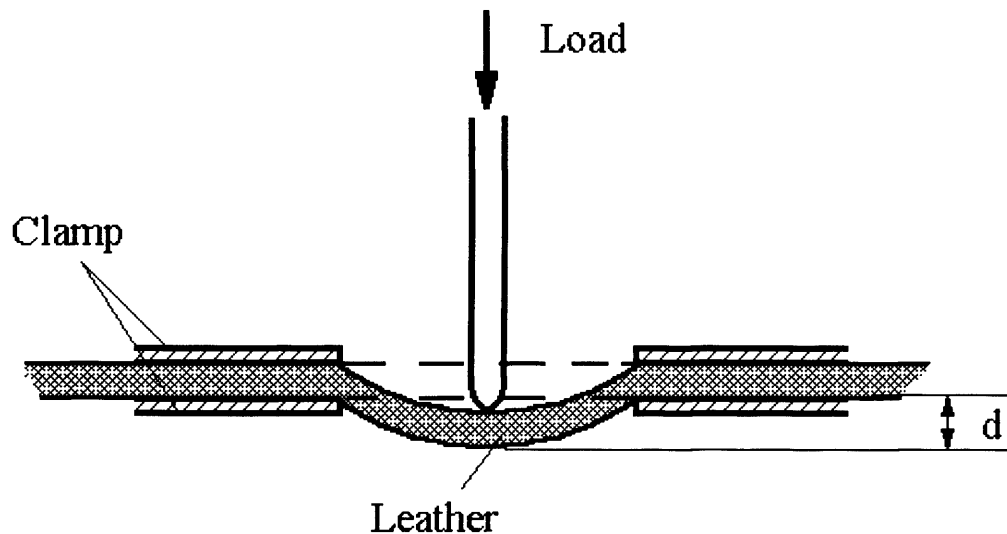


Figure 1.9 Illustration of the principle of the BLC Softness gauge.

1. 2. 3. 5 *Torsion*

Some other tests on softness measure the force when the leather sample is in torsion ^[4, 57]. The specimen is clamped between two clamps one of which can be rotated to a certain angle. The force needed is recorded. The larger the force, the harder is the leather sample.

1. 2. 3. 6 *Dynamic and Static Compression*

As another form of deformation, the compression response of leather has also been studied. Palm et al ^[57] applied a dynamic compression to leather, and afterwards, as in the application of this kind of approach to polymer materials, they measured the real modulus E' and the imaginary modulus E'' . In Palm's research, E' was taken as the parameter which best described leather softness since E' covered a much broader range of values than E'' . The results obtained by applying such a method around the whole of the hide were compared with those obtained by other methods such as dynamic flexure and torsion. Apparent density was also measured. Results from the comparison were found to be very controversial for leather, but unanimous for polymer materials such as plasticised and unplasticised polyvinyl chloride. It was claimed that the highest modulus (most rigid) measured by these dynamic techniques may be associated with the most randomised interwoven fibre structure, indicated by the

small variations found in tensile moduli with respect to the test specimen's orientation to the backbone. As a result of this randomised fibre structure, there are many more fibre-to-fibre cross contacts with no possibility of the fibres slipping alongside each other at low strains; thus there is strong resistive force to compression (high modulus).

Lokanadam et al ^[1] studied the behaviour of different light leathers under successive static compressive loads. The compressive strains produced under different loads were measured. They found that the slopes of plots of logarithm of load against thickness of the sample were closely related to the subjective assessments of leather softness made by a group of experienced tanners. Wang's study ^[58] on goatskin leathers also identified a strong correlation between the compressive strain at a given compressive stress and the softness as hand graded by a group of assessors. It was also reported that the degree of compressive strain decreased with the apparent density of the leathers. This result disagreed with the results reported by Palm ^[57]. In dynamic compression studies he found that higher density did not necessarily indicate higher (dynamic) compression modulus which was used to describe the softness of leather in his research.

1. 2. 3. 7 Other Methods

Recently Kellert and Wolf ^[59] developed an automatic softness tester; *Figure 1.10*. A clamped leather strip hangs vertically with the free end just in contact with a measuring cell. When the clamped sample is turned by a motor drive to a certain angle the force on the cell is measured.

Heidemann ^[60] suggested that both the pulse rate and pulse energy of acoustic emission produced during the deformation of leather are related to structural characteristics of leather. He states that if leather is hard the sound wave caused by an internal "breaking event" migrates more or less undisturbed to the sensor, while in soft leather, most of the sound energy is easily absorbed. He is of the opinion that really soft leather develops no sound ^[60]. Kronick et al ^[48, 49, 61] carried out extensive research on this subject and concluded that at low strains acoustic emission was due to the breaking of adhesions. On a second extension there was no acoustic emission up to the strain reached in the first cycle (Kaiser effect) and the sample was softer.

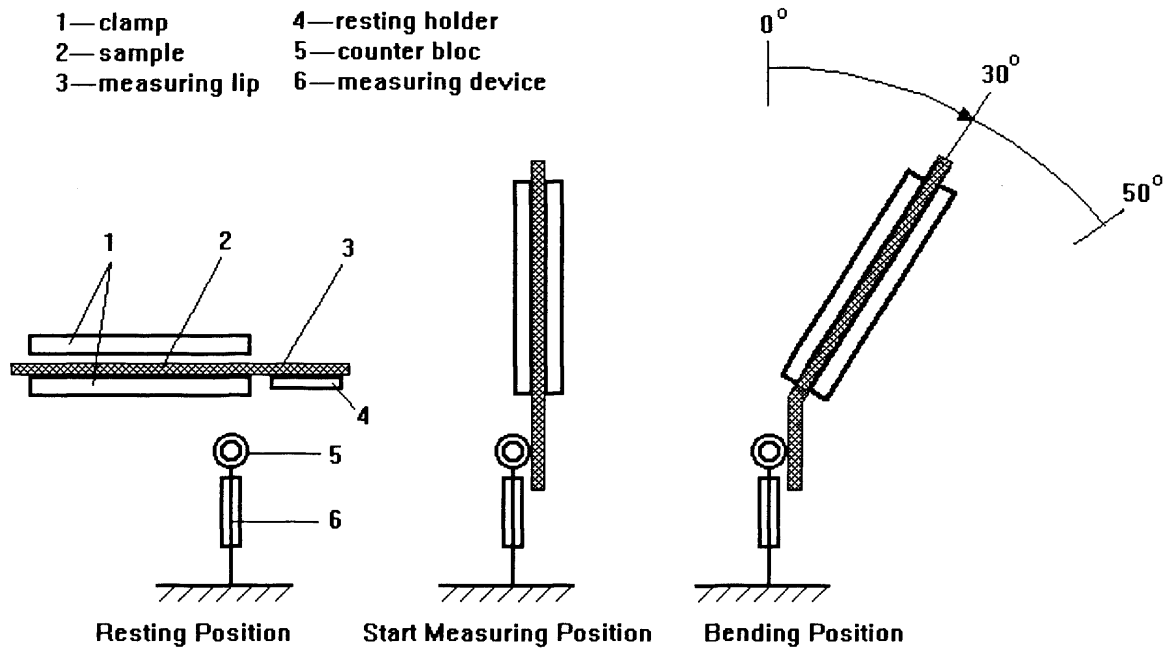


Figure 1.10 Softness meter of Kellert and Wolf.^[60]

1. 2. 4 Factors Affecting Leather Softness

1. 2. 4. 1 The Original Material

Leathers made from different kinds of skins have different intrinsic softness and show different characteristics. These differences are due not only to different species of animal but also to different breeds in the same kind of animal ^[8, 44, 58]. These differences are mainly attributed to:

- i) The constitution of skin, such as the fat content, shape, size and distribution of hair follicles, and the ratio of grain to corium thickness layer.
- ii) The size of collagen bundles, their shape (wavy or straight) and the weave pattern of collagen fibres.

In fact, due to the heterogeneity of leather, even samples from the same hide will behave rather differently depending on the location of the sampling area. Fibre orientation also plays very important role in this case.

1. 2. 4. 2 Processes in the Tannery — Chemical Treatment

From tanners' experiences it is believed that each process step can influence the final softness of leather^[2]. In essence leather making removes substances which are not needed, but

preserves and crosslinks the collagen fibres which are the main constituent of leather. Further added materials (dyes, fatliquors) can assign to the leather a certain property. Covington et al^[2] studied how each main process carried out in the tannery influences the mechanical properties of leather, especially its softness. It was concluded that:

- i) Soaking and bating make little contribution to the softness of the final product under their experiment conditions.
- ii) Liming and fatliquoring both influence the softness significantly, and among these two, fatliquoring having stronger influence. Without liming, fibres do not split or open up into constituent sub-units (fibrils), while without fatliquoring an opened-up structure can restick again during drying.
- iii) For the same type of fatliquor, the smaller the size of the dispersing particles in the emulsion, the softer is the leather.
- iv) Softness is correlated with tear strength, i.e. softer leathers have a higher tear strength.

It is worth emphasising that conclusion i) was only based on the particular experimental conditions used. It is known that the bating process involves enzymatic proteolysis of collagenous and noncollagenous residues in the skin. Various unwanted debris in and around follicles in the papillary layer, impurities formed from fat, residual epidermis, sweat and tallow glands remaining after the liming process are easily removed by bating^[62, 63, 64]. Bating can also digest, dissolve, or weaken elastin fibres. Hence bating can play a role in obtaining a softer and fuller product. Properly controlled bating is particularly important in dealing with pig skin and sheep skin where there is more elastin than in bovine hide^[65].

Deliming with carbon dioxide instead of a weak acidic solution results in a softer leather with a finer surface structure^[66]. This effect is partly because carbon dioxide can improve the fat removal process and increase the ability of the leather to bind with chromium. Using carbon dioxide in deliming enables all the calcium to be removed without the leather becoming loose and weakened.

1. 2. 4. 3 Processes in the Tannery — Mechanical Treatment

Softening effects exerted in the tannery are classified as either of chemical origin or due to mechanical stress imposed in operations such as staking^[67]. The former endows the leather with the potential for softness and the latter is concerned with realising this potential.

Different leather drying methods and techniques influence leather structure in different ways and do play an important role in determining the feel, handle, softness, area, thickness

and even the colour^[68]. During the first drying, shrinkage occurs at all levels; i. e., molecular, fibril, fibre and the gross fibre structure (the interwoven fibre bundles). The effect of drying on the structure of the first two levels may be markedly influenced by the processes of liming, tanning and fatliquoring. Generally speaking, drying under tension using techniques such as nailing, toggling, pasting or vacuum drying (under certain conditions) yields a thinner and firmer leather^[69]. Freeze drying is claimed to produce a soft leather^[70], since the frozen water trapped inside the leather structure sublimates under the high vacuum condition, thus inhibiting the usual collapse of the fibrous structure.

Vibratory staking is the most widely used procedure for mechanical softening. Several systems are available. In one case (e.g. Cartigliano), two large nearly parallel plates, one with a matrix of pins and the other with a matrix of holes, vibrate at a set frequency. Leather is conveyed by elastic conveyor bands between the plates where it is subjected to vibratory mechanical action (*Figure 1.11*). The Molissa Vibratory Staker is similar except that both upper and lower plates have pins.

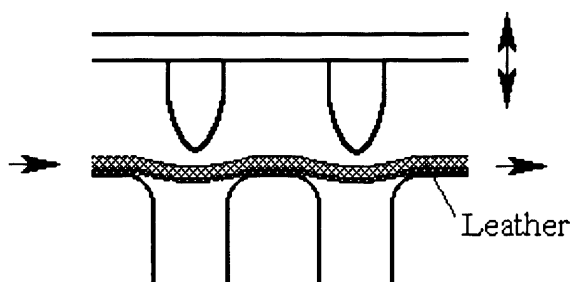


Figure 1.11 Demonstration of Cartigliano staking machine.

Softness can also be increased by milling which involves tumbling of a large number of leathers simultaneously in a dry, rotating drum where the leather is deformed multidirectionally by being bent, stretched and compressed. After milling the area is greatly reduced and the grain pattern becomes coarse^[71].

It has been recognised that the presence of some water in the leather prior to staking or milling will influence the softening results^[71], but no systematic studies have been carried out on why and how the existence of water and the amount of the water content affects the final mechanical behaviour of the leather.

1.3 The Aim of the Project

When a piece of leather is to be judged for softness, a person normally takes the product in hand, and applies a number of actions, namely stretching, bending, and compressing on it. As a result, the resistances to these different types of deformation are assessed. Softness

measuring instruments mentioned above either involve a combination of different deformations — loop test, ST300 softness gauge for example, — or overlook some basic parameters of leather such as thickness. Therefore, it is necessary to understand how leather responds to each deformation and how the parameters of the material and process conditions influence the softness and judgement of the softness.

The project had several aims: (i) establish procedures which characterise the resistance of leather to deformation in tension, bending and compression; (ii) understand further the mechanism of deformation and the relationship between the mechanical properties of leather and its microstructure; (iii) determine the influence of some key processes used in the tannery (such as staking and fatliquoring) on the behaviour of leather; and (vi) optimise the conditions of leather manufacture, such as water content of leather prior to being staked, and the frequency, amplitude and number of vibrations applied during staking.

Chapter two introduces the methodology involved in the research. Chapter three focuses on an understanding of the bending behaviour of leather. Both material type and measurement conditions were considered. Chapter four concentrates on the description and analysis of the deformation behaviour of leather under compression. Chapter five discusses the results obtained from differential scanning calorimetry (DSC) experiments which are used to understand how the water content prior to staking affects the softening effect of such a mechanical action. Chapter six concerns an investigation of the influence of staking amplitude, frequency and duration on leather softness by simulating staking action on a Dartec dynamic testing machine. The final chapter summarises the main conclusions of this research and makes suggestions for further work.

CHAPTER 2

MATERIALS AND EXPERIMENTAL METHODS

2. 1 Materials — Sources and Characterisation

2. 1. 1 Main Material

The main material used in this research was wet blue bovine hide processed at Garston's Tannery of Highfield Leathers Ltd. (Liverpool). Split material arrived in two batches, each batch containing five hides. Differences between the two batches were considered to be small and in any case were not of concern since for each particular set of experiments, sampling was from the same batch. The hides had been split in the limed condition, because this results in more uniform hide thickness and produces a more even property distribution in the finished product^[72]. The splitting machine was set such that the final crust leather had a thickness of 2.0 ± 0.5 mm. The processing history of the wet blue used in this research is listed in *Appendix I*.

On receipt the wet blue hides were carefully sealed and individually wrapped in plastic films. Thereafter the hides were stored in a cool storing room until further treatments were needed.

Further treatments on the wet blue leather fell into two categories; either fatliquoring or a parallel procedure in which no fatliquor was added. Following such treatment the leathers were toggle dried. Details of these procedures which were carried out in the tannery at BSLT are given in *Appendix II*. Attention was paid to avoiding any significant unwanted mechanical action on the crust leathers while they were handled, since the main aim of the project was to investigate how controlled mechanical action (e.g. vibratory staking) influences the deformation characteristics of the leather.

2. 1. 2 Leathers for Thickness-Bending Tests

In the thickness-bending tests, several pieces of thick leather were used. These samples included (1) a chrome tanned, fully finished leather piece with thickness up to 3 mm and (2) a half side of crust leather with a full thickness (i.e. without being split in the tannery) of 4.0 ± 0.5 mm made from a wet blue which was from the same tannery that supplied the main materials.

2. 1. 3 Materials Subjectively Characterised for Softness

A particular set of leather pieces, obtained from BLC*, was used in a comparison of various deformation tests. These samples had been used in an earlier study of leather softness^[4]. The set comprised 8 pieces of finished leather with different degrees of softness as judged by hand feel. These pieces were randomly numbered from 1 to 8 when they were subject to hand feel judgement. The thickness of the leathers in this set was around 1 mm, and a subjective grading of softness was known.

2. 2 Experimental Methodology

2. 2. 1 Instrumentation and Experimental Techniques

2. 2. 1. 1 Quasi-Static Mechanical Testing

Quasi-static mechanical tests were carried out using an Instron 1122 testing machine in a conditioned laboratory in which the temperature (20° Celsius) and relative humidity (65%) were kept constant. This machine could produce a range of cross head speeds from 0.5 mm min⁻¹ to 1000 mm min⁻¹.

Tests involving three types of deformation were carried out using the Instron 1122 testing machine:

1) Tensile Test

Sample size

Two sample sizes were used:

a) A rectangular shaped sample with a total length 200 mm and width 25 mm. The distance between the two pairs of grips was 100 mm (*Figure 2.1 (a)*).

b) A dumbbell shaped sample with a gauge length of 50 mm and width 10 mm; *Figure 2.1 (b)*. This is the standard specimen for tensile testing of leather^[73].

Given that a sample size is sufficient for measuring accurately the property of leather under investigation, then the smaller the sample size, the smaller should be the difference between the adjacent samples. So in most cases, dumbbell shaped samples were used. In fact, only in a preliminary investigation of topographical variability was the rectangular shape

* BLC, The Leather Technology Centre, Leather Trade House, Kings Park Road, Moulton Park, Northampton, NN3, 1JD, U.K.

used.

The thickness of the specimen was measured prior to testing using the standard thickness gauge^[74]. Leather was placed in the thickness gauge between the two flat surfaces. An initial pressure (5 N cm^{-2}) was gently applied and the thickness recorded five seconds after the pressure was fully loaded. A mean value at three or five evenly spread points (depending on the size of the sample) along the test length was taken as the thickness of the specimen.

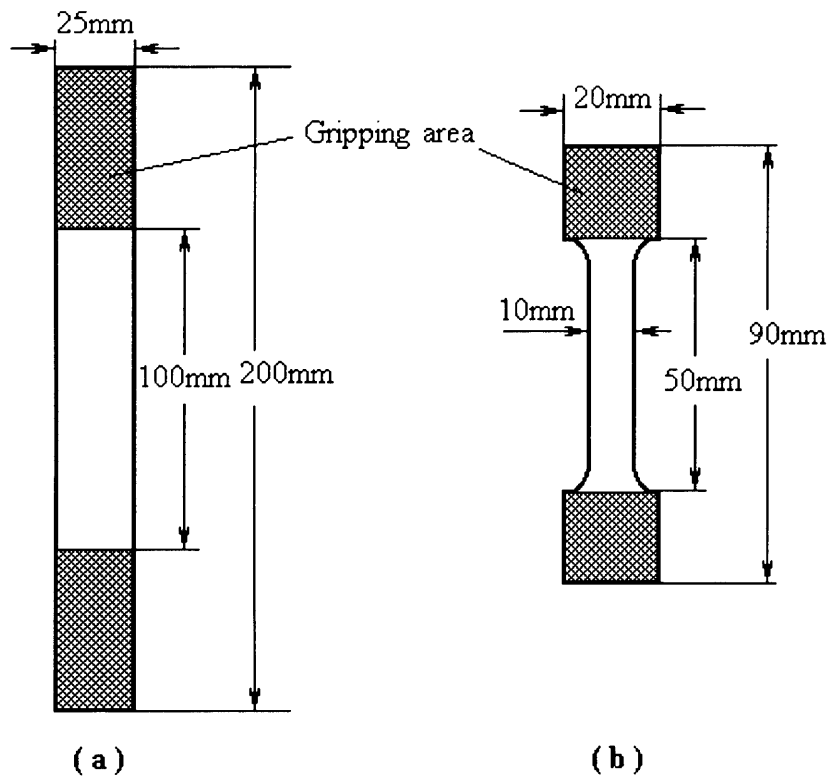


Figure 2.1 Samples used for tensile test.

Testing Method

The specimen was clamped firmly between the upper and lower grips. The distance between the pair of grips was set to meet the requirement of the initial testing length of the sample. When loading, the sample was kept as flat and straight as possible without applying a noticeable initial load — which could be monitored on the load monitor display of the testing machine. Depending on the experiment the upper grips were driven apart until either the specimen broke or a certain separation was achieved. A set cross head speed of 100 mm min^{-1} was used for tensile testing.

Calculation

In a uniaxial tensile test (*Figure 2.2*), when applying a load of F , the stress of the sample in the direction of stretching axis was calculated as follows:

$$\sigma = \frac{F}{A_0} \quad (2 - 1)$$

Where A_0 is the initial area of the sample cross section (mm^2), and σ is the stress in the unit of MPa^* . The tensile strength of the sample was obtained using the equation (2-1) when F was the load at break.

The strain, ε , along the direction of the applied force was calculated using equation (2-2), where l_0 and l are the initial length of the sample and length after stretching respectively.

$$\varepsilon = \frac{l - l_0}{l_0} \times 100\% \quad (2 - 2)$$

Strain at break was obtained when l was the breaking length of the sample.

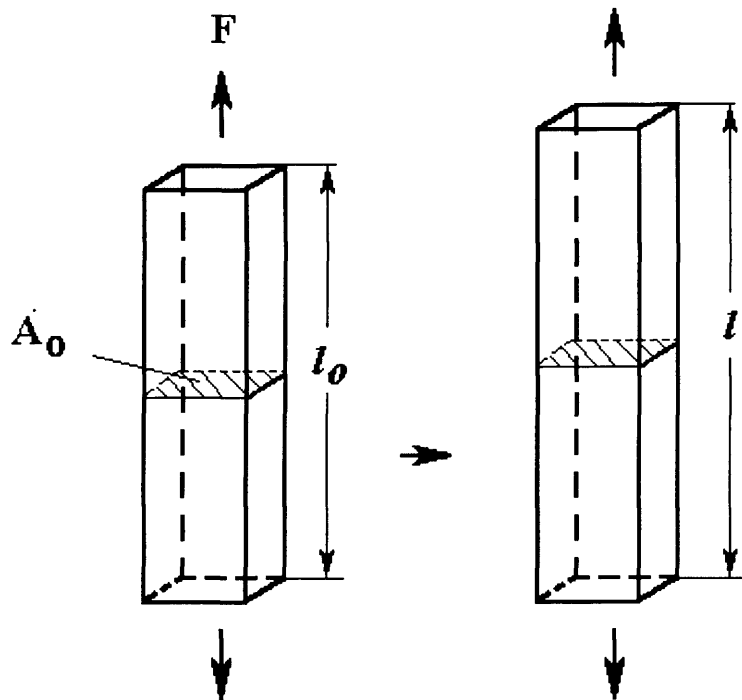


Figure 2.2 Deformation when a strip sample is under uniaxial stretch.

2) Bending Test

The set up for the bending test on the Instron 1122 is shown in *Figure 2.3*. A probe attached to the cross head was driven down to deform the specimen by pressing down on the centre of the span. The force exerted due to the bending deformation was measured by a very sensitive load cell (capable of measuring force to ± 0.001 N with a minimum full scale of 0.1 N). A rectangular shaped specimen was mounted on the top of the two supporting rollers which sat in the semicircular slots on the supporting unit. The distance between the two supporting rollers could be set at 30, 40, 50, 60 or 70 mm by dropping the rollers into the appropriate slots. The maximum strain in such a bending test is estimated no more than 6%. The surface of the supporting rollers was very smooth, minimising the friction between the roller and sample. A representation of the bending test is shown in *Figure 2.4*.

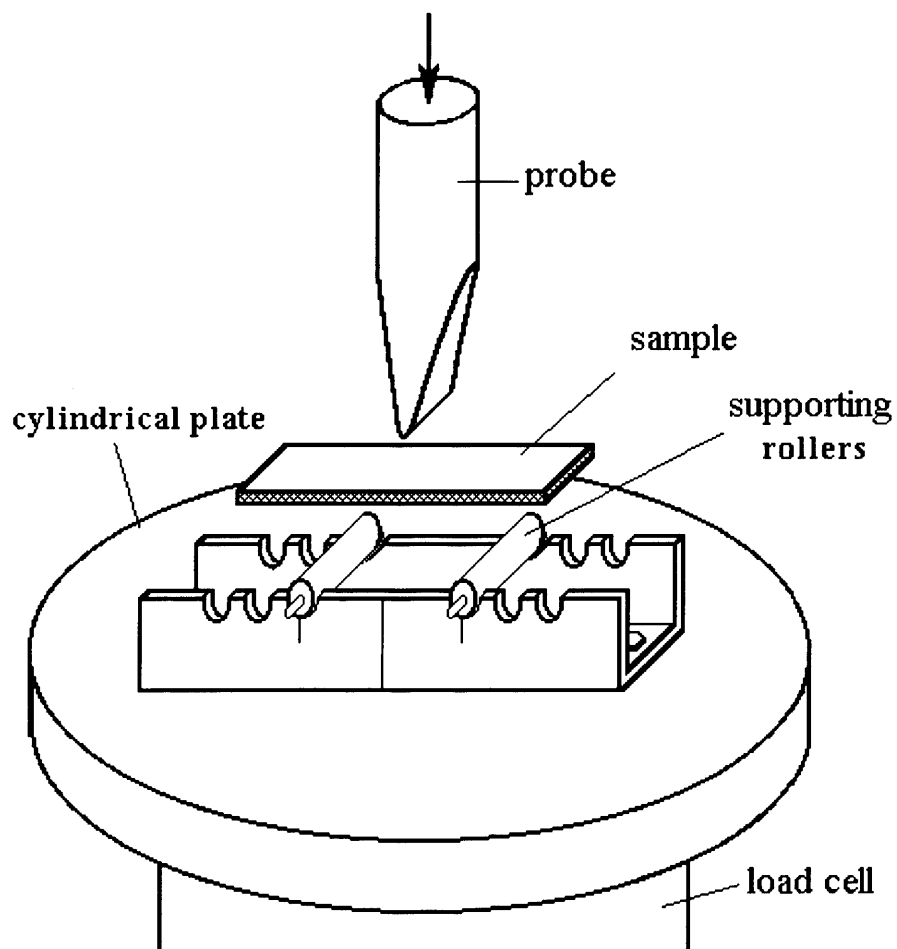


Figure 2.3 The set-up of bending test.

* $1\text{Pa} = 1\text{ N m}^{-2}$

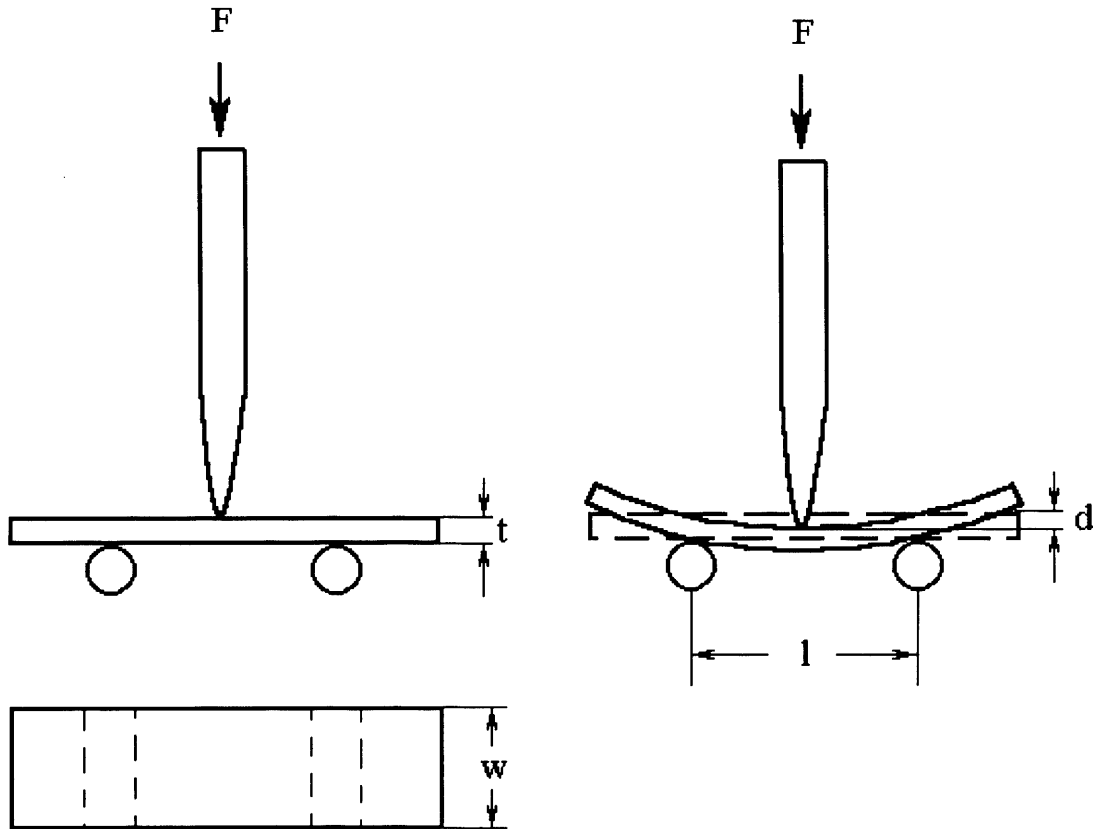


Figure 2.4 Geometry of the three-point bending test.

3) Compression Test

A disc shaped sample, diameter 12 mm, was placed on a flat plate attached to the load cell. A flat-headed probe which was attached to the upper cross head was driven down to compress the sample. Compression stress, σ , was calculated using equation (2-3):

$$\sigma = \frac{F}{A_0} \quad (2-3)$$

where F is the force applied (N), and A_0 is the area of the flat surface of the probe, expressed in mm^2 .

Compressive strain, ε , was given by

$$\varepsilon = \frac{t - t_0}{t_0} \times 100\% \quad (2-4)$$

where t_0 and t are respectively initial thickness and thickness under compression.

To obtain the equilibrated force under a given compression, the slowest speed of the

cross head was used; i. e. 0.05 mm min^{-1} . Cross head movement and, at the same time, the remaining thickness of the sample, were measured using a micrometer dial gauge with an accuracy of 0.01 mm

2. 2. 1. 2 Dynamic Mechanical Testing

Tests were performed on a hydraulically activated dynamic testing machine^{*}, which was able to apply a controlled oscillatory loading at frequencies between 0.1 and 50 Hz.

Two kinds of experiment were carried out using the Dartec machine. One experiment applied dynamic mechanical actions on a leather strip. The sample was alternately stretched and allowed to retract at different frequencies, amplitudes and for various numbers of cycles (*Figure 2.5*). The other experiment simulated the vibratory staking action of a modern staking machine. A small device was designed to fit on the dynamic testing machine (*Figure 2.6*). Basically this device involves two plates, one connected to the load cell and activator, the other to the base of the testing machine. The upper plate could move vertically up and down but two guiding rods inhibited relative rotational movement of the upper plate. A matrix of pins was mounted on the upper plate whereas the lower plate contained a matrix of holes. Leather sheets with widths of 150 mm and variable lengths (in the range 400 ~ 600 mm) were fed through between the two plates whilst the pin matrix moved in and out of the hole matrix at a controlled frequency, amplitude and for a given number of cycles. The geometry of pins and holes was similar to that used in modern staking machines such as those manufactured by Cartigliano^{*}.

^{*} Manufactured by Dartec Ltd, Stourbridge, England

^{*}Officine di Cartigliano s. p. a.

36050 Cartigliano
Vias. Givsseppez
VICENZA
ITALY

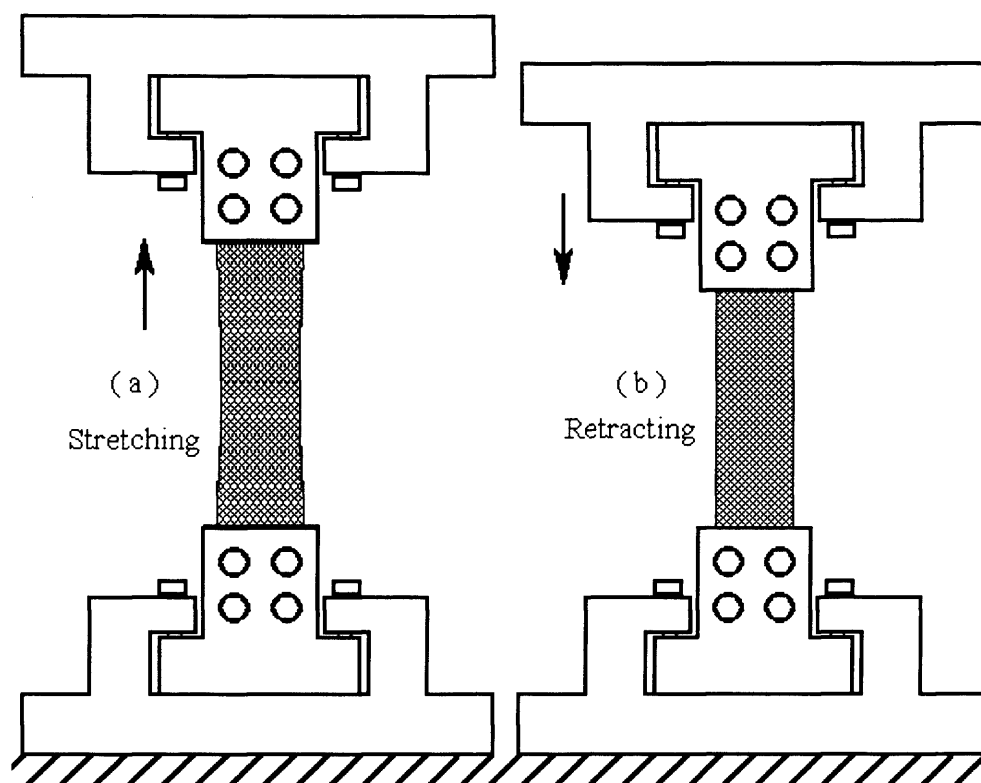


Figure 2. 5 Illustration of dynamic stretching on a leather strip.

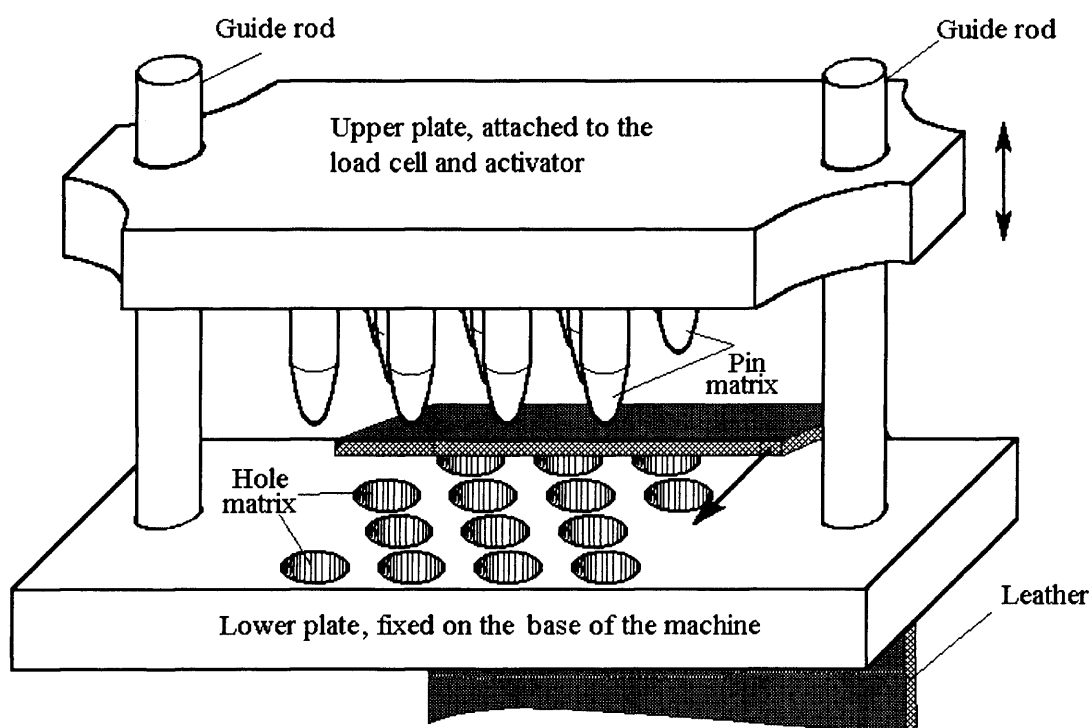


Figure 2.6 Staking device installed on Dartec.

2. 2. 1. 3 Differential Scanning Calorimetry (DSC)

A Mettler TC10A DSC was used to measure the amount of freezable water in samples of wet leather.

Sample preparation

Two methods were used to prepare leather samples with different moisture contents prior to either being staked in the tannery or analysed by DSC. One approach conditioned samples above saturated salt solutions. The second approach directly added water by spraying or soaking, then letting the water evaporate in a controlled way until the required water content was reached.

For moisture content in the leather less than about 55% on a dry weight basis *, the required moisture content was obtained by placing the sample in a sealed cabinet at constant relative humidity for a period of time until equilibrium was achieved. Different levels of relative humidity were obtained by using various saturated salt solutions in the cabinet where a relative humidity meter was installed. The salt solutions and relative humidities obtained are listed in table 2.1.

When the RH reached equilibrium, leather samples (size 35~40 mm × 45~50 mm) were placed on the punctured deck above the solution. At least one week was allowed for the sample to reach equilibrium in a given humidity.

Table 2. 1 R.H% obtained over different saturated salt solutions.

Saturated salt solution	R. H obtained at 20° C / %
Potassium Acetate	23
Conditioned Room	65
NaCl	75
KCl	85
K ₂ SO ₄	97
H ₂ O	100

A moisture content greater than 55% could not be reached by the above method. So the amount of additional water needed to reach the required moisture content was calculated in anticipation and an amount of water which was somewhat greater than the calculated

amount was sprayed on the two surfaces of the sample. The leather then was sealed in polyethylene film, and sufficient time was allowed for the moisture concentration to reach equilibrium. Water content was measured after equilibrium had been reached. If the water content was much higher than needed, the leather was taken out to evaporate in the conditioned room for some time and then was sealed again until a new equilibrium was achieved. Water content was then measured. If necessary this process would be repeated until approximately the required water content was reached. Higher moisture contents were also obtained by soaking the leather in water. The leather was then placed on a rack in the conditioned room. Excessive water was allowed to evaporate gradually until the water content reached the required value. When measuring water content of leather which was moisturised either by spraying water on it or by soaking in water, attention was always paid to (a) ensuring equilibrium had been reached before the measurement by sampling on two following days and the difference of the water contents of the two samples was no larger than 5%; and (b) ensuring water had dispersed or penetrated evenly over the whole piece of leather.

Water Content Measurement

A piece of leather, having approximately 3 grams dried weight, was cut into small cubes, and conditioned with the original sample from which it had been cut. When equilibrated, the cubes were immediately weighed and placed in an oven at 100° C for 5 hours. The analysis procedure was completed using the standard leather testing method^[75]. Moisture content (%) on a dry weight basis was calculated using the following equation:

$$\text{Water content (\%)} = \frac{G_1 - G_2}{G_2} \times 100 \quad (2 - 5)$$

where G_1 and G_2 are the weights of sample before and after drying respectively.

Differential Scanning Calorimetry measurement

Conditioned leather pieces were always kept in a sealed polyethylene bag until required. For DSC analysis, the sample was sealed in an aluminium capsule in order to maintain the original water content. The temperature was reduced from room temperature to -50° C, at a speed of 5° C min⁻¹, held at -50° C for 10 min, then returned to room temperature at a speed

* dry weight basis: the weight of all substances contained in sample except water. Same in later sections.

of $3^{\circ} \text{C min}^{-1}$. Further details are given in *Chapter 5*.

2. 2. 2 Data Collection and Handling

For the quasi-static mechanical experiments on the Instron machine, results were recorded using both the dedicated chart recorder and an IBM 386 PC which received a load proportional voltage signal via a 16 bit A-D converter (Strawberry Tree ACPC16). Software Labtech Notebook* was used for the original data collection. The data acquisition frequency could be controlled. Higher collecting rates, 10 to 30 readings per second, were used in the low strain range to allow detailed analysis of the results. Meanwhile, the chart recorder provided a direct indication of the force-deformation curve and also a hard copy as a security against losing information during computer data collection.

For each test, original raw data collected by the computer were saved to a unique file. Data in each file were then further processed using either self-developed QBASIC programmes or, in some cases, worksheet software such as Microsoft Excel® or QuattroPro®. The aims was as follows:

- i) Accurate determinations of the starting point of the force-deformation curve
- ii) Quick calculation of certain variables, such as the stress at a given strain, strength, elongation.
- iii) Further calculation of specific parameters and theoretical simulation of the experimental data.

Point (iii) will be discussed later. The necessity of (i) is discussed below.

Considering the whole stress – strain curve, or more broadly, the force – deformation curve, both force and deformation should ideally start at zero. However, this condition is almost impossible to achieve for the following reasons. The noise of the electric signal from the load cell produces a fluctuating reading. Even when a filter was used this fluctuation was still considerable in some tests especially when the most sensitive load ranges were used. Further the precise zero is difficult to define because the initial strain is uncertain. In spite of precautions, the sample mounted for the test was never perfectly straight. Also in some tests (bending, compression), the protrusion of short fibre ends from the surface gave a small load signal not truly representative of the whole sample. This was particularly so when the tests were carried out using the most sensitive load ranges.

Fluctuations caused by electrical background noise were minimised by applying a

* Laboratory Technologies Corporation, 400 Research Drive Wilmington MA 01887 British agents Adept

consecutive five points smoothing to the original data; the principle of which is schematically shown in *Figure 2.7*.

Figure 2. 8 (a)~(d) compares the original, once smoothed, twice smoothed and three times smoothed graphs (in the low strain region) of a tensile test.

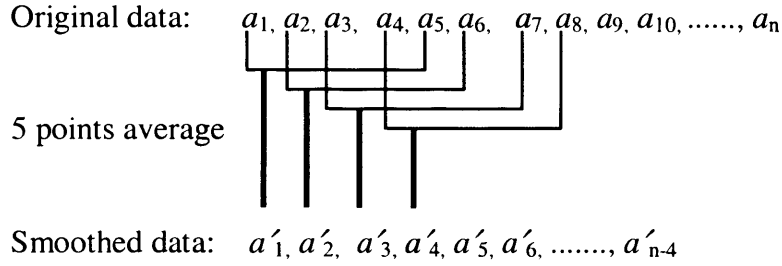


Figure 2.7 The 5 point smoothing scheme.

The starting point of the force – deformation curve was determined by processing the smoothed data as follows:

- i) The mean force, $F_{Av.}$, was calculated over n consecutive forces F_i before the point A (with the force value F_{n+1}) from where the force started to increase continuously. This

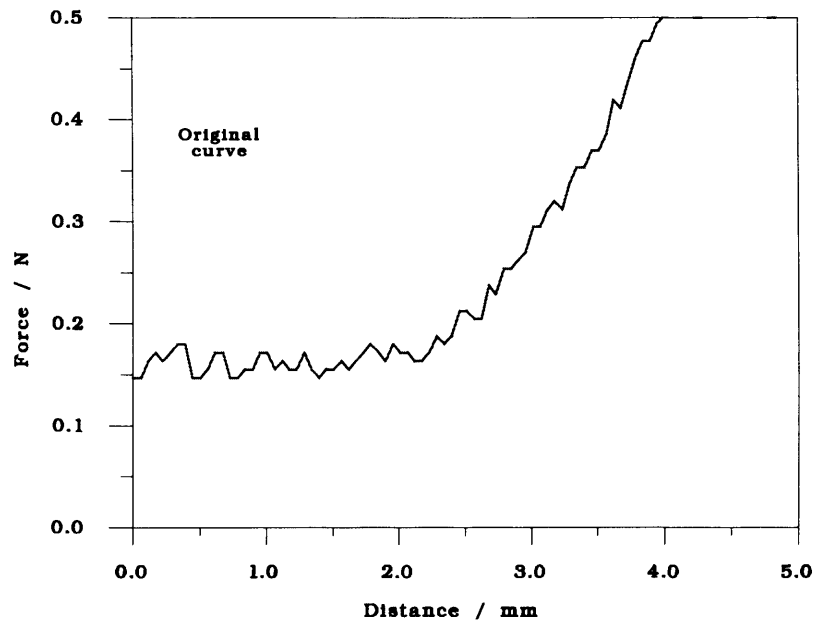
mean value was given by:
$$F_{Av.} = \frac{\sum_{i=1}^n F_i}{n} \quad (2 - 6)$$

- ii) The standard deviation, s , of $F_1, F_2, \dots, F_n$ was calculated by:

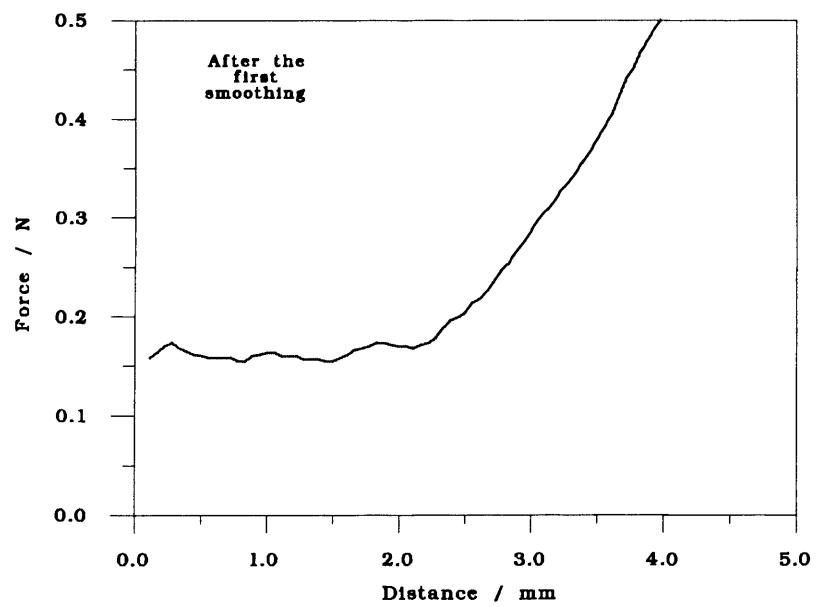
$$s = \sqrt{\frac{\sum_{i=1}^n (F_i - F_{Av.})^2}{n}} \quad (2 - 7)$$

- iii) The starting point B then was defined as the point where $F_B - F_A = s$.

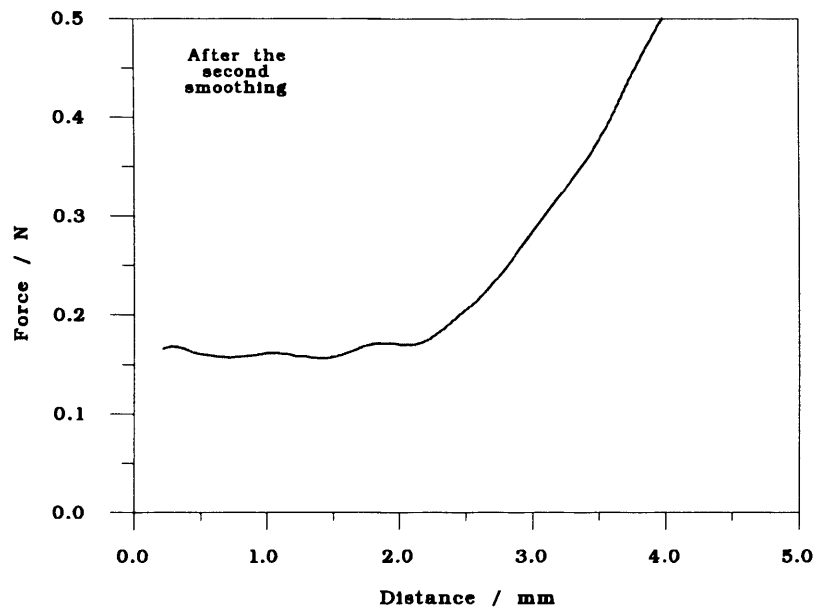
Three QBASIC programmes were developed for handling data from the tensile test, bending test and compression test. Relative calculations such as changing force to stress, distance to strain, finding the stress value at a given strain were also carried out using these programmes.



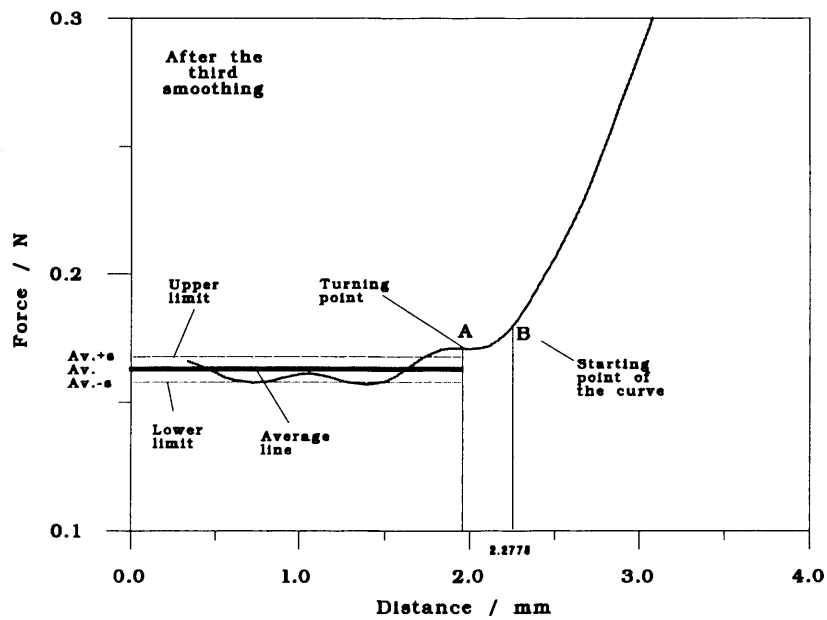
(a)



(b)



(c)



(d)

Figure 2.8 The procedure for smoothing and initialising the original data.

CHAPTER 3

BENDING BEHAVIOUR OF LEATHER

3. 1 Introduction

When a person judges the softness of a piece of material, the “feel” of that material is obtained by stretching, bending and compressing the material using his hands. When these actions are carried out, several types of force are applied, namely tensile, bending, and compressive. In such a subjective evaluation it is likely that the extension is no more than ~5%. The degree of compression should also be small. Certainly the largest amplitude of deformation will be associated with bending of the material and it is thus reasonable to assume that bending deformation plays a decisive role in judging the softness of a leather. Therefore, investigating and understanding the fundamental bending behaviour of leather is crucial for improved understanding of softness. The three point bend test geometry is the method of choice for other classes of material. It is a well controlled test and lends itself to theoretical analysis. Although it has been applied to assess the bending behaviour of other materials, no publications have been found concerning the application of this method to the analysis of leather behaviour. This chapter reports an investigation into how the dimensions of the sample (width, length and thickness), test condition (degree of bending) and the process used to make the leather affect the resistance of leather to bending deformation. The relationship between these variables and bending resistance is analysed from both theoretical and empirical standpoints. Comparisons are made between (a) the softness characterised by the three point bend test, (b) softness assessed by other instrumental methods, and (c) softness judged subjectively.

3. 2 Theoretical Background

The following is an outline of the standard theory of beam bending. (For further detail see reference [76,77] and *Appendix III*.)

3. 2. 1 Simple Elastic Beam Theory

For an ideal elastic material subject to a transverse force applied in the middle of a beam supported at each end (*Figure 3.1*), the resistance to bending deformation is described by equation (3-1):

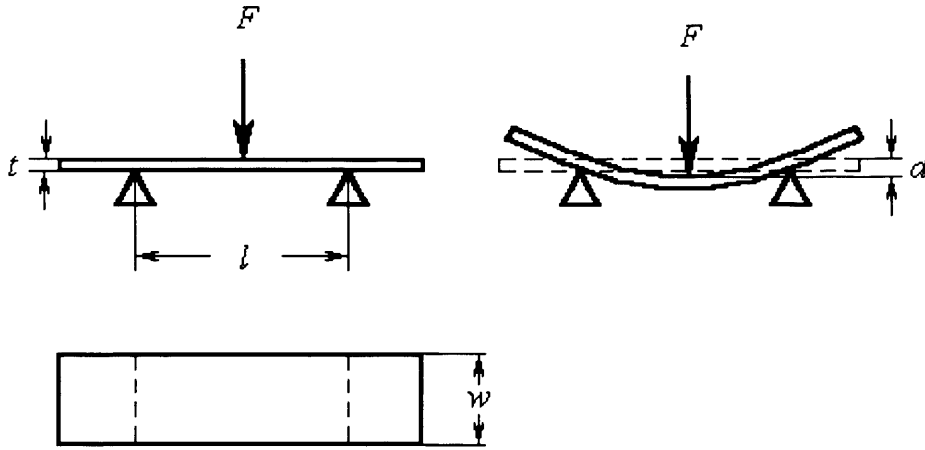


Figure 3.1 Three point bending of a beam.

$$F = E \frac{4 d w t^3}{l^3} \quad (3 - 1)$$

where F — force applied to bend the beam to a depth d .

l — distance between the two supporting points.

w — width of the beam.

t — thickness of the beam.

E — Young's modulus.

The Young's modulus is an intrinsic material parameter which is independent of the size of the sample and defined by equation (3 - 2a):

$$E = \frac{\Delta \sigma_x}{\Delta \epsilon_x} \quad (3 - 2a)$$

where $\sigma_x = F/A$ is the internal stress along x axis while a beam is extended by a normal force F acting over a cross sectional area A in the direction of x , and ϵ_x is the resulting strain along the x axis:

$$\epsilon_x = \frac{l_1 - l_0}{l_0} \quad (3 - 3)$$

where l_0, l_1 are the length of sample before and after extension respectively.

Two basic assumptions are made in the deduction of equation (3 - 1):

(1) The extension behaviour of the material can be described by Hooke's law, i.e.

$$\epsilon_x = \frac{\sigma_x}{E} \quad (3 - 2b)$$

and

(2) Deformation is by pure bending (see Figure 3.2), i. e.

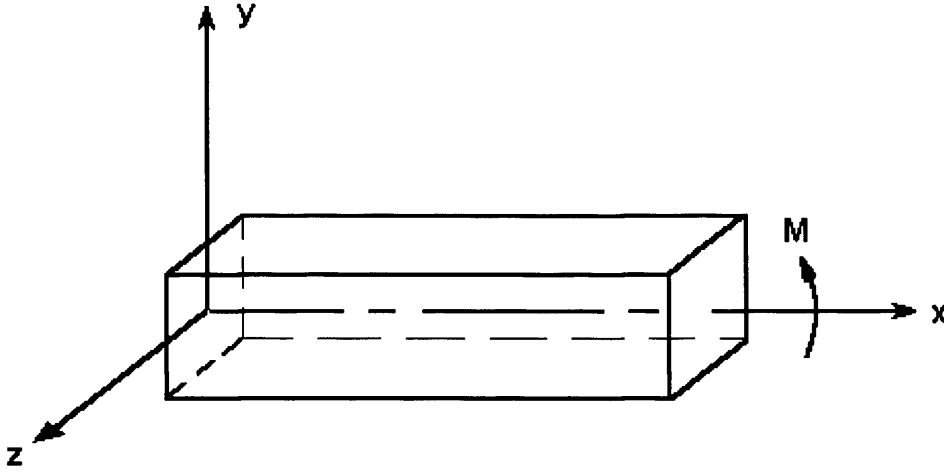


Figure 3.2 A beam under a bending moment M .

$$\sigma_y = \sigma_z = \tau_{xy} = \tau_{xz} = \tau_{yz} = 0$$

$$\sigma_{x|at\ y} = \frac{E\ y}{R} \quad (3 - 4a)$$

or:

$$\frac{1}{R} = \frac{M_r}{E I_c} \quad (3 - 4b)$$

where σ_i is the internal stress along the i axis, τ_{ij} is the shear force on the ij plane, y is the distance from the xz plane, R is the curvature at the point concerned, M_r is the resultant internal moment and I_c is the second moment of the cross sectional area of the beam with respect to the neutral axis parallel to the z axis (see *Appendix III*). The product of EI is defined as bending stiffness of the beam.

Under these two assumptions, when a beam is under the action of a bending moment as shown in *Figure 3.3*, we have:

$$\frac{1}{R} = \frac{d\theta}{ds}$$

$$\frac{1}{R} = \frac{\frac{d^2 y}{dx^2}}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{\frac{3}{2}}}$$

Since:

$$\frac{dy}{dx} \ll 1$$

therefore

$$\tan \theta = \frac{dy}{dx} \approx \theta$$

$$\frac{1}{R} = \frac{d\theta}{ds} \approx \frac{d\left(\frac{dy}{dx}\right)}{ds}$$

$$ds = \sqrt{1 + \left(\frac{dy}{dx}\right)^2} \quad dx \approx ds$$

$$\frac{d\theta}{ds} = \frac{d^2y}{dx^2} = \frac{1}{R}$$

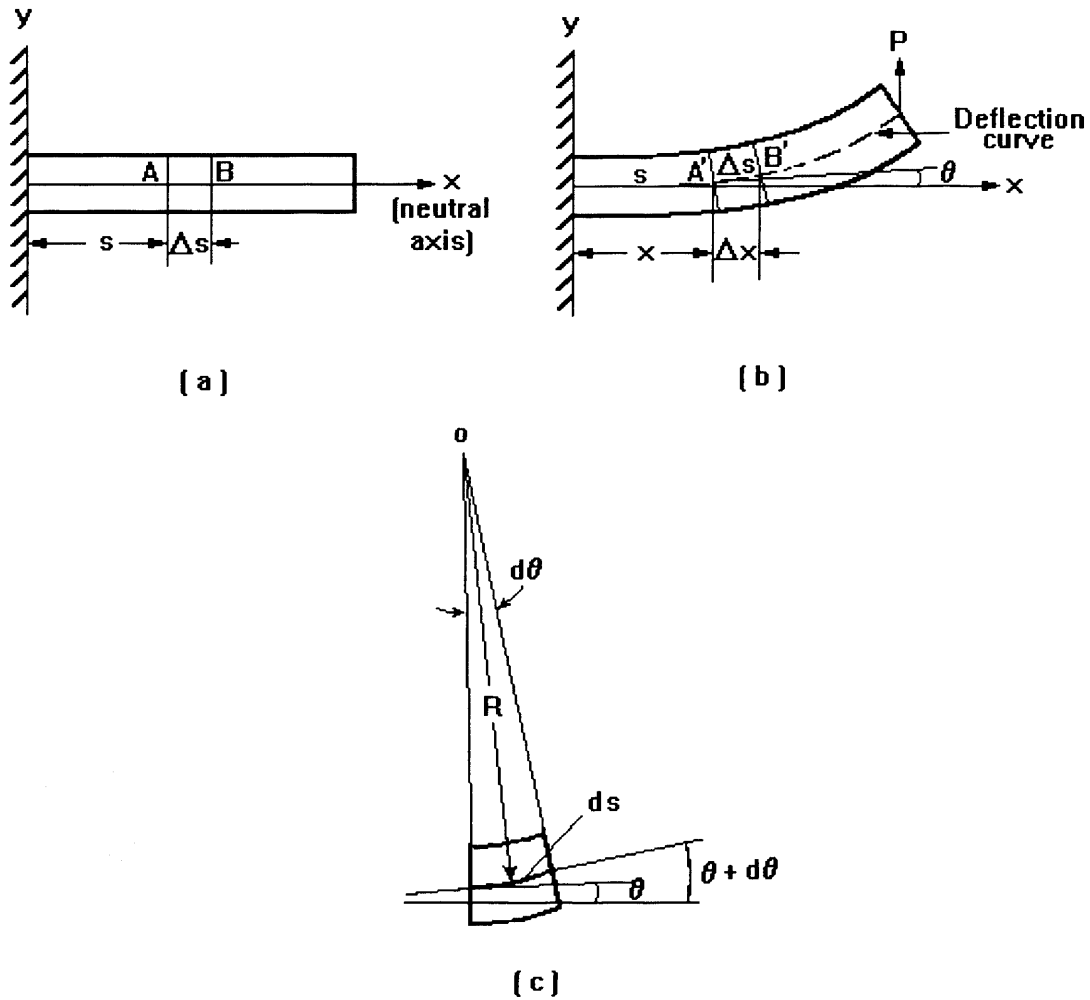


Figure 3.3 Analysis of pure bending.

Because

$$\frac{1}{R} = \frac{M}{EI}$$

therefore, there exist two linear differential equations:

$$\frac{d\theta}{ds} = \frac{M}{EI} \quad (3-5)$$

and

$$\frac{d^2y}{dx^2} = \frac{M}{EI} \quad (3-6)$$

Thus, for the bending deformation shown in Figure 3.4 (a),

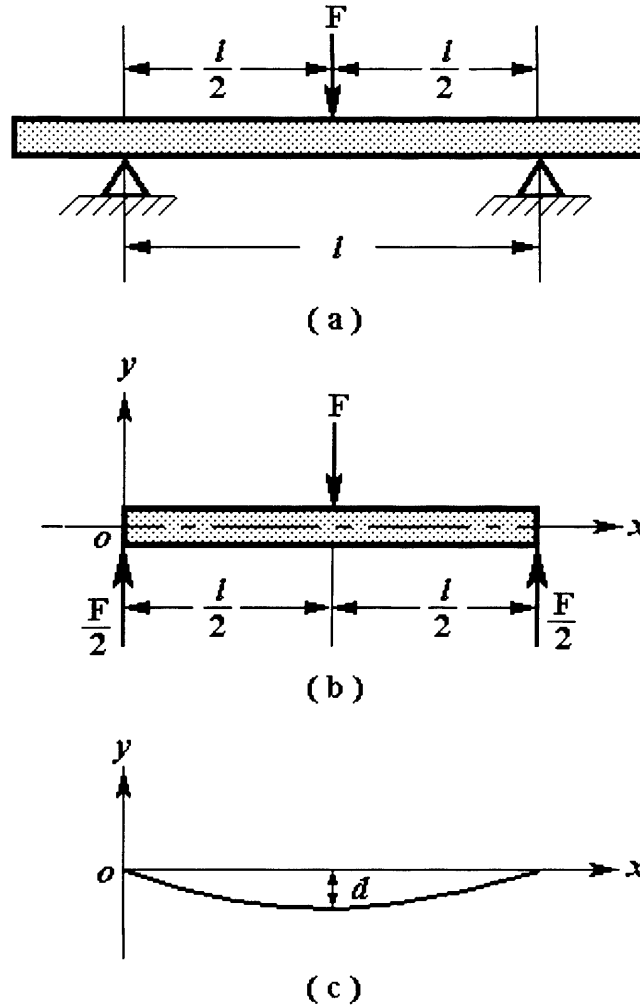


Figure 3.4 A beam subject to a single transverse force at the middle.

the maximum deflexion d at the midpoint of the beam can be found by discriminating differential equations (3 - 5) and (3 - 6) with boundary conditions and we have

$$F = \frac{4Edwt^3}{l^3} \quad (3 - 1)$$

The application of the above equation requires that 1) the material is elastic, i.e. the stress strain behaviour can be described using Hooke's law; and 2) the shear strains do not significantly influence the deformation.

3. 2. 2 Some Deviations from Simple Linearity

3. 2. 2. 1 Different Moduli in Tension and Compression

Suppose that Hooke's law still applies in both tensile and compressive deformation, only that the moduli are different in these two deformations, say E_T when under tension and E_C when

under compression, then:

$$e_T = \frac{\sigma_{xx,T}}{E_T}$$

and

$$e_C = \frac{\sigma_{xx,C}}{E_C}$$

where e_T , e_C are strains under tension and compression respectively, $\sigma_{xx,T}$ and $\sigma_{xx,C}$ stand for the stresses under the two types deformation.

$$M = \frac{E_T}{R} \left(\frac{wt^3}{12} \right) \left(\frac{2\sqrt{E_T/E_C}}{1 + \sqrt{E_T/E_C}} \right)^2$$

When $E_T = E_C = E$, the ideal equation (3-4b) is recovered, and a modulus in bending is defined as:

$$E_B = E_T \left(\frac{2\sqrt{E_T/E_C}}{1 + \sqrt{E_T/E_C}} \right)^2$$

Detailed deductions of the above equation see reference [76]. The influence of the difference between E_T and E_C on the bending modulus E_B is illustrated in *Figure 3.5*.

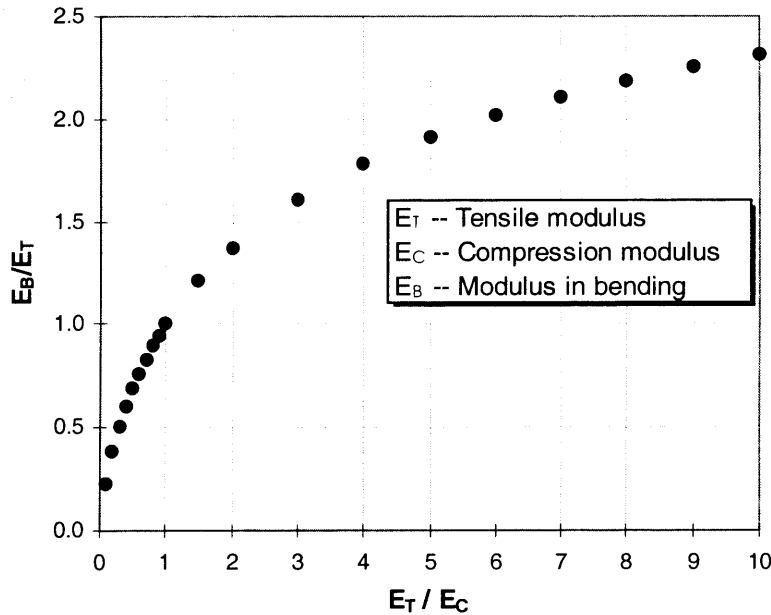


Figure 3.5 The relationship between E_B/E_T and E_T/E_C

From *Figure 3.5*, we can see that E_B is equal to E_T when $E_T = E_C$, E_B/E_T increases as E_T/E_C increases, but there is a limit for E_B/E_T as $E_T/E_C \rightarrow \infty$.

3. 2. 2. 2 Shear Deflections in Beams

In fact, pure bending loading conditions are seldom encountered in an actual engineering problem. Much more commonly the resultant internal reaction consists of a bending moment and a shear force. The presence of the shear force indicates a variable bending moment in the beam. The relationship between shear force and the change in bending moment is given by equation (3-7),

$$Q = \frac{dM}{dx} \quad (3-7)$$

where Q is the resultant shear force on the section.

Based on equation (3-7), Williams^[76] derived an equation for total deflection d at the centre of a three-point bending beam:

$$d = d_B + d_S = \frac{Fl^3}{48EI} \left[1 + 3\left(1 + \frac{\nu}{2}\right) \frac{t^2}{l^2} \right]$$

where d_B – the central bending deflection in a simply supported beam

d_S – the central shear deflection in the same beam

ν – Poisson's ratio defined as

$$\nu = \left| \frac{e_{(transverse)}}{e_{(axial)}} \right|$$

E, I, F, l, t – same meaning as in equation (3-1)

The bending and shear deflections in the three point loading system is shown in *Figure 3.6*.

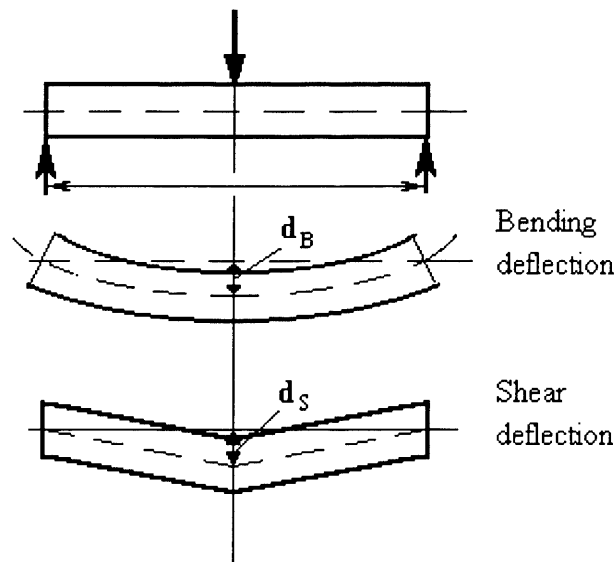


Figure 3.6 Shear and bending deflection in a beam.

3. 2. 2. 3 Further Discussion About the Shear Force

One of the requirements for pure bending is that:

$$\sigma_y = \sigma_z = \tau_{xy} = \tau_{xz} = \tau_{yz} = 0$$

So strictly speaking, the presence of the shear force and the resulting shear stresses and shear deformation, would not produce pure bending. Plane sections would no longer remain plane after bending and the geometry of the actual deformation would become considerably more involved. However, when the length of a beam is much larger than the dimensions of the cross section, the deformation of the shear force is relatively small. The assumption is still valid that the longitudinal axial strains are still distributed in the same manner as for pure bending. So the load stress relationship (equation (3 - 4a) or (3 - 4b)) under pure bending for ideally elastic materials is still considered valid, i. e.

$$\sigma_{|at\ y} = \frac{M_r y}{I} \quad (3 - 4c)$$

Experience and experimental work indicate that this assumption is sufficiently accurate for most practical purposes ^[77].

Figure 3.7 (a) shows a simply supported beam with a single transverse load P . For convenience, a rectangular cross section has been chosen, as shown in Figure 3.7 (b).

Figure 3.7 (c) shows the free-body diagram of the portion of the beam between section (1) and (2) in (a). The vertical shear forces on these sections produce a change in bending moment denoted by ΔM . Figure 3.7 (d) shows a free-body diagram of a slice of the beam extending between section (1) and (2) and having its lower surface $abeh$ at a distance u above the neutral surface of the beam.

The change in bending moment between sections (1) and (2) makes it reasonable to expect that the normal stress σ_1 and σ_2 on the areas $ahgd$ and $befc$ is different. Therefore, the resultant horizontal force F_{1x} on the section (1) would be different in magnitude from the resultant force F_{2x} on the section (2). Equilibrium would require the existence of a horizontal shear force ΔF_x on the surface $abeh$. This horizontal shear force can be expressed in terms of normal stresses:

$$\begin{aligned} \sum \vec{F}_x &= 0 \\ F_{2x} - F_{1x} + \Delta F_x &= 0 \\ \Delta F_x = F_{1x} - F_{2x} &= \int_{ahgd} \sigma_1 da - \int_{befc} \sigma_2 da \end{aligned}$$

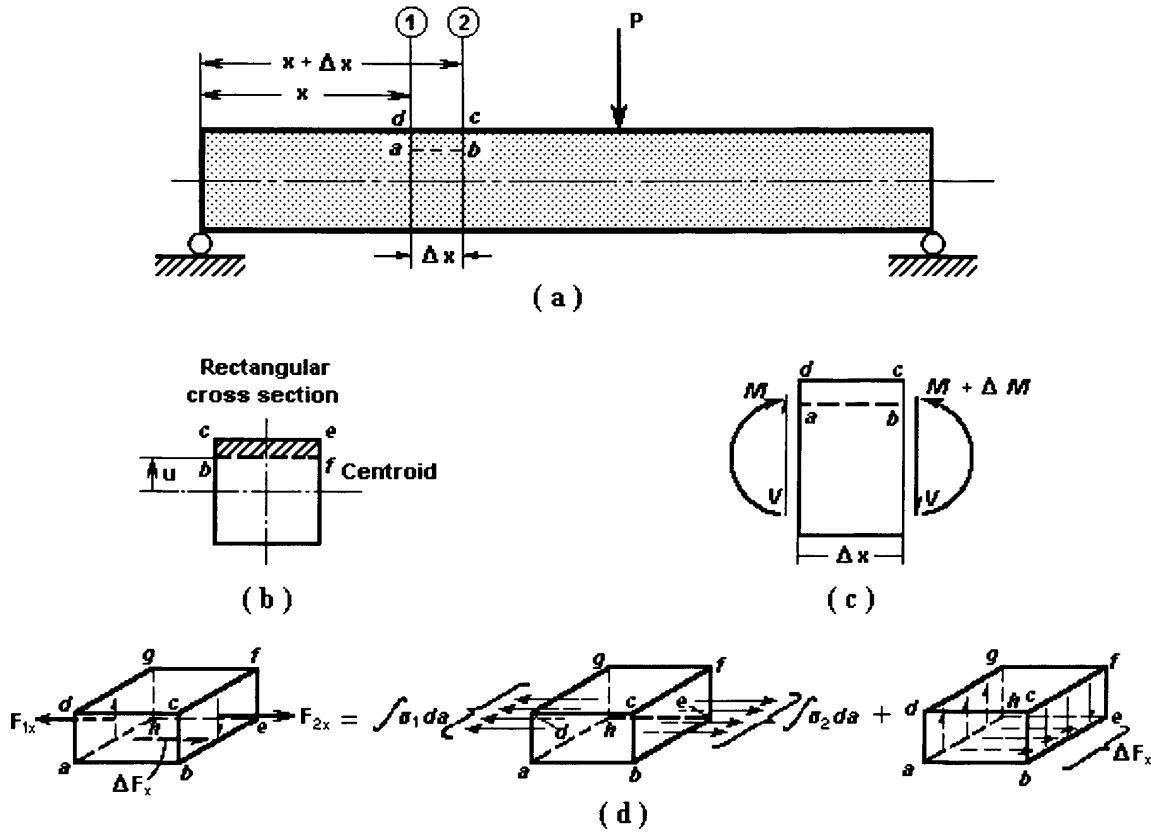


Figure 3.7 A simply supported beam with a single transverse load P at the middle ^[78].

$$\Delta F_x = \int_{befc} (\sigma_1 - \sigma_2) da \quad (3 - 8)$$

The existence of such longitudinal shear forces can be illustrated using a simple experiment.

Suppose that several planks or slabs are stacked one on top of the other without fastening, as shown in *Figure 3.8 (a)*, then when a transverse force P is loaded on the stack, the stack will deform in a way as shown in *Figure 3.8 (b)*. If there is no friction between the slabs, the ends of the slab will become staggered due to the existence of the shear force ΔF_x . Each slab behaves as an independent beam, and the total resistance to bending of n slabs is approximately n times the resistance for one slab alone.

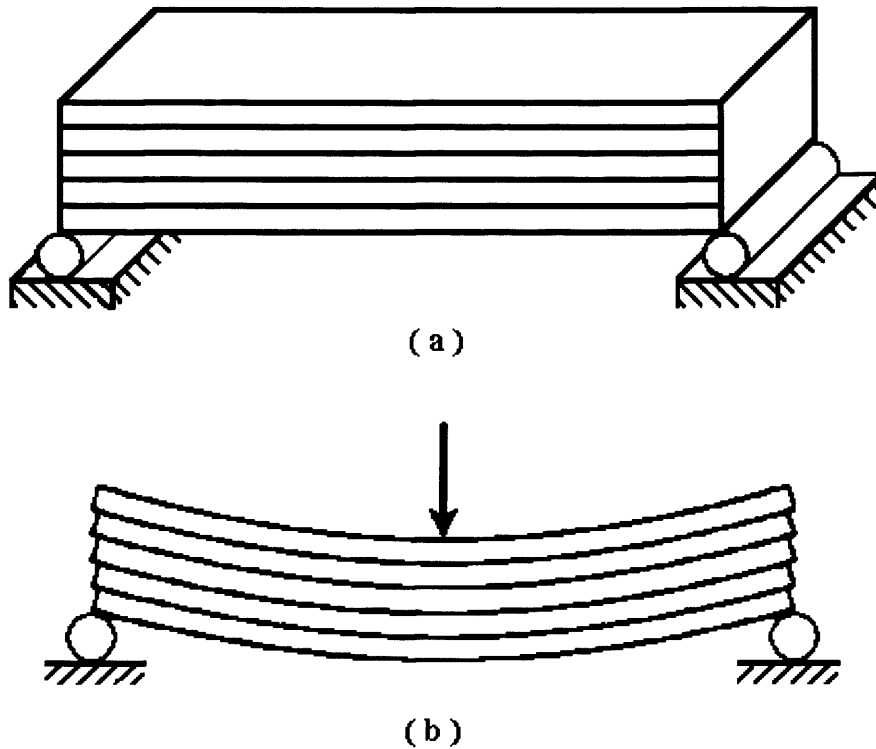


Figure 3.8 The deformation of a stack of slabs when bent^[77].

If the slabs are fastened together to prevent their sliding on one another, or in other words, to increase the friction between the slabs, the entire assembly can be taken as a single beam having a thickness equal to n times the thickness of one slab; then before fastening,

$$P \propto nt^3 \quad (3 - 9)$$

and after fastening,

$$P \propto (nt)^3 \quad (3 - 10)$$

where t is the thickness of one slab.

Here the conditions “before fastening” and “after fastening” indicate two extreme situations. In one situation there is no friction between the slabs. In other words the friction between the slabs is so small compared with the longitudinal shear forces produced by the variable bending moment in the whole assembly that it can be neglected. Hence the slabs are free to slide on one another when the stack is bent. In the other situation the friction between the slabs is comparable to the coherent internal force inside one slab. Hence the whole assembly can be regarded as one piece of homogeneous material which has the same properties as one slab. Thus the load stress relationship under pure bending for ideally elastic materials can be applied, supposing that the assumption made before is met.

For leather material, the magnitude of Young's modulus E is in the range of $10^0 \sim 10^2$ MPa, which is much smaller than the general engineering materials whose Young's modulus E is in the range of $10^8 \sim 10^{10}$ MPa. Thus leather is much more deformable than the general elastic engineering materials when subject to an external transverse force in bending, and the deformation effect of the shear force cannot be completely neglected. Two important questions centre on the effect of the shear force and the way the shear force influences the properties of the leather.

3. 2. 2. 4 Sandwich beams

In this case, beams made with three laminated layers — two skins of material of one modulus, separated by another material of different modulus — are considered.

For the sandwich beam of width w and total thickness t with a bottom skin of thickness h_1 , and a top skin of thickness h_2 as shown in Figure 3.9, Williams^[76] derived an equation which describes the stiffness S in a three-point bending test (for the deduction, see reference [76]), i. e.

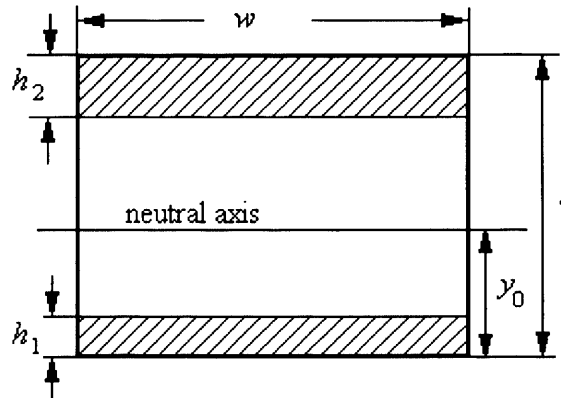


Figure 3.9 Cross section of a sandwich beam.

$$S = \frac{wt^3}{12} E_s \left\{ 4 - 4 \left(\frac{E_s - E_c}{E_s} \right) \left[\left(1 - \frac{h_2}{t} \right)^3 - \left(\frac{h_1}{t} \right)^3 \right] \right. \\ \left. - 3 \frac{\left[1 - \left(\frac{E_s - E_c}{E_s} \right) \left(1 - \left(\frac{h_2}{t} \right)^2 - \left(\frac{h_1}{t} \right)^2 \right) \right]^2}{\left[1 - \left(\frac{E_s - E_c}{E_s} \right) \left(1 - \left(\frac{h_1}{t} + \frac{h_2}{t} \right) \right) \right]} \right\} \quad (3 - 11)$$

where S – an equivalent stiffness to EI

E_s – Young's modulus of the top and bottom skin

E_C – Young’s modulus of the middle part

w – width of the beam

h_1, h_2, t have the meanings as shown in *Figure 3.9*.

Thus any beam bending problem may be solved in the usual fashion except that EI is replaced by the function S computed from the values for the beam.

3. 3 Experimental Procedure

3. 3. 1 Three Point Bending

Experimental procedure and data acquisition for three-point bending have been discussed in 2. 2. 1. 1 and 2. 2. 2 respectively.

3. 3. 2 Materials Used and Sampling

Two investigations were undertaken. In the first, a method was designed to obtain a series of samples in which the parameters of sample size such as width, length and thickness, and the test conditions such as the depth of the bending deflection were varied. This bending set of experiments used samples from one side of a commercially sourced, finished chrome tanned leather. Samples with different thickness were obtained using splitting machine. These samples were identified as “set sample group” AI to $AVII$ with each group having the same thickness and containing 25 individual samples a_{ij} , where $i, j = 1, 2, 3, 4, 5$ representing different width and length. The second investigation focused on the influence of sample thickness on bending behaviour and the influence of the sample process history on the relationship between thickness and bending behaviour. Samples for this second experiment were obtained from various sources and were prepared differently. They were identified as “sample x ” or “sample group x ”. Details of sample sources and locations, process history and sizes are listed below.

The sampling location for set sample group $AI \sim AVII$ and sample 1 is shown in *Figure 3.10*. The meaning of each individual sample from sample set group AI is listed in table 3. 1(a)

The sample groups $AII, AIII, AIV, AV, AVI$, and $AVII$ had the same arrangement as group AI shown in table 3. 1(a) except that their thickness differed from AI . The thicknesses of groups $AII, AIII, AIV, AV, AVI$, and $AVII$ were 2.08, 1.68, 1.55, 1.25, 1.00, and 0.77 mm respectively. Different values of thickness were obtained by splitting samples in a splitting machine. Individual samples for these six sets are listed in table 3.1(b).

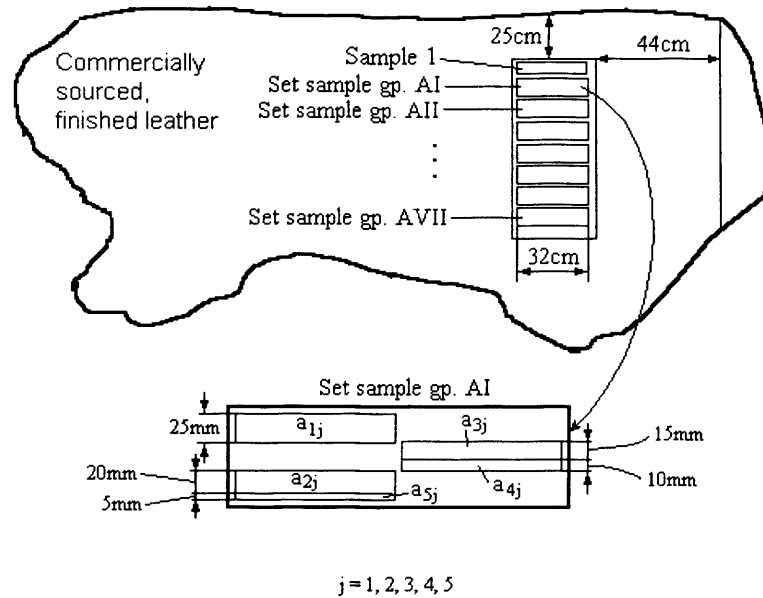


Figure 3.10 Sampling location for set sample group AI ~ AVII, and sample 1.

Samples with different thicknesses from leather which had undergone different processing history were prepared as follows. All samples were fatigued.

Sample 1, commercially sourced, chrome tanned and finished leather from the same side as the set sample groups. The different thicknesses were obtained by gradually buffing the corium side with emery paper. The action of buffing was slow.

Sample 2, from the leather sourced as wet blue, was toggle dried and had not been staked. The different thicknesses were obtained by shaving gradually from the corium side with a high speed grinder.

Sample 3, also from the leather sourced as wet blue, was toggle dried, but in this case was staked. The different thicknesses were obtained using the same method as used for sample 2.

Sample 4, prepared in the same way as sample 3, was shaved from the grain side.

Sample group 5 was again from leather sourced as wet blue, toggle dried and staked. However the different thicknesses were obtained using a splitting machine. This meant that samples with different thicknesses came from different regions on the hide, but they were cut from positions as close together as possible. All test samples contained the grain layer.

The sampling locations of sample group 2 to sample group 5 are shown in *Figure 3.11*.

Sample group 6 (1) and (2) were from the set sample group AI~AVII (commercially sourced finished leather). Again different thicknesses were obtained using the splitting

machine. Sample groups 6(1) and (2) were different in sample width.

Table 3. 1(a) Testing samples of set sample group AI

Group	Thickness t / mm	Sample	Width of sample w / mm	Length between supporting points l / mm	Remark
AI	2.44	a ₁₁	25	30	
		a ₁₂	25	40	
		a ₁₃	25	50	
		a ₁₄	25	60	
		a ₁₅	25	70	
		a ₂₁	20	30	
		a ₂₂	20	40	
		a ₂₃	20	50	
		a ₂₄	20	60	
		a ₂₅	20	70	
		a ₃₁	15	30	
		a ₃₂	15	40	
		a ₃₃	15	50	
		a ₃₄	15	60	
		a ₃₅	15	70	
		a ₄₁	10	30	
		a ₄₂	10	40	
		a ₄₃	10	50	
		a ₄₄	10	60	
		a ₄₅	10	70	
		a ₅₁	5	30	
		a ₅₂	5	40	
		a ₅₃	5	50	
		a ₅₄	5	60	
		a ₅₅	5	70	

Table 3.1(b) Set sample group AII~AVIIGroup AII, $t = 2.08$ mm

$w \setminus l$	30	40	50	60	70
25	a ₁₁	a ₁₂	a ₁₃	a ₁₄	a ₁₅
20	a ₂₁	a ₂₂	a ₂₃	a ₂₄	a ₂₅
15	a ₃₁	a ₃₂	a ₃₃	a ₃₄	a ₃₅
10	a ₄₁	a ₄₂	a ₄₃	a ₄₄	a ₄₅
5	a ₅₁	a ₅₂	a ₅₃	a ₅₄	a ₅₅

Group AIII, $t = 1.68$ mm

$w \setminus l$	30	40	50	60	70
25	a ₁₁	a ₁₂	a ₁₃	a ₁₄	a ₁₅
20	a ₂₁	a ₂₂	a ₂₃	a ₂₄	a ₂₅
15	a ₃₁	a ₃₂	a ₃₃	a ₃₄	a ₃₅
10	a ₄₁	a ₄₂	a ₄₃	a ₄₄	a ₄₅
5	a ₅₁	a ₅₂	a ₅₃	a ₅₄	a ₅₅

Group AIV, $t = 1.55$ mm

$w \setminus l$	30	40	50	60	70
25	a ₁₁	a ₁₂	a ₁₃	a ₁₄	a ₁₅
20	a ₂₁	a ₂₂	a ₂₃	a ₂₄	a ₂₅
15	a ₃₁	a ₃₂	a ₃₃	a ₃₄	a ₃₅
10	a ₄₁	a ₄₂	a ₄₃	a ₄₄	a ₄₅
5	a ₅₁	a ₅₂	a ₅₃	a ₅₄	a ₅₅

Group AV, $t = 1.25$ mm

$w \setminus l$	30	40	50	60	70
25	a ₁₁	a ₁₂	a ₁₃	a ₁₄	a ₁₅
20	a ₂₁	a ₂₂	a ₂₃	a ₂₄	a ₂₅
15	a ₃₁	a ₃₂	a ₃₃	a ₃₄	a ₃₅
10	a ₄₁	a ₄₂	a ₄₃	a ₄₄	a ₄₅
5	a ₅₁	a ₅₂	a ₅₃	a ₅₄	a ₅₅

Group AVI, $t = 1.00$ mm

$w \setminus l$	30	40	50	60	70
25	a ₁₁	a ₁₂	a ₁₃	a ₁₄	a ₁₅
20	a ₂₁	a ₂₂	a ₂₃	a ₂₄	a ₂₅
15	a ₃₁	a ₃₂	a ₃₃	a ₃₄	a ₃₅
10	a ₄₁	a ₄₂	a ₄₃	a ₄₄	a ₄₅
5	a ₅₁	a ₅₂	a ₅₃	a ₅₄	a ₅₅

Group AVII, $t = 0.77$ mm

$w \setminus l$	30	40	50	60	70
25	a ₁₁	a ₁₂	a ₁₃	a ₁₄	a ₁₅
20	a ₂₁	a ₂₂	a ₂₃	a ₂₄	a ₂₅
15	a ₃₁	a ₃₂	a ₃₃	a ₃₄	a ₃₅
10	a ₄₁	a ₄₂	a ₄₃	a ₄₄	a ₄₅
5	a ₅₁	a ₅₂	a ₅₃	a ₅₄	a ₅₅

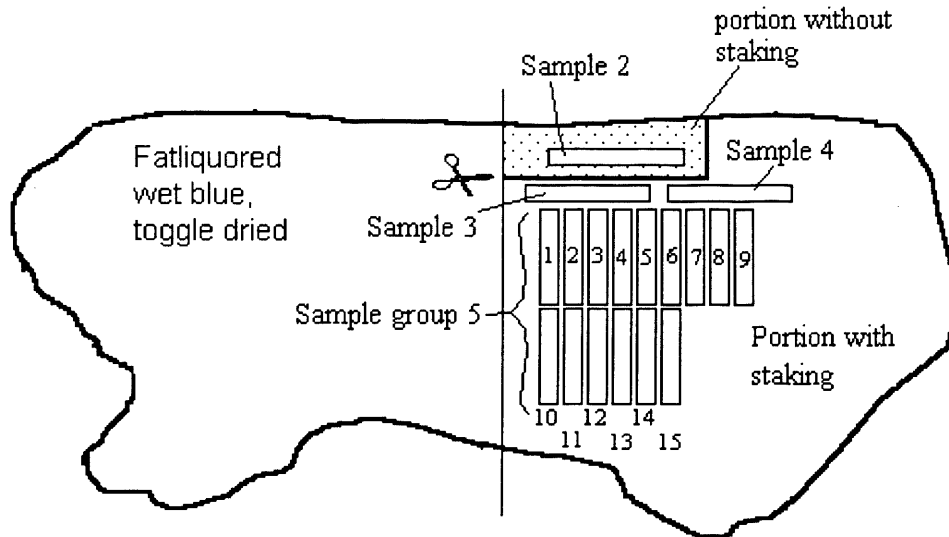


Figure 3.11 Sampling locations of sample 2 ~ 5.

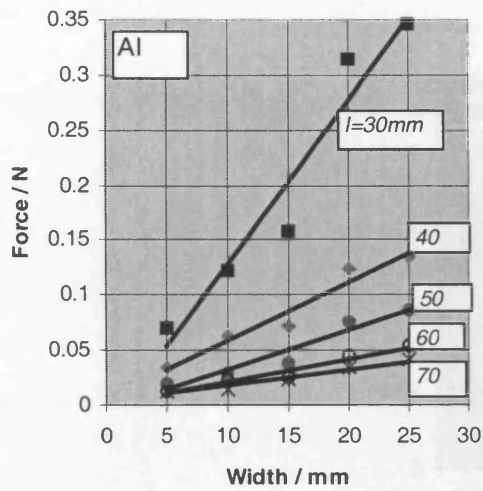
All the samples mentioned above had been conditioned in a conditioning room, where the temperature (20° Celsius) and relative humidity (65%) were kept constant for a period long enough to reach equilibrium prior to test.

3. 4 Results and Discussion

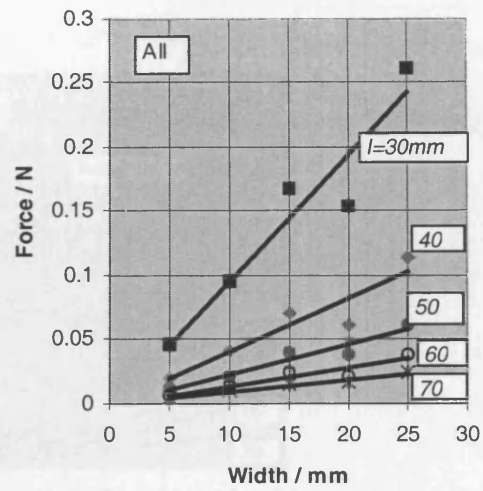
3. 4. 1 Force As a Function of Sample Width

3. 4. 1. 1 Results

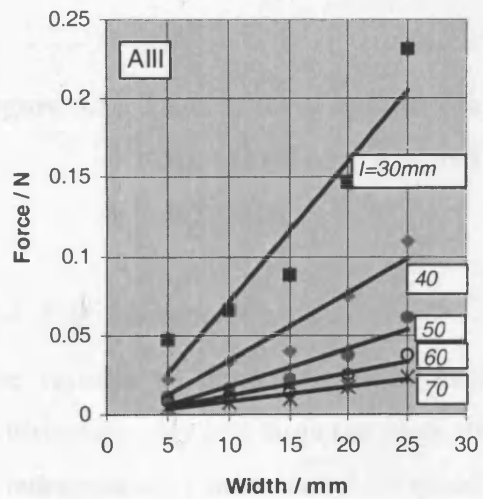
These experiments used the commercially sourced finished leather. Figures 3.12 (a) ~ (g) show the dependence of transverse force, F , on the sample width, w , for a series of samples with different length and thickness.



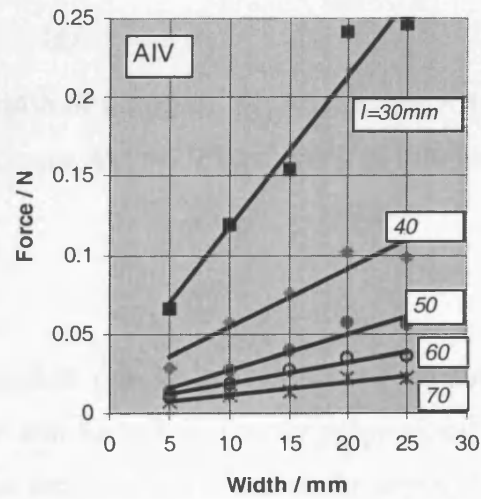
(a)



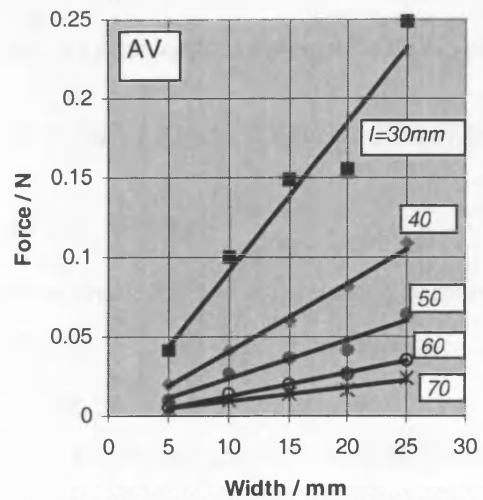
(b)



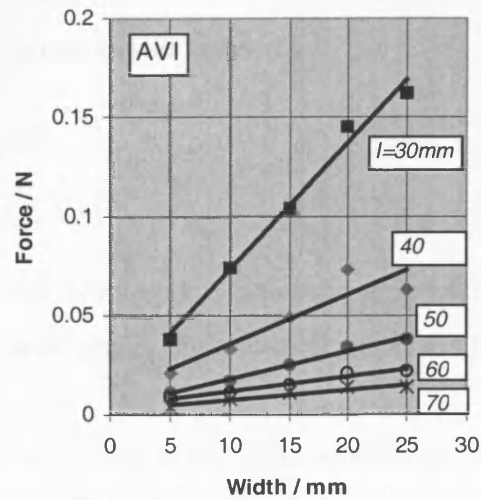
(c)



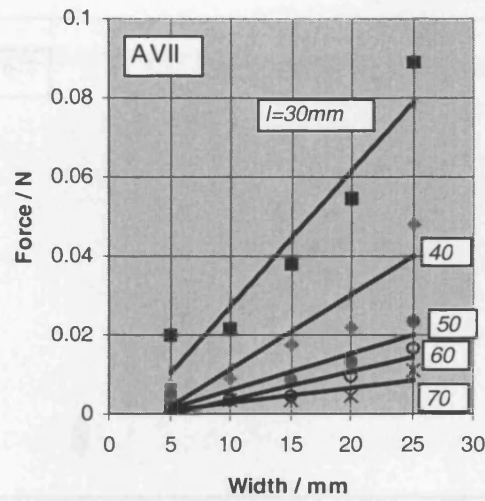
(d)



(e)



(f)



(g)

Figure 3.12 Plots of force against the width of samples. AI: $t=2.44$ mm, AII: $t=2.08$ mm, AIII: $t=1.68$ mm, AIV: $t=1.55$ mm, AV: $t=1.25$ mm, AVI: $t=1.00$ mm, AVII: $t=0.77$ mm.

3. 4. 1. 2 Discussion

The variable w seems to play an independent role in the relationship of force to bending deformation. By and large the plots show that force F is directly proportional to the variable w independent of other sample dimensions such as l and t , and of the depth of the probe d at which the force is measured.

Thus: $F \propto w$

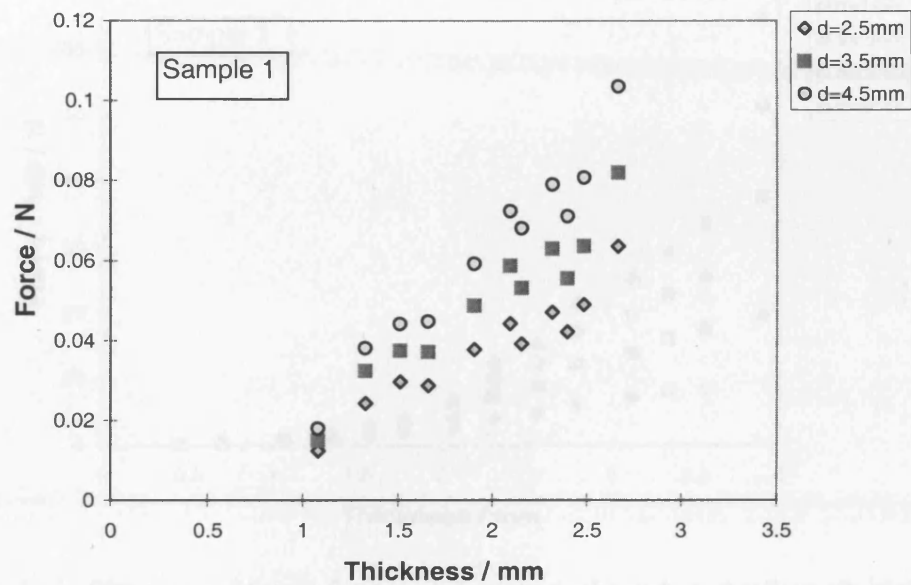
This result accords with equation (3-1) for linear elastic materials.

3. 4. 2 Force Against Sample Thickness

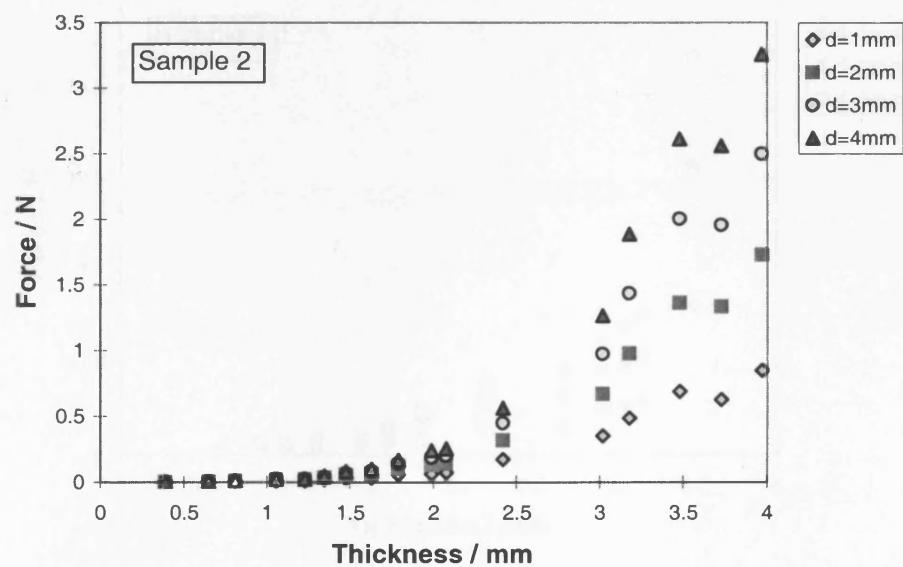
3. 4. 2. 1 Results

Results from the force-thickness bending test for sample 1 to sample group 6 are summarised in Figure 3.13 (a)~(g). The logarithm of force against logarithm of thickness for each sample is shown in Figure 3.14 (a)~(g).

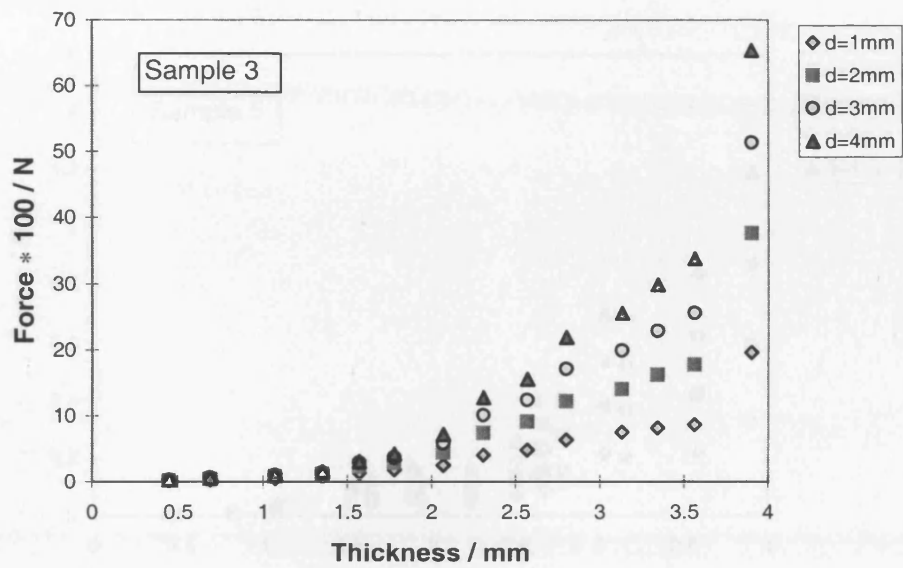
Different samples (sample groups) were used to highlight whether or not factors apart from thickness itself influence the F - t pattern. These factors include:



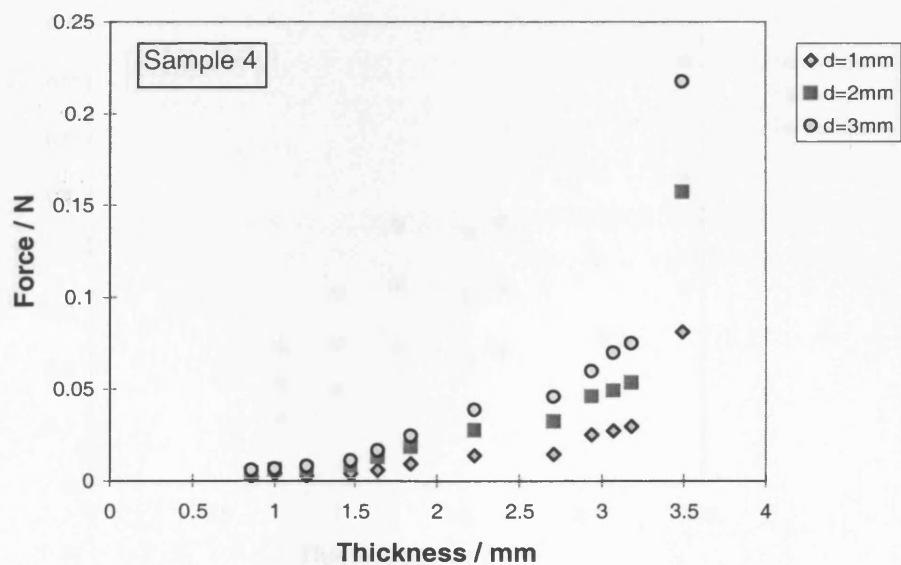
(a) Sample 1. $l=50\text{mm}$, $w=15\text{mm}$, fully treated commercial leather, buffed gradually with emery paper from the corium side.



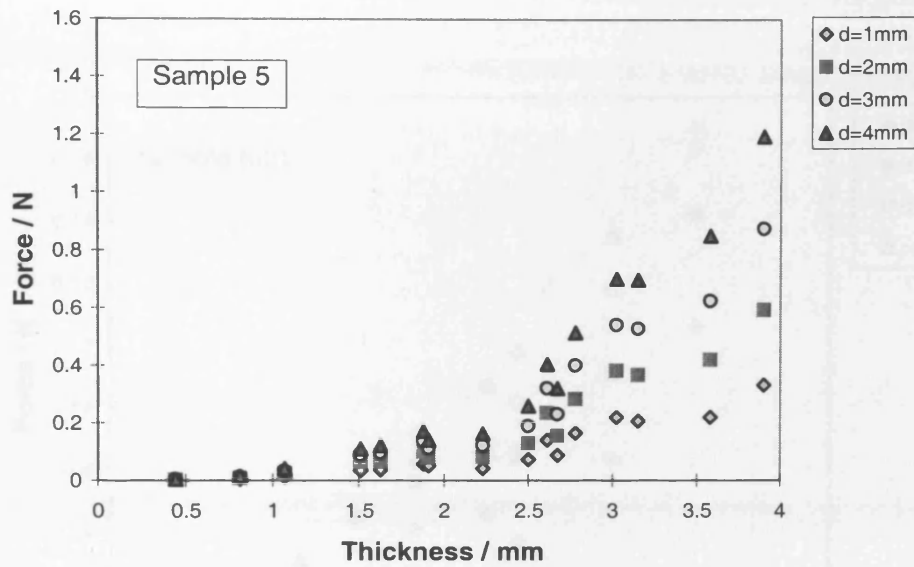
(b) Sample 2. $l=50\text{mm}$, $w=15\text{mm}$, fatliquored, unstaked, shaved gradually with high speed grinder from the corium side.



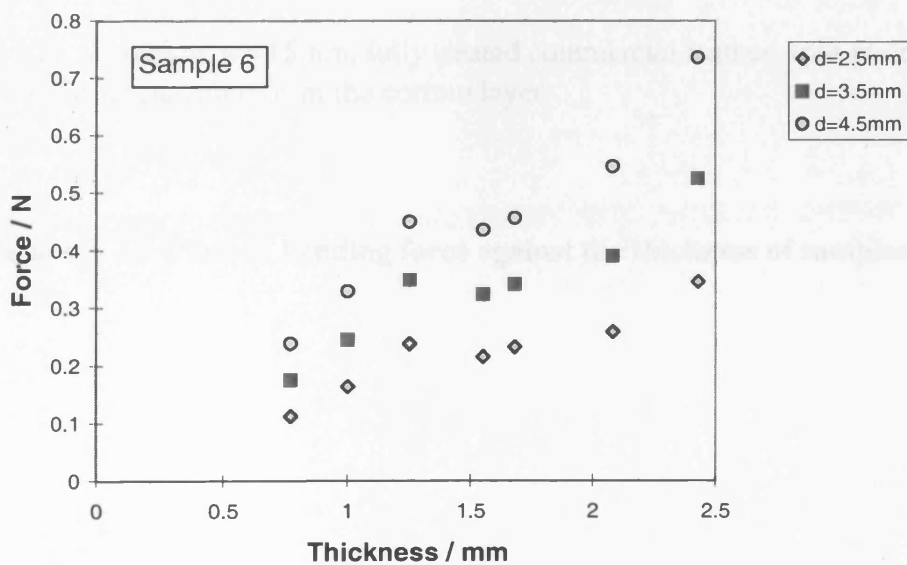
(c) Sample 3. $l=50\text{mm}$, $w=15\text{mm}$, fatliquored, staked, shaved gradually with high speed grinder from the corium side.



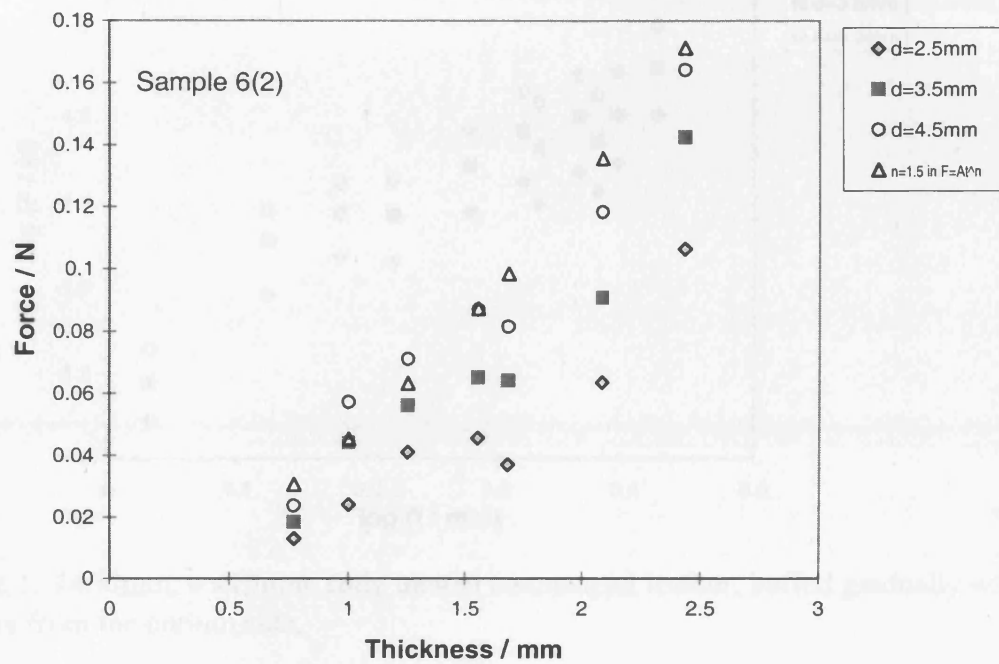
(d) Sample 4. $l=50\text{mm}$, $w=15\text{mm}$, fatliquored, staked, shaved gradually with high speed grinder from the grain side.



(e) Sample 5. $l=50\text{mm}$, $w=25\text{mm}$, fatliquored, staked, split to different thickness via splitting machine from the corium layer.

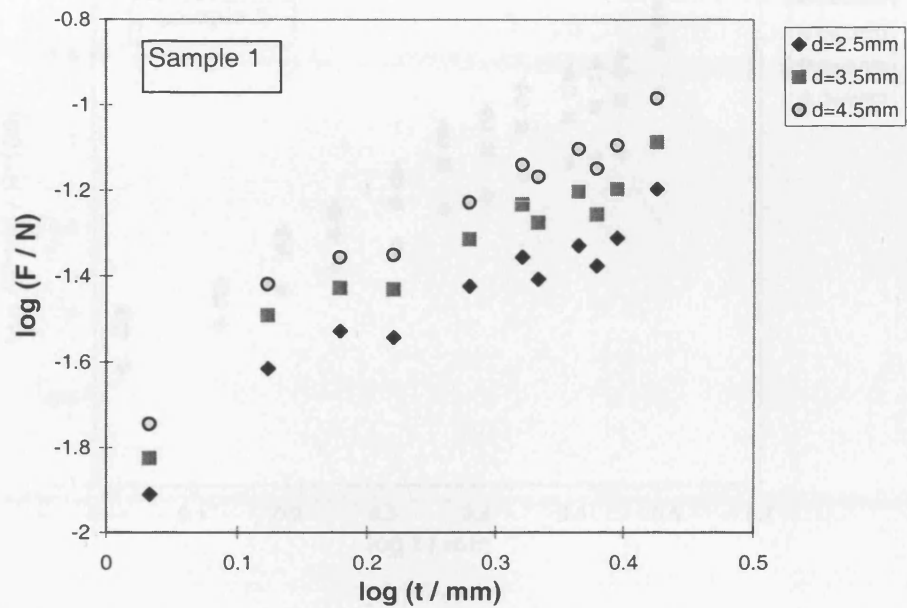


(f) Sample 6 (1). $l=30\text{mm}$, $w=25\text{mm}$, fully treated commercial leather, split to different thickness via splitting machine from the corium layer.

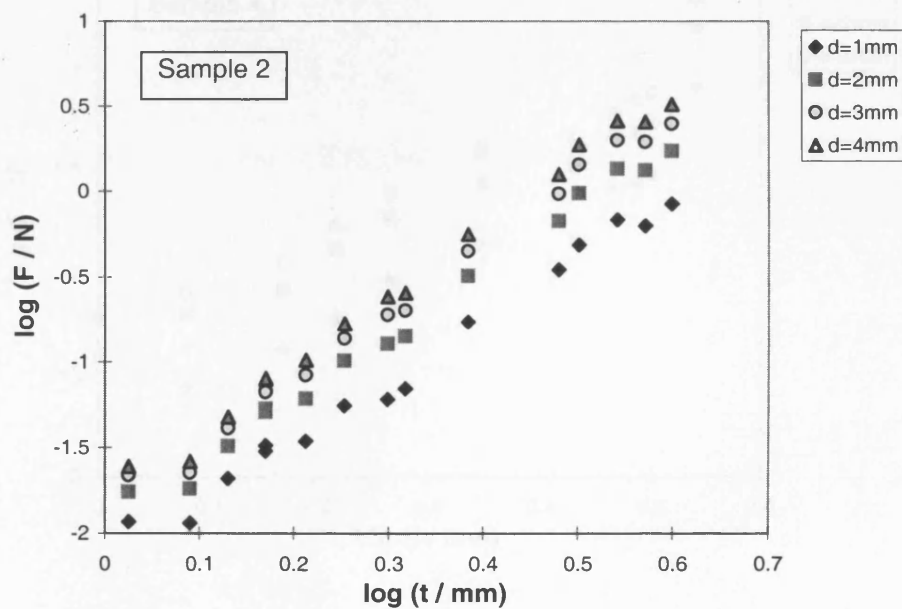


(g) Sample 6(2). $l=40\text{mm}$, $w=15\text{mm}$, fully treated commercial leather, split to different thickness via splitting machine from the corium layer.

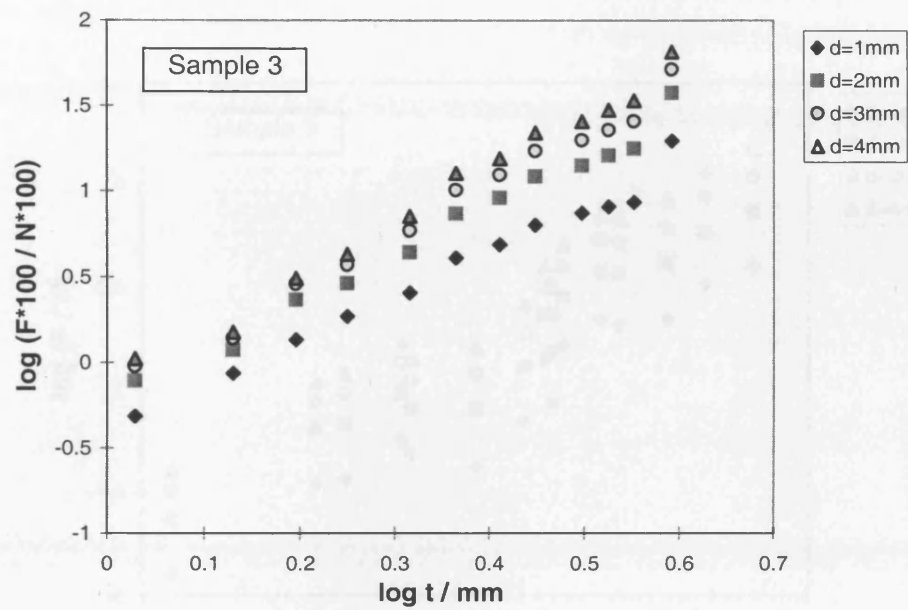
Figure 3. 13 Plots of bending force against the thickness of samples.



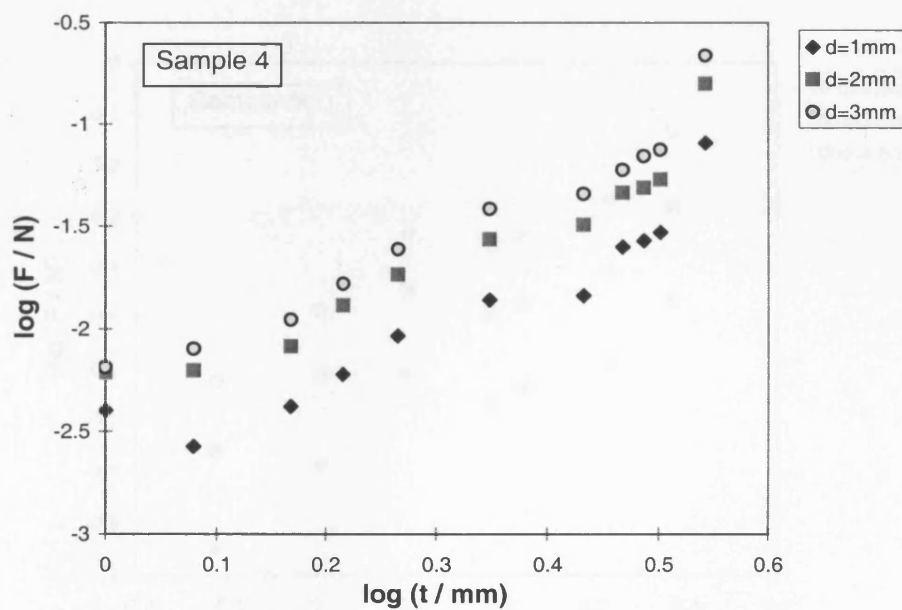
(a) Sample 1. $l=50\text{mm}$, $w=15\text{mm}$, fully treated commercial leather, buffed gradually with emery paper from the corium side.



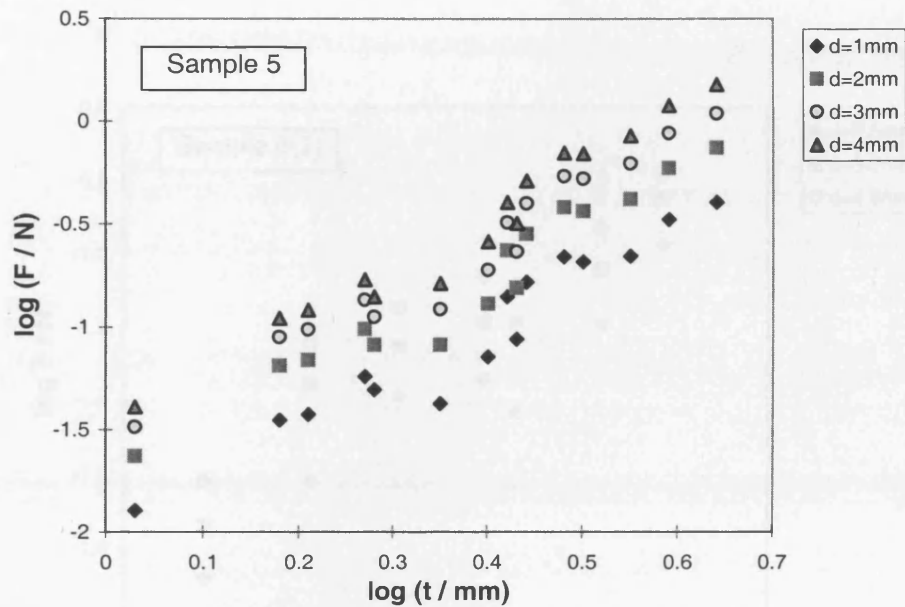
(b) Sample 2. $l=50\text{mm}$, $w=15\text{mm}$, fatliquored, unstaked, shaved gradually with high speed grinder from the corium side.



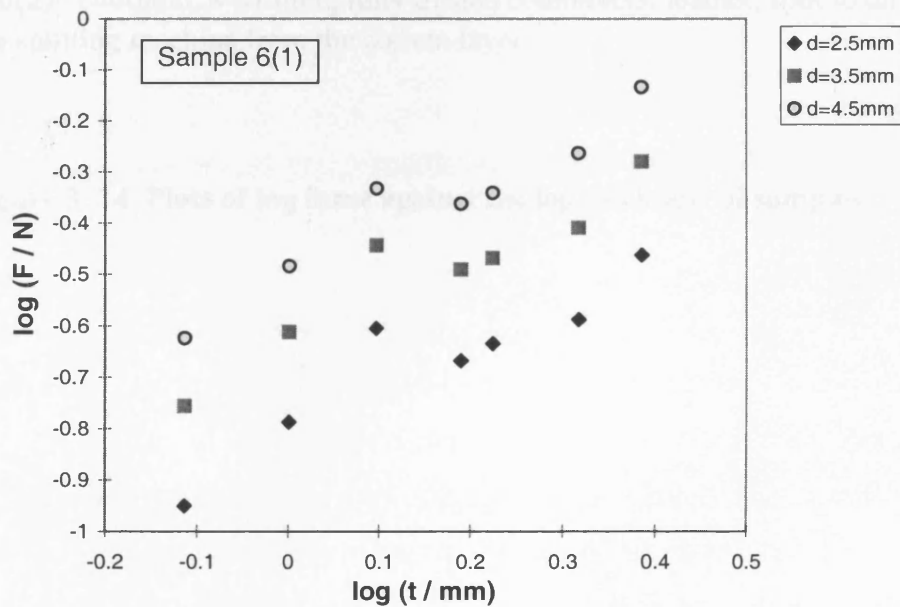
(c) Sample 3. $l=50\text{mm}$, $w=15\text{mm}$, fatliquored, staked, shaved gradually with high speed grinder from the corium side.



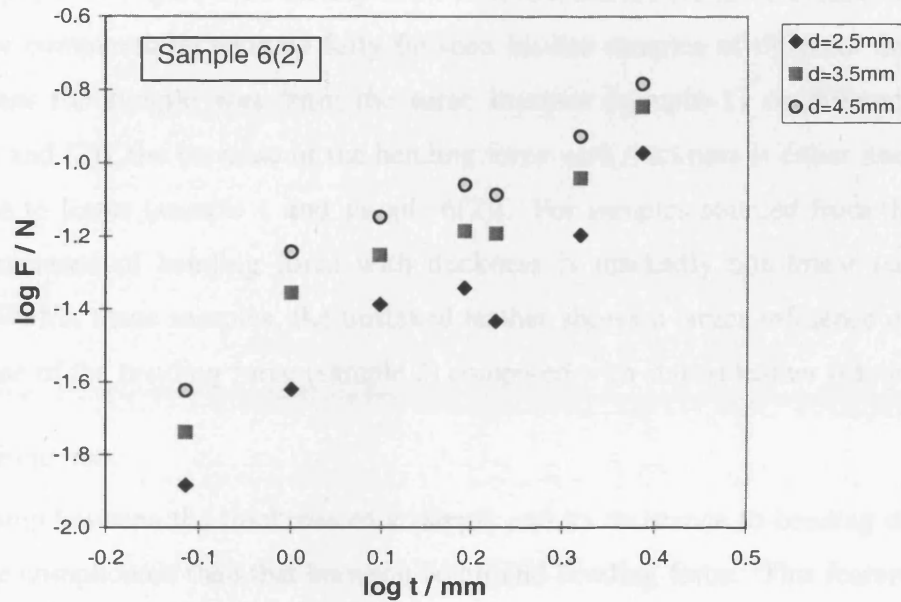
(d) Sample 4. $l=50\text{mm}$, $w=15\text{mm}$, fatliquored, staked, shaved gradually with high speed grinder from the grain side.



(e) Sample 5. $l=50\text{mm}$, $w=25\text{mm}$, fatliquored, staked, split to different thickness via splitting machine from the corium layer.



(f) Sample 6 (1). $l=30\text{mm}$, $w=25\text{mm}$, fully treated commercial leather, split to different thickness via splitting machine from the corium layer.



(g) Sample 6(2). $l=40\text{mm}$, $w=15\text{mm}$, fully treated commercial leather, split to different thickness via splitting machine from the corium layer.

Figure 3. 14 Plots of log force against the log thickness of samples.

- i) different manufacturing processes and sample preparation;
- ii) sampling locations from same or different regions of the hide; and
- iii) sample dimensions l and w .

The graphs in *Figure 3.13* clearly show different characteristics for differently treated samples. For commercially sourced fully finished leather samples of different thickness, no matter whether the sample was from the same location (sample 1) or different locations (sample 6(1) and (2)), the increase of the bending force with thickness is either linear (sample 6(1)) or close to linear (sample 1 and sample 6(2)). For samples sourced from the wet blue leather, the increase of bending force with thickness is markedly non-linear (sample 2 to sample 5). Within these samples, the unstaked leather shows a larger influence of thickness on the increase of the bending force (sample 2) compared with staked leather (samples 3-5).

3. 4. 2. 2. Discussion

The relationship between the thickness of a sample and its resistance to bending deformation is much more complicated than that between width and bending force. This feature is largely attributable to the following.

- 1) The modulus of leather is considerably smaller than that of ideally elastic engineering materials, resulting in a larger resultant shear force when the sample is deformed in bending;
- 2) Leather is not a homogeneous material and it shows isotropic characteristics in mechanical properties. This observation is highlighted in a comparison of the behaviour of tension and compression;
- 3) The typical grain and corium two layer structure each with different mechanical properties will also contribute to the deviation from the ideal theory.

Furthermore, the two layers also undergo different changes when they are processed in the tannery. This is due to differences in the microstructure of the two layers. Therefore, when the approximate pure bending model is applied to leather, large deviations from the theoretical model are inevitable. In order to understand the relationship between sample thickness and its resistance to bending deformation, we start with simple theory and then extend the analysis by considering the influence of other factors that may cause a deviation from the ideal bending behaviour.

According to equation 3-4(b), the standard theory of bending gives that

$$M = \frac{IE}{R}$$

The stiffness of the beam, S , is given by

$$S = EI$$

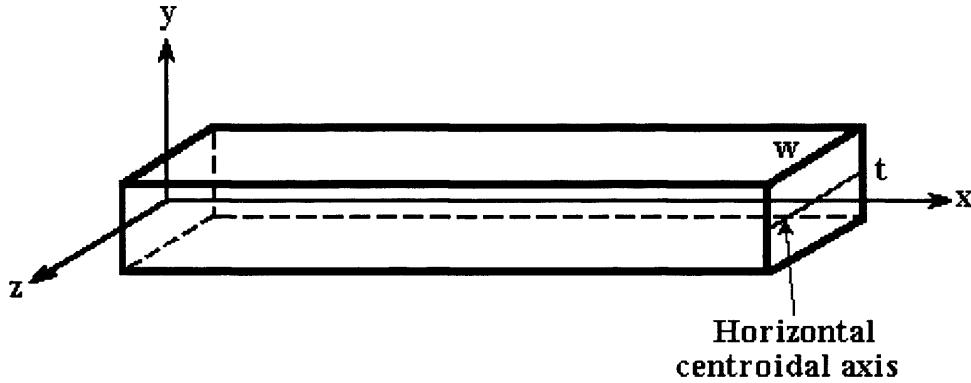


Figure 3.15 A rectangular beam with width w and thickness t .

For a rectangular beam, width w and thickness t as shown in *Figure 3.15*, the second moment of the cross sectional area about its horizontal centroidal axis I is given by

$$I = \int_{\text{cross section}} y^2 da = \frac{wt^3}{12}$$

Therefore, the bending stiffness: $S = \frac{wt^3}{12} E$

or $S \propto t^3$

For leather, if the results are in accord with a general relationship of the form:

$$S \propto t^n$$

then we may determine, n , and compare the latter with theoretically expected value, namely 3.

n can be obtained from the slope of $\log F \sim \log t$ plot. The n values of sample 1 to sample 6 are listed in table 3. 2.

It is clear that in no case is $n = 3$ as expected from theory. Rather n varies from as low as 1.0 to as high as 3.5 depending on the leather type and sample preparation route.

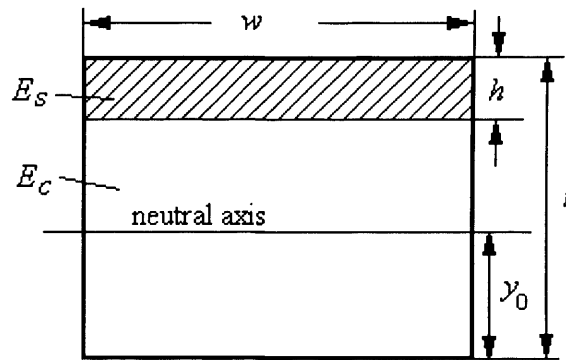
A. Explanation of bending stiffness $S \propto t^n$ where $n \neq 3$

As discussed in section 3.2.2.4, for a sandwich beam which has three laminated layers, stiffness $S = EI$ can be expressed according to Williams using equation 3-11. A special case of interest is when $h_1 = 0$ — i.e. there are only two different layers (shown in *Figure 3.16*) — as this is the case of leather structure. This gives (let $h_2 = h$):

Table 3.2 Indices n for samples 1– 6

Sample	History of process	n	l	w
1	Completely treated commercial, /gradually buffed to different thickness t	1.5~1.6	50	15
2	Ustk /grinder shaved to different t	3.3~3.5	50	15
3	Stkd /grinder shaved to different t	2.3~2.6	50	15
4	Stkd /grinder shaved (from grain) to different t	2.2~2.3	50	15
5	Stkd /split to different t	2.5~2.6	50	25
6(1)	Completely treated commercial, /split to different t	1.0	30	25
6(2)	Same as 6(1)	1.5~1.6	50	15

stk — staked; uskd — unstaked

**Figure 3.16 Cross section of a two- layer beam.**

$$S = \frac{wt^3}{12} E_s \left\{ 4 - 4 \left(\frac{E_s - E_c}{E_s} \right) \left[\left(1 - \frac{h}{t} \right)^3 \right] - 3 \frac{\left[1 - \left(\frac{E_s - E_c}{E_s} \right) \left(1 - \frac{h}{t} \right)^2 \right]^2}{\left[1 - \left(\frac{E_s - E_c}{E_s} \right) \left(1 - \frac{h}{t} \right) \right]} \right\} \quad (3 - 12)$$

$$\text{or:} \quad S = \frac{wt^3}{12} E_1 \left\{ 4 - 4 \left(1 - \frac{E_2}{E_1} \right) \left(1 - \frac{h}{t} \right)^3 - 3 \frac{\left[1 - \left(1 - \frac{E_2}{E_1} \right) \left(1 - \frac{h}{t} \right)^2 \right]^2}{\left[1 - \left(1 - \frac{E_2}{E_1} \right) \left(1 - \frac{h}{t} \right) \right]} \right\} \quad (3 - 13)$$

where E_1 and E_2 stand for the moduli of the grain and corium layers respectively; t is the

thickness of the whole sample, and h is the thickness of grain layer which is normally in the range 1 ± 0.2 mm.

For homogeneous material, that is to say, when $E_1 = E_2$, equation 3-13 reduces to the equation describing standard bending theory,

$$S = wt^3/12$$

However one unique characteristic of leather is that it contains two distinguishable layers. Thus leather can be regarded as a laminated material. We can see how the standard theory ($S = wt^3/12$) is modified by a given set of layer dimensions and moduli.

In the case of fatliquored leather, we assume the ratio h/t varies from 1 (all grain) to 1/4, since the thickness of the leather samples ranges from about 1 mm to up to about 4 mm.

When the ratio of E_2/E_1 is not 1, then the dependence of S on t will not be the same as required by the standard theory. This results in a deviation of n from 3 if we still assume that the dependence of S on t can be approximately described by an equation having the form, $S \propto t^n$. The consequences of this approximation are illustrated in *Figure 3.17*. The solid line represents the case where $E_2 = E_1$, i.e. $S \propto t^3$. The lines above this solid line show the situation where $E_1 < E_2$ which can be described approximately in the form of $S \propto t^n$ where $n > 3$. The lines below the solid line show the case where $E_1 > E_2$ which can also be closely described by $S \propto t^n$ where $n < 3$.

In practice the ratio of E_2/E_1 varies according to the process history of leather. Tensile test on the separate grain and corium layers of two different samples yielded the results and are shown in *Figure 3.18 (a)~(b)*.

The results shown in *Figure 3.18 (a)* are from the grain and corium layers of fatliquored and staked crust leather. In this case, the ratio of moduli $E_2/E_1 \approx 0.49$ where $E_1 = 9$ MPa and $E_2 = 4.4$ MPa (moduli measured at low strains $< 5\%$). The low strain region was selected in order to avoid large deviations from linearity. After substituting E_1 and E_2 in equation 3-13 with the actual values of grain and corium moduli, an $S \sim t$ relationship can be obtained as shown in *Figure 3.19 (a)* plot 2. When using the power law to represent this plot, the best fit is for $n = 2.69$; *Figure 3.19 (a)* plot 3. For the unstaked leather, O'Leary's ^[79] work on the same leather as used in this work (with a separate fatliquoring process) showed that the ratio of E_2/E_1 was approximately 2.5 where $E_1 \approx 5.5$ MPa, and $E_2 \approx 14$ MPa. In this case, the index for the power law best fit is 3.4; *Figure 3.19 (c)*.

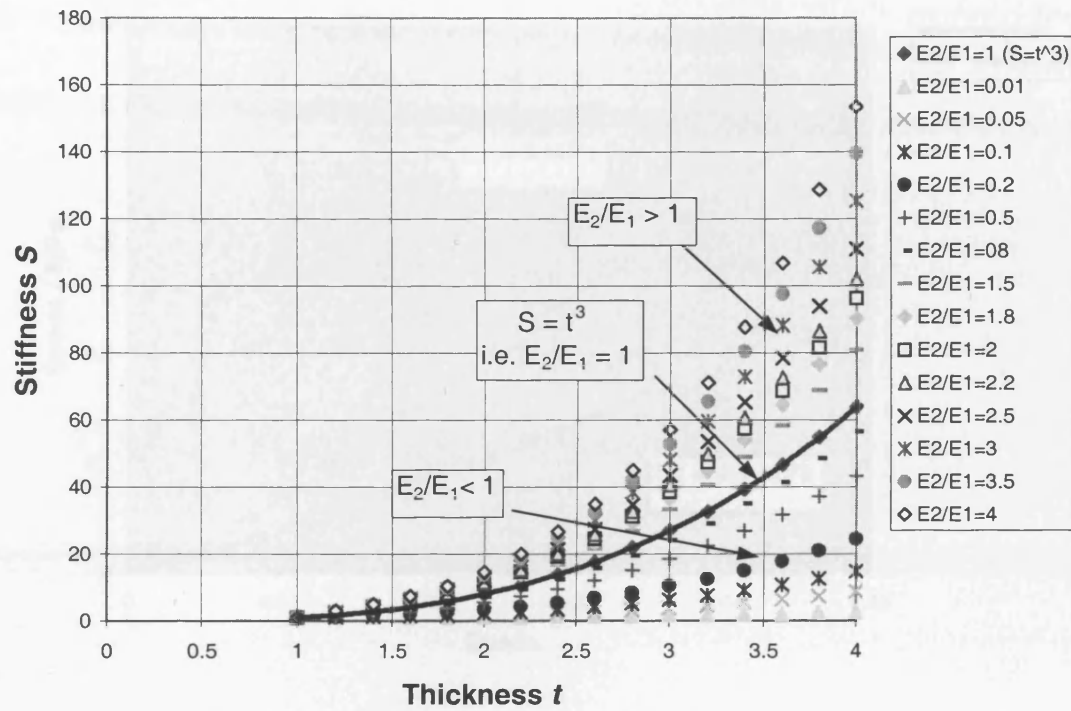
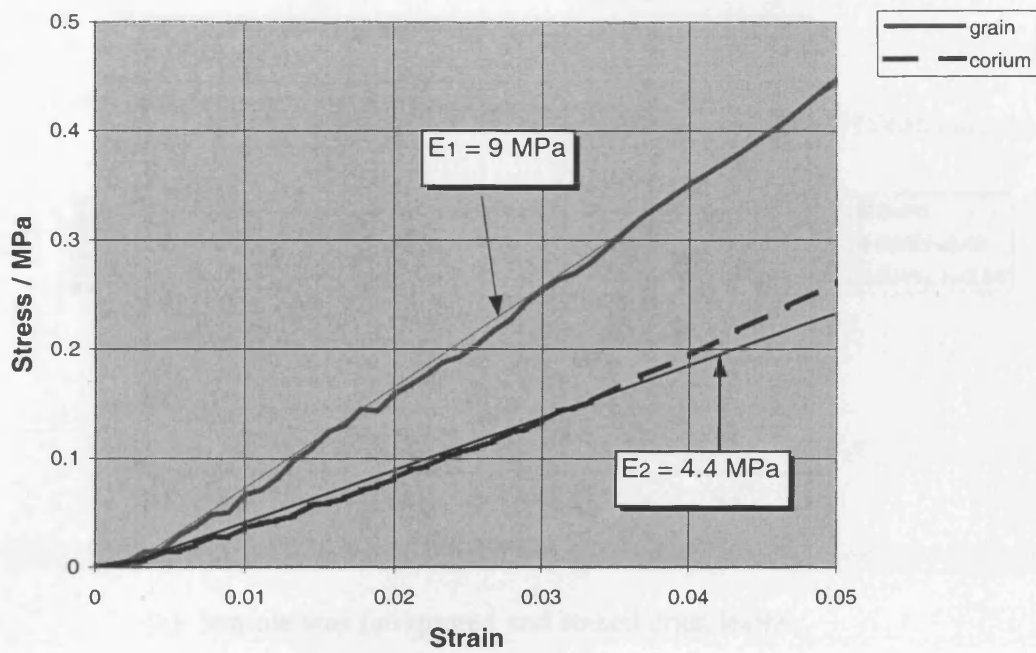
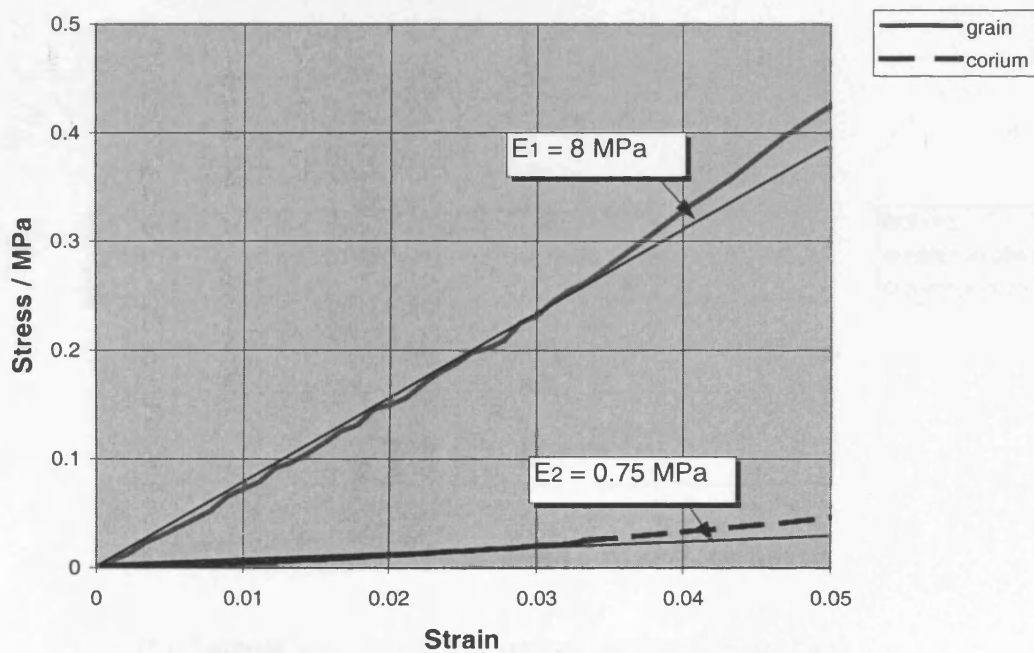


Figure 3.17 The influence of different ratio of E_2/E_1 on the apparent power index n in the equation of $S = t^n$.



(a) Fatliquored and staked crust leather.

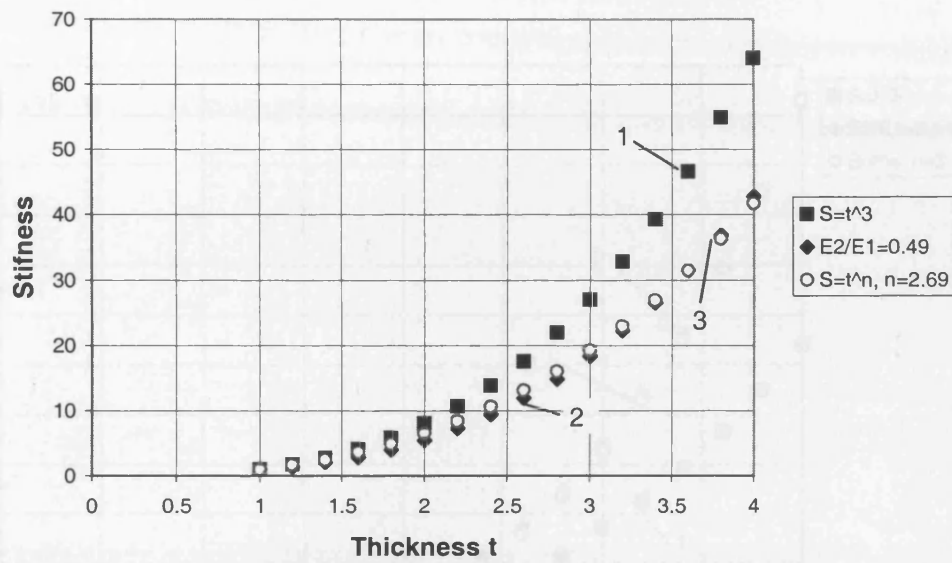


(b) Fully treated commercial leather.

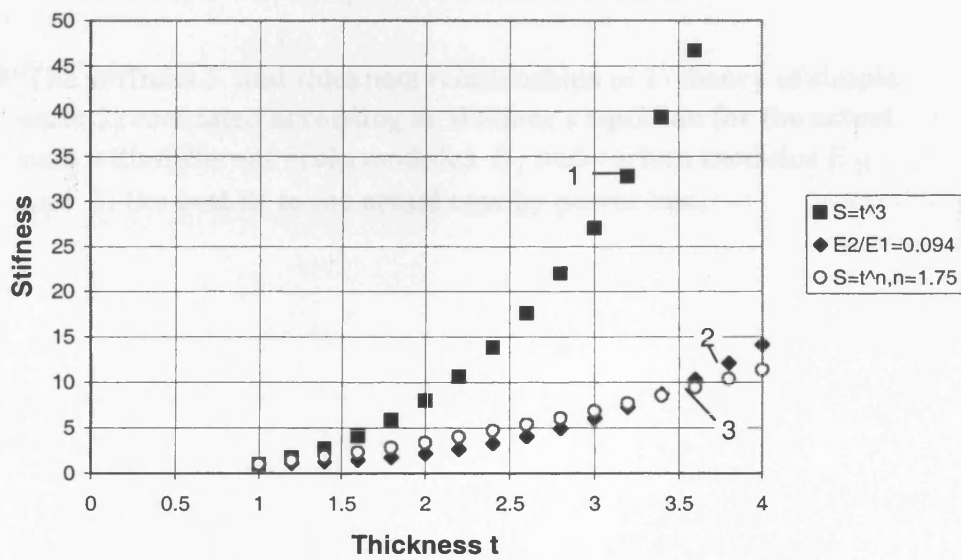
Figure 3. 18 Tensile behaviour of grain and corium layers.

(a)--- fatliquored and staked crust leather

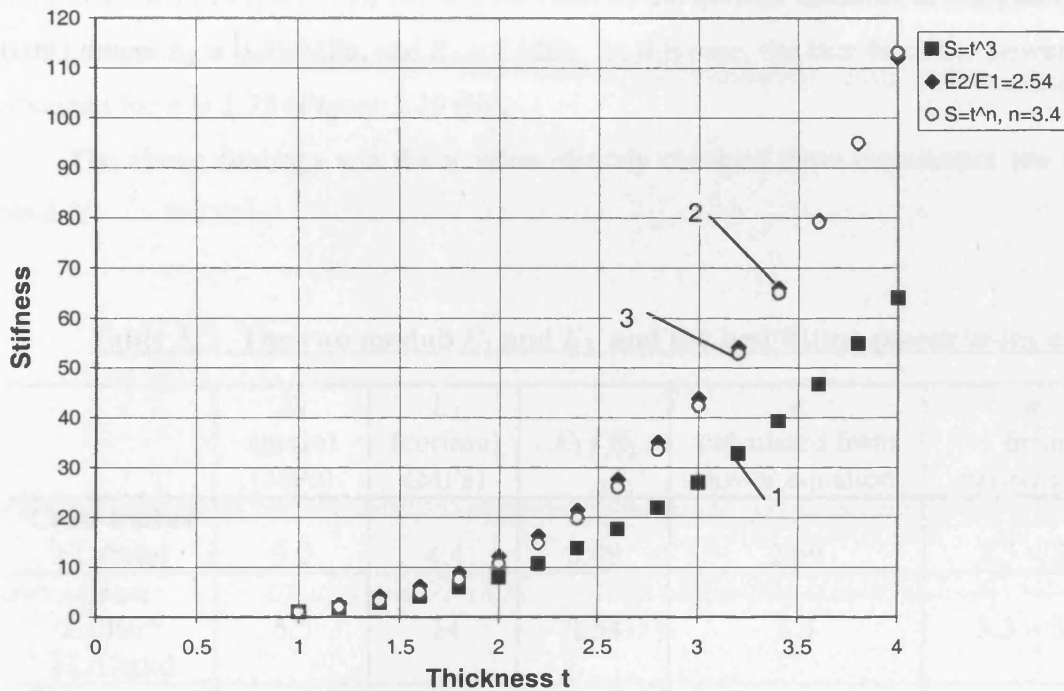
(b)--- fully treated commercial leather



(a) Sample was fatigued and staked crust leather.



(b) Sample was completely treated commercial leather.



(c) Sample was fatliquored and unstaked leather.

Figure 3. 19 The stiffness S and thickness relationships of 1) theory of simple case; 2) caculated according to William's equation for the actual case with different grain modulus E_1 and corium modulus E_2 ; and 3) the best fit to the actual case by power law.

The tensile behaviour of the grain and corium layers of the finished commercial leather is shown in *Figure 3.18 (b)* and the ratio of the corium modulus to the grain modulus is 0.093 where $E_2 = 0.75$ MPa, and $E_1 = 8$ MPa. In this case, the best fit of the power function is obtained for $n = 1.75$ (*Figure 3.19 (b)*).

The above findings and the n value directly obtained from experiment are listed the table 3.3

Table 3.3 The two moduli E_1 and E_2 and the best fitting power index n

	E_1 (grain) (MPa)	E_2 (corium) (MPa)	E_2 / E_1	n calculated from power equation	n from experiment
Crust leather FL/Stkd	9.0	4.4	0.49	2.69	2.5 ~ 2.6
Crust leather* FL/Ustkd	5.5	14	2.54	3.4	3.3 ~ 3.5
Fully treated commercial leather	8	0.75	0.093	1.75	1.5 ~ 1.6

*— data is from reference [79]

Generally speaking, for fatliquored unstaked crust leather, it is not unreasonable that $E_1 < E_2$ since the deposition of fat liquor is expected to be greater in the surface layers. Thus more fatliquor will be present in the grain layer than in the corium. However, staking seems to have had a more significant effect on the corium layer than on the grain, leading to a reduction in E_2/E_1 . For the commercially sourced leather, the grain layer had been coated with some finishes, which appear to endow it with a much higher modulus than that of the corium.

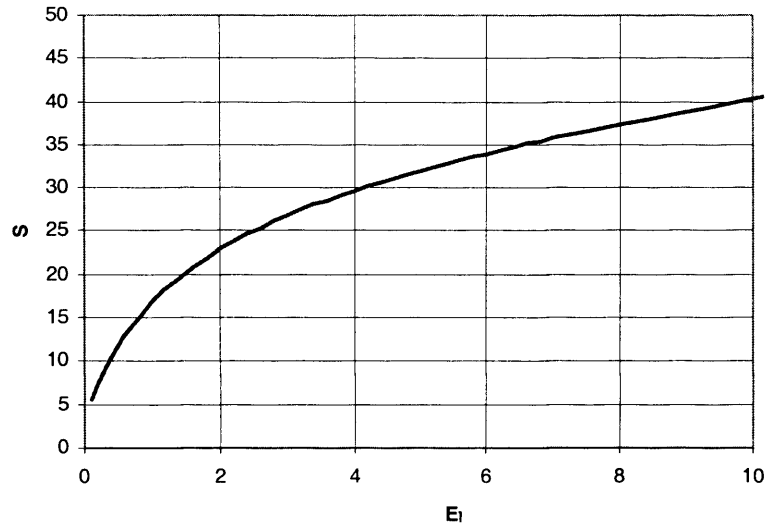
Comparing the indices obtained from the simulation by the power function to Williams's equation (3-13), and the indices in the experimental cases (table 3.3), it is apparent that there is a high degree of accordance between them. Thus we may conclude that the deviation of the dependence of bending behaviour on t of leather from that of the simple, ideal elastic material is mainly due to the "laminated" structure of leather and the different moduli the two layers possess.

Traditionally, the product of EI is defined as the flexural rigidity or the bending stiffness of the beam, which includes both the material parameter E and the size and shape of a sample (included in I , the second moment of area). Obviously in equation (3-13), stiffness S

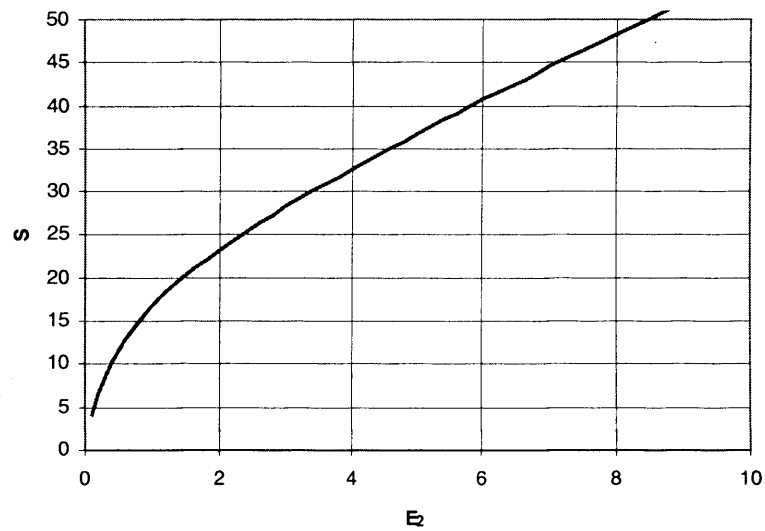
describes the bending stiffness of a sample with a laminated structure. There are several variables affecting the magnitude of S in different ways. The expression for S is composed of two factors: (i) the factor outside the bracket which is equivalent to EI for a homogeneous material and contains the variables E_1 and t , and (ii) the modifying factor within the bracket which contains a further three terms with one term being a constant, and the other two containing the variables E_2/E_1 and also t . *Figure 3.17* also shows how these variables would affect both the stiffness and the deviation from a homogeneous material calculation.

The first factor will increase as thickness increases while the second factor changes in different degrees as t increases depending on the ratio of E_2/E_1 — it decreases when $E_2/E_1 < 1$ but increases when $E_2/E_1 > 1$. On the whole the larger the ratio of E_2/E_1 , the larger influence of t on the stiffness S . In other words, thickness plays a different role in influencing the softness of leather in different leather samples with various processing histories. The ratio of E_2/E_1 also affects the stiffness of leather having a given thickness. Samples with a large value of E_2/E_1 possess larger value of S . Although increases in both E_1 and E_2 result in an increased S , they affect it in a different manner. As shown in *Figure 3.20 (a) and (b)*, the increase of S is affected more sharply by an increase in E_2 than by an increase in E_1 . This feature indicates that the application of finishes on the grain surface will be invariably be at the cost of losing some bending softness of the material. However achieving the full potential of the softness of the corium layer could act as compensation to such a loss.

Suppose that the bending stiffness S can be used as a measure of the softness of leather, then S can be predicted knowing the following variables: grain modulus E_1 , corium modulus E_2 , grain thickness and the parameters of the size of the testing samples. Noticing that the value of S calculated in this way includes the influence of the sample thickness which obviously does not always influence S the same way, we may eliminate the influence of t on the softness by finding the best fitted power index in the power function of $S \propto t^n$ according to *Figure 3.17*. That is to say, given the ratio E_2/E_1 , we are able to find the corresponding curve in *Figure 3.17* and subsequently the power index n . Thus the influence of t on the softness of leather can be accounted for approximately by using t^n to divide into the calculated S . This procedure allows comparison of the softness of two samples with different thickness.



(a)



(b)

Figure 3.20 The influence of E_1 and E_2 on the stiffness.

B. Further discussion

When the shear force is also considered as discussed in 3. 2. 2. 2, i. e.

$$d = \frac{Fl^3}{48EI} \left[1 + 3\left(1 + \frac{\nu}{2}\right) \frac{t^2}{l^2} \right]$$

where ν is Poisson's ratio, and the other symbols have the same meaning as before. After rearranging we have

$$F = \frac{48EI}{dl^3} \frac{1}{\left[1 + 3\left(1 + \frac{\nu}{2}\right) \frac{t^2}{l^2} \right]}$$

where the second factor $\frac{1}{\left[1 + 3\left(1 + \frac{\nu}{2}\right) \frac{t^2}{l^2} \right]}$ is slightly smaller than one, since in most cases, $t^2 \ll l^2$.

Hence the power index n is slightly lower if the power function is still used to describe the “laminated” leather. In other words, the magnitude of n should be slightly smaller than the n calculated from the power equation, resulting in a closer approach to the experimental data. So the Williams equation (3-13) for laminated material can be used to describe the bending behaviour of leather when the moduli of the grain and corium layer and the thickness of the grain layer, are known.

3. 4. 2. 3 The Relationship Between Resistance to Bending Deformation and the Length Between Supporting Points and the Depth of Bending

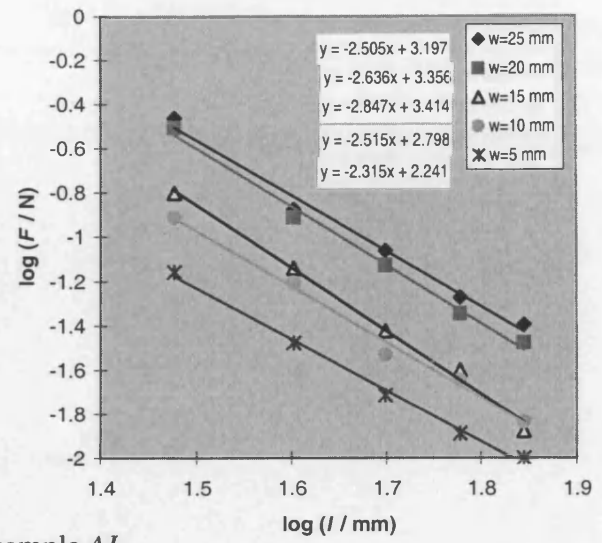
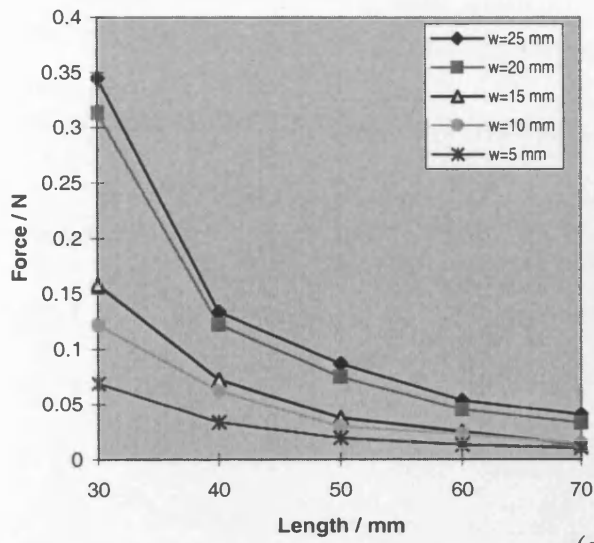
From the bending test of sample group AI ~ AVII, we obtained a series of plots of F against the sample length (between the two supporting points), l , which are shown in *Figure 3.21 (a) ~ (g)*. It can be concluded that

$$F \propto l^{-(2 \sim 3)}$$

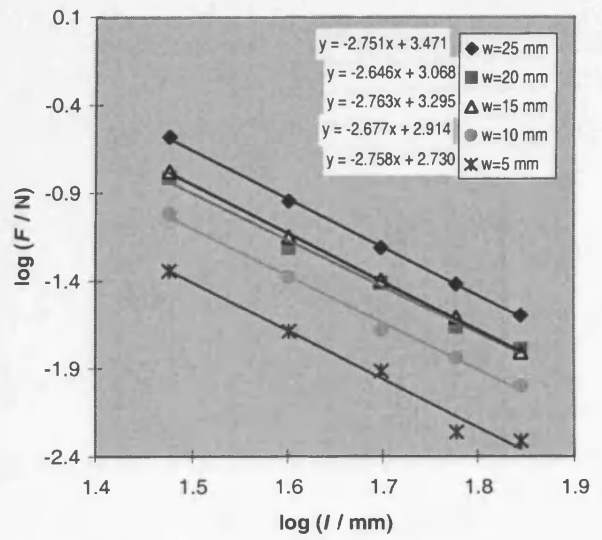
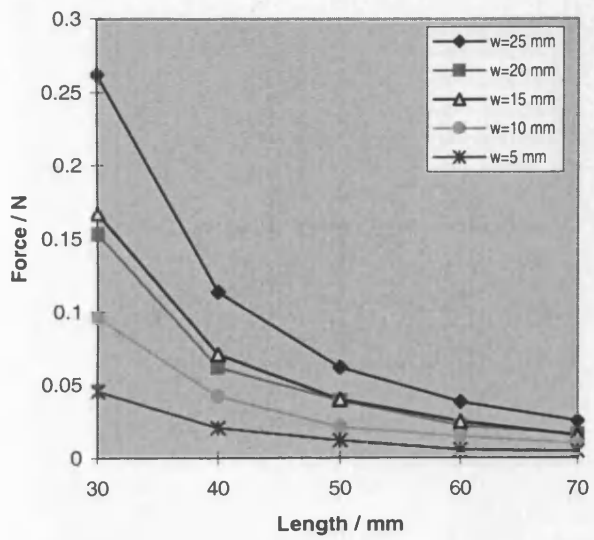
Compared with the ideal case where $F \propto l^{-3}$ (equation 3-1), the absolute value of the power index of l in the practical case is *smaller* than in the standard theory. The situation is now compared with the bending case where a relatively large deflection happens.

The basic assumption of the ideal bending theory is that the distortions are so small that no change in the geometry of the beam needs to be included in the analysis. This assumption is valid for most practical problems where the modulus of the material is high. However, for materials with a low modulus such as leather, the three point bending test leads to a relatively large deflection of the beam.

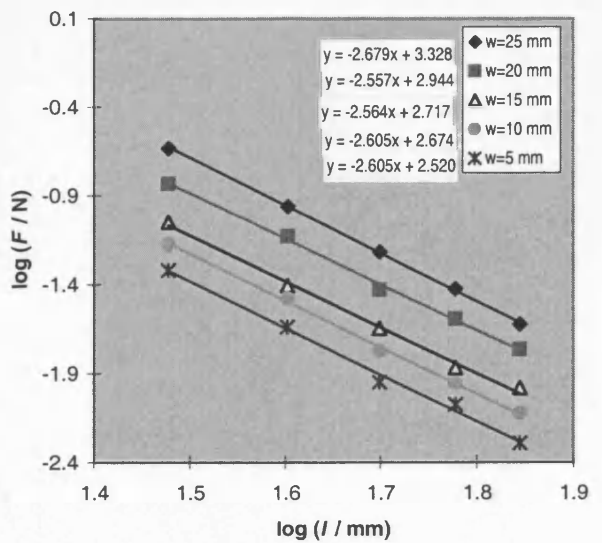
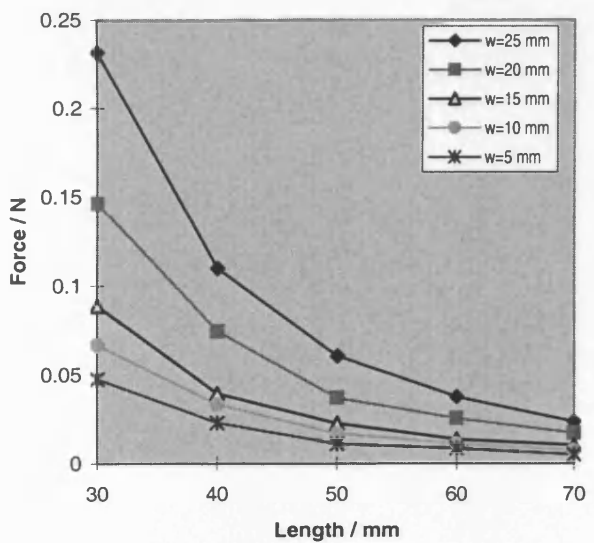
Consider a simply supported beam of length l with a central load F as shown in *Figure 3.2*:



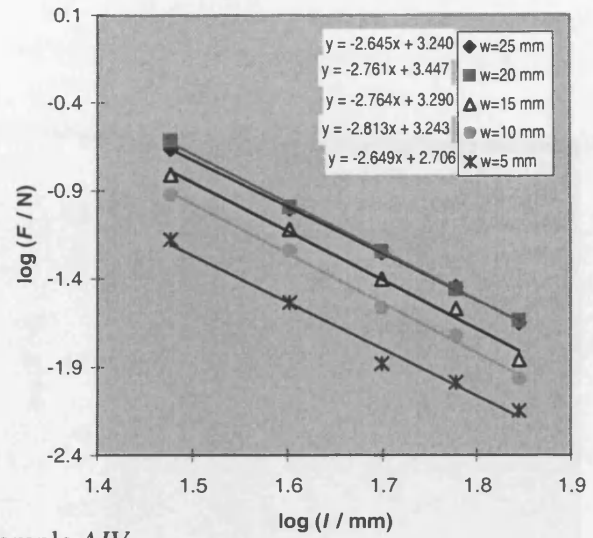
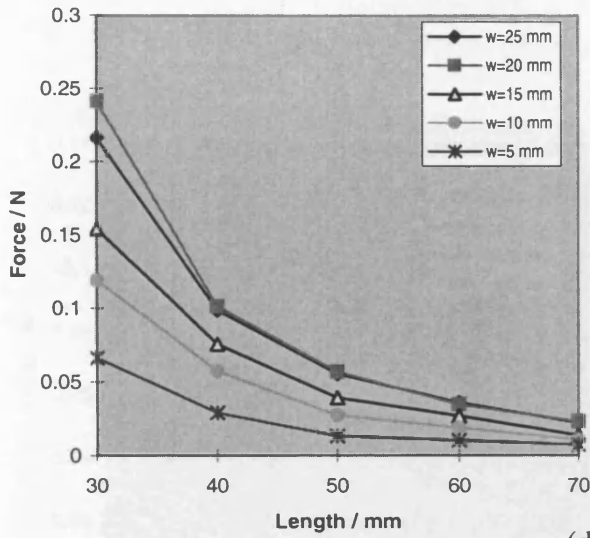
(a) sample AI



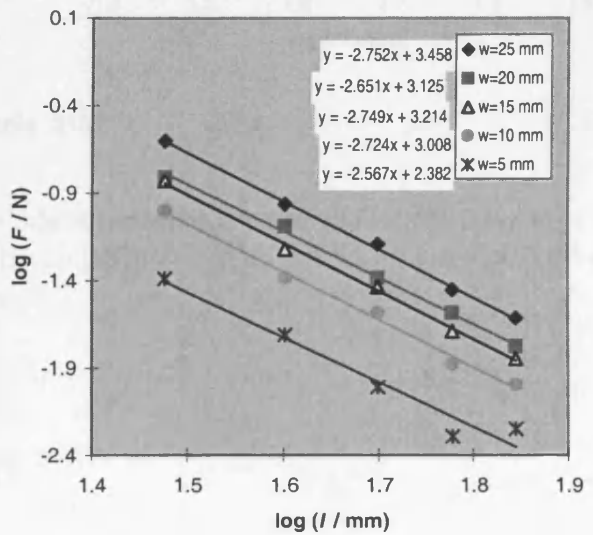
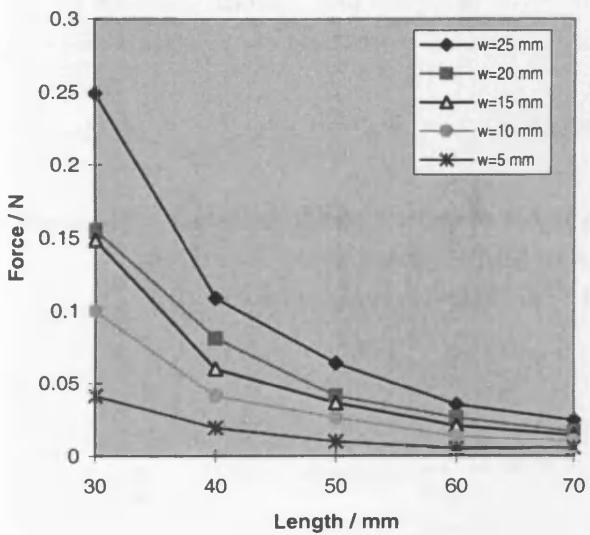
(b) sample AII



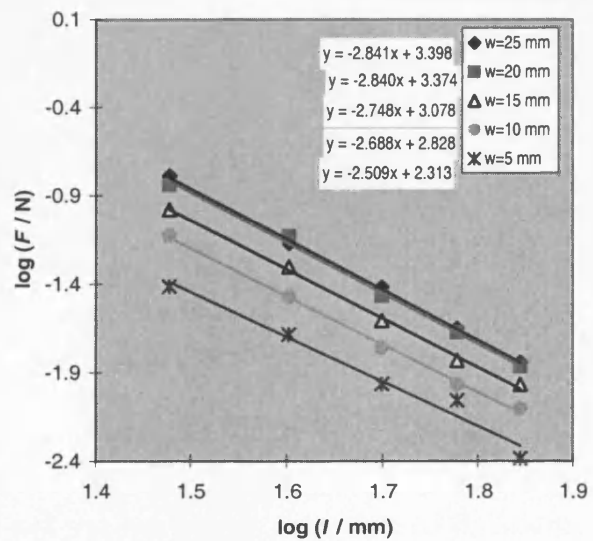
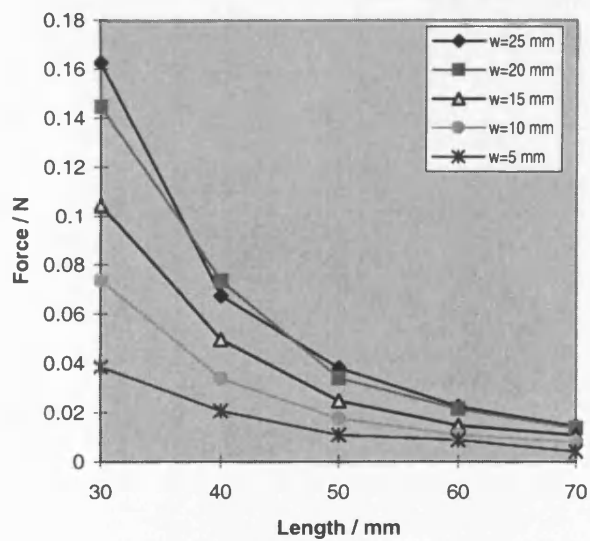
(c) sample AIII



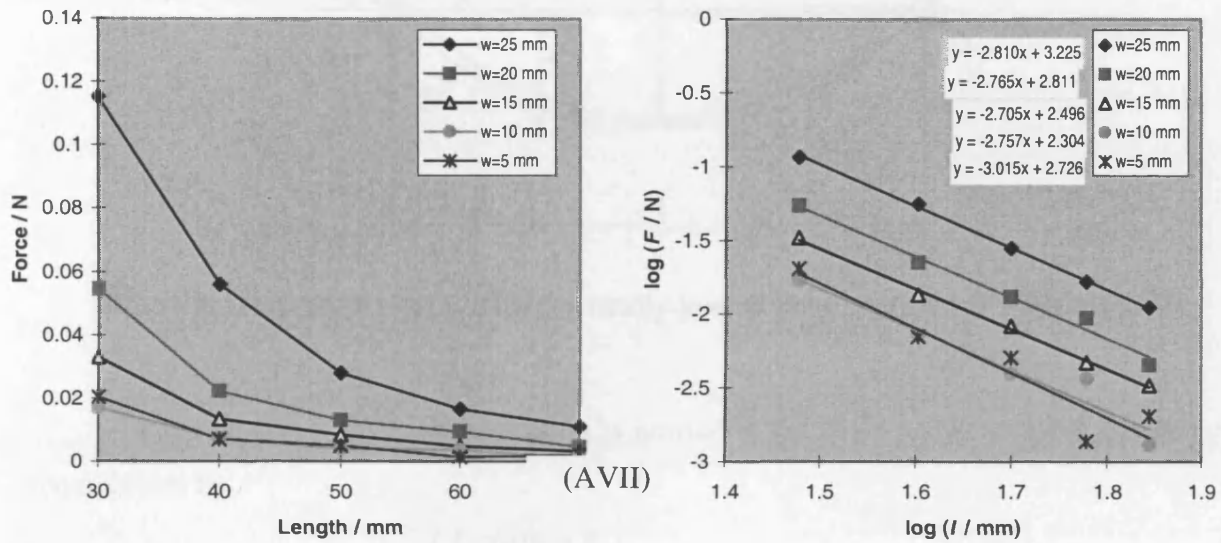
(d) sample AIV



(e) sample AV



(f) sample AVI



(g) sample AVII

Figure 3.21 Bending force F (or $\log F$) at $d = 2.5\text{mm}$ against the sample length l (or $\log l$).

AI: $t = 2.44\text{ mm}$, AII: $t = 2.08\text{ mm}$, AIII: $t = 1.68\text{ mm}$, AIV: $t = 1.55\text{ mm}$, AV: $t = 1.25\text{ mm}$,
 AVI: $t = 1.00\text{ mm}$, AVII: $t = 0.77\text{ mm}$.

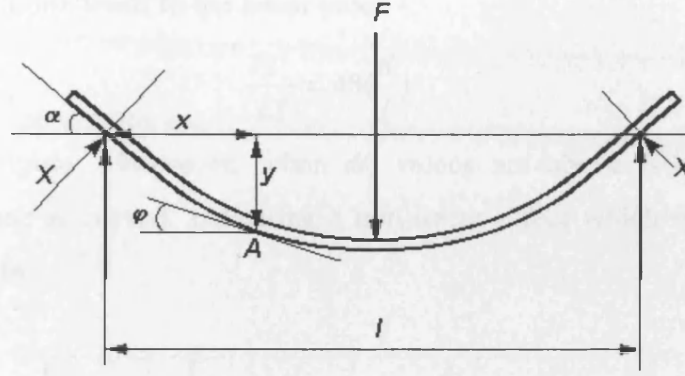


Figure 3.22 A simply supported, centrally loaded beam with large deflections^[76].

The reaction X at the contact point is normal to the beam and is given at mechanical equilibrium by

$$2 X \cos \alpha = F$$

The bending moment at point A is given by

$$M = - (X \cos \alpha \cdot x + X \sin \alpha \cdot y)$$

If conventional bending theory is applicable, we have:

$$M = \frac{EI}{R}$$

Here R is the local radius of curvature given by

$$R = \frac{ds}{d\phi} \quad (3-14)$$

where s is the length of the beam and ϕ is the angle between the tangent line of a certain point of the beam and the x axis. The last form of the equation after taking account of large deflection was given by Williams^[76]:

$$\left. \begin{aligned} \frac{1}{2} \left(\frac{Fl^2}{EI} \frac{1}{\cos \alpha} \right)^{\frac{1}{2}} &= - \int_0^\alpha \cos \phi \sin^{-\frac{1}{2}}(\alpha - \phi) d\phi \\ \text{and} \quad \frac{d}{l} \left(\frac{Fl^2}{EI} \frac{1}{\cos \alpha} \right)^{\frac{1}{2}} &= - \int_0^\alpha \sin \phi \sin^{-\frac{1}{2}}(\alpha - \phi) d\phi \end{aligned} \right\} \quad (3-16)$$

Thus a solution is obtained by choosing any value of α from which a value of Fl^2/EI is formed using the first equation. Substituting this together with α yields d/l from the second equation and hence d/l may be plotted versus Fl^2/EI .

The integrals in equation (3-16) are not soluble analytically but can be solved by numerical methods using a computer. The resulting plot is given in Figure 3.23^[76]. For small

values of d/l the solution tends to the linear case:

i.e.
$$\frac{Fl^2}{EI} = 48\left(\frac{d}{l}\right)$$

as shown in the figure. However, when d/l values are above 0.05, the errors become significant. The line is curved, indicating a non-linear effect which in this case is entirely geometrical in origin.

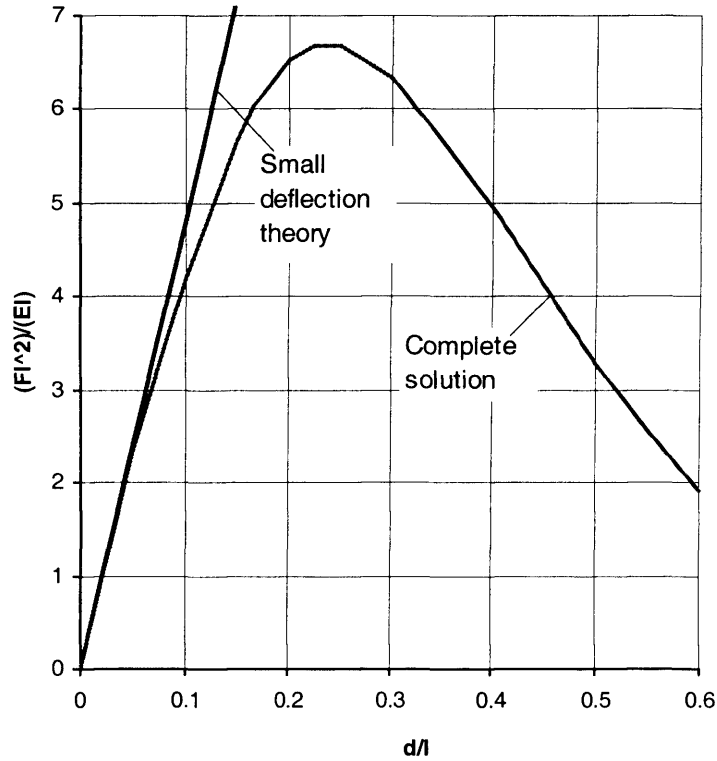


Figure 3.23 Deflection of a simply supported, centrally loaded beam ^[76].

We consider only the segment before the maximum point of the curve, i. e. the range of d/l between 0.06 ~ 0.2. We then apply the power function to the $Fl^2/(EI)$ vs. l/d plot for the purpose of comparison with what was obtained from the experiments with leather, as shown in Figure 3.24,

It is found that the best fit to the curve can be represented approximately by the power function:

$$\frac{Fl^2}{EI} \propto \left(\frac{l}{d}\right)^{-0.7}$$

or in another form:

$$F \propto l^{-2.07} = l^{-2.7}$$

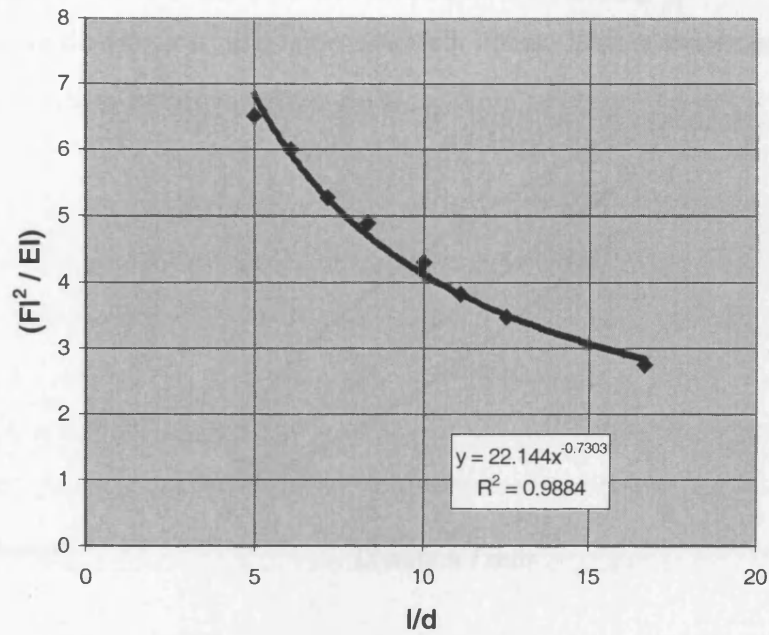


Figure 3.24 In large deflection, influence of l/d on the bending force

which gives an explanation for the observed case of the leather samples for which $F \propto l^{-(2-3)}$ where the ratio of d/l falls into the region of $0.05 \sim 0.13$. It is worth noting that the leathers used possessed relatively low moduli and so in practice, large deflections will occur on handling.

3. 5 An Empirical Equation Describing the Softness of Leather

3. 5. 1 The Experimental Bending Phenomena of Different Leather Materials

From observations and comparisons of all the samples with various processing histories which have been subjected to bending tests, several features are noted. On one hand absolute bending force certainly reflects the flexural rigidity. On the other hand, the shape of the bending curve and how the bending force depends on the length of the sample may also be considered to be of importance for characterising the softness of sample. Some basic characteristics of the bending test behaviour may be stated as follows:

- 1) There are three basic types of bending curve for leather samples with different process histories. These three types can be approximately described by a power function $F \propto d^\alpha$ where the power index α of the depth d in a bending test varies for different leather

samples. In other words, three kinds of shapes of bending curve were noted: concave upwards, concave downwards, and approximately linear. This is shown in *Figure 3.25*.

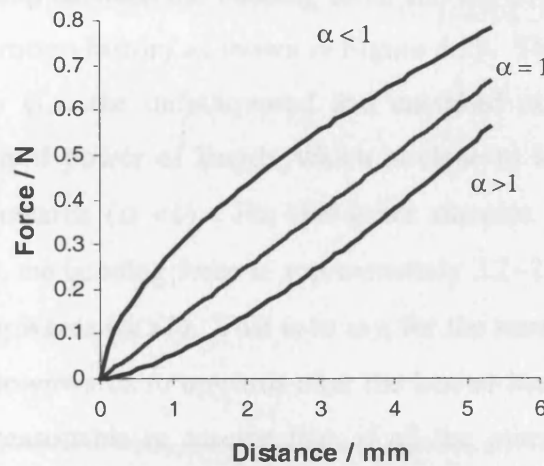


Figure 3.25 Three basic types of bending behaviour.

Figure 3.26 shows the actual bending curves of 2 mirror samples (symmetrical to the backbone of the hide) selected from unfatigued crust leather, one before staking, the other after staking.

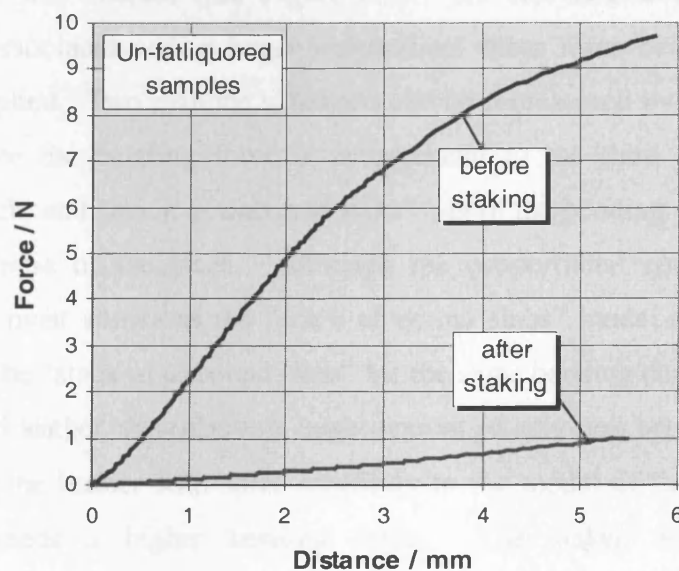


Figure 3.26 Two typical types of actual bending tests.

Figure 3.26 shows that the changes caused by staking action on leather are reflected mainly in two aspects: one is that the bending force needed at a certain bending depth is

dramatically reduced after staking, another is that the shape of the bending curve has changed from an $\alpha < 1$ type to an $\alpha > 1$ type.

2) The relationship between the bending force and the length of the sample appears to vary according to the process history as shown in *Figure 3.27*. The results showed that for the hardest type of leather (i.e. the unfatliquored and unstaked sample) the bending force is approximately 2.9 to third power of length, which is close to standard theory, and its $F \sim d$ curve is concave downwards ($\alpha < 1$). For the softer samples (i.e. those which had been fatliquored and staked), the bending force is approximately 2.2~2.5th power of length, and its $F \sim d$ curve is concave upwards ($\alpha > 1$). That is to say, for the same leather, the curve type will change from concave downwards to upwards after the leather has gone through the softening process. Hence it is reasonable to assume that, if all the other parameters of two leather samples are the same, the softer one is more likely to assume the $\alpha > 1$ type of $F \sim d$ curve.

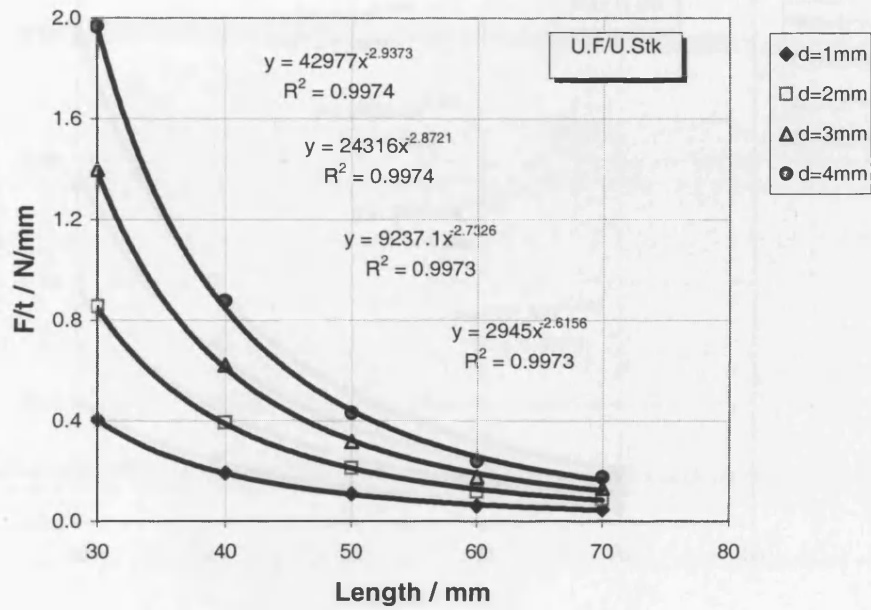
3. 5. 1. 1 Why Differences in Bending Stiffness

It is known that the fibres at different hierarchical levels inside leather adhere to each other and this is especially significant for leather before staking and without fatliquoring^[80]. It is reasonable to relate these adhesions to the bending model of a stack of bound slabs as discussed earlier in this chapter (see *Figure 3.8*). We can assume that strong adhesion between fibres is associated with a larger longitudinal shear force being produced when a bending force is applied. Two extreme situations can be represented by the models “stack of bound slabs”, where the bending force is proportional to the third power of the whole thickness of the stack, and “stack of unbound slabs” where the bending force is in proportion to the whole thickness of the stack. Although the proportional constants in these two situations differ, in most situations the “stack of bound slabs” model requires much higher bending force than the “stack of unbound slabs” for the same bending depth.

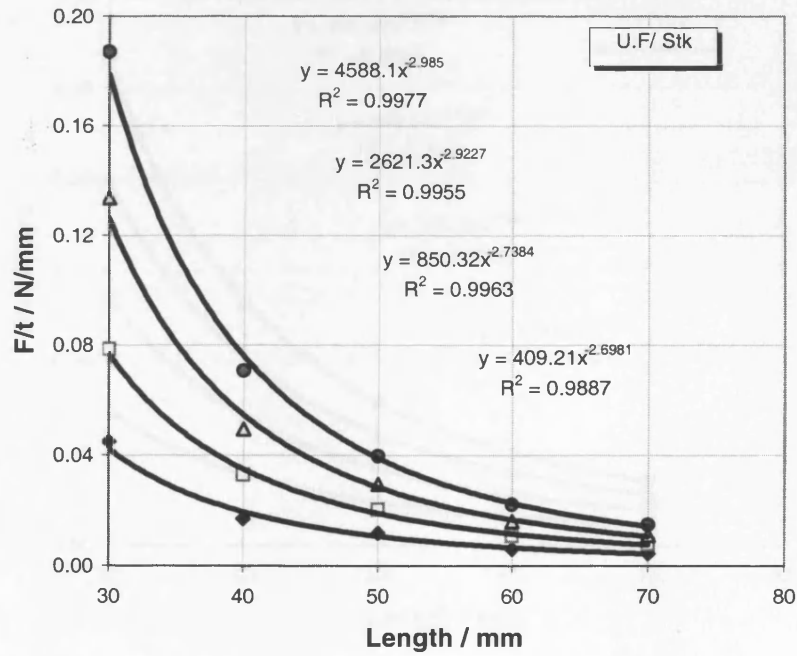
For unstaked leather, the relatively large amount of adhesion between the fibres in all hierarchies endows the leather with some similarity to the model of “stack of bound slabs” which generally needs a higher bending force. The staked leather with reduced interconnection between fibres may be more like the model of “stack of unbound slabs”.

3. 5. 1. 2 Why Differences in $F \sim d$ Curve Shape

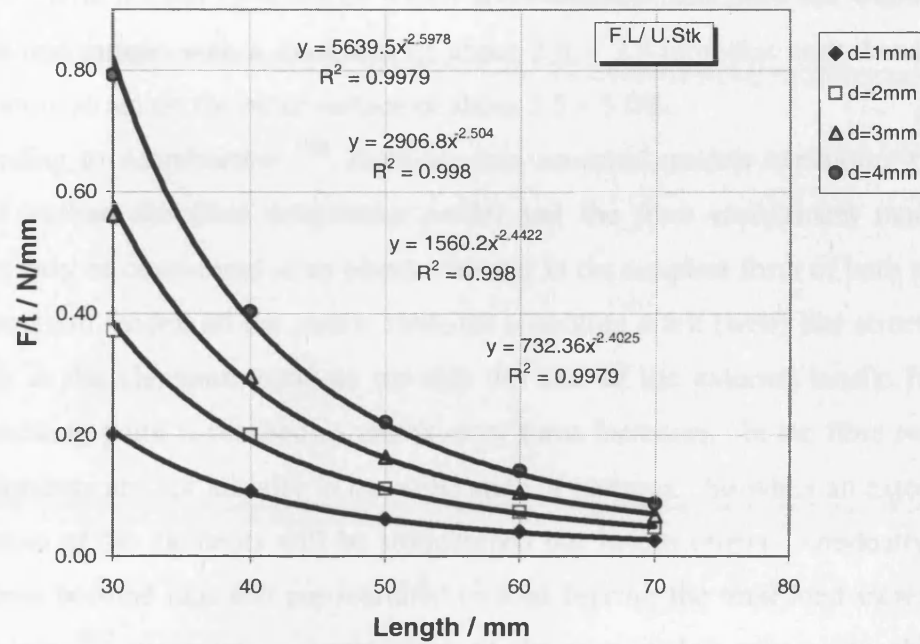
When a bending test was carried out, the part of the sample beneath the neutral axis will be stretched and the part of the sample above the neutral axis will be subject to compression. As



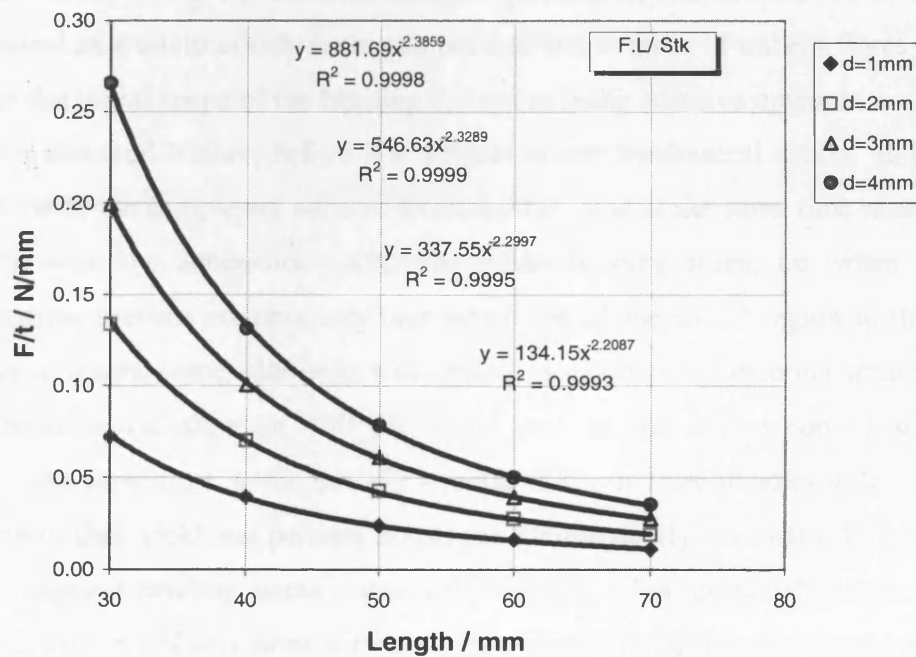
(a)



(b)



(c)



(d)

Figure 3. 27 The relationship between bending resistance F and the length between supporting points l . Where U. stands for Un-, FL. stands for fatliquored, and Stk. stands for staked.

can be seen from *Figure 3.26*, when $d < 2$ mm, the curve for the unstaked sample is actually concave downwards instead of upwards which approximately describes the whole bending curve. For a test sample with a thickness of about 2.0 ~ 2.5 mm, this early bending stage gives a maximum strain on the outer surface of about 2.5 ~ 3.0%.

According to Attenburrow ^[10], there are two accepted models explaining the tensile behaviour of leather: the fibre orientation model and the fibre recruitment model. The collagen fibre may be considered as an elastic element in the simplest form of both models. In the fibre orientation model, all the elastic elements constitute a felt (web) like structure. The web reshapes as the elements orientate towards the axis of the external tensile force until finally the breaking point is reached as the external force increases. In the fibre recruitment model, the elements are not initially in the same state of tautness. So when an external force is applied, some of the elements will be straightened out before others. Gradually as more and more fibres become taut and are recruited to load bearing the total load increases non-linearly. Wright ^[81] suggested a combination of the two models where the elements in different degrees of waviness comprise the felt like web in its initial state. However when the sample is stretched, fibres between hinge points unbend then reorientate into the strain axis. It is reasonable to say that as the initial bending progresses, the tensile modulus of the portion below the neutral axis continuously increases because the number of unbent fibres increases. This results in the initial shape of the bending $F-d$ curve being concave upwards.

For the unstaked leather, before it is subject to any mechanical action, all fibres and fibre bundles inside the sample are adhered to each other. And at the same time many are, in a wavy state between the adhesions. After the initial bending stage, i.e. when the fibres between adhesions become continuously taut which makes the initial region in the bending curve concave upwards, some adhesions will undergo tension as the external stretching force increases. Breakage and slippage will occur and lead to the destruction of some weak adhesions. At the same time, some initially straight fibres or fibre bundles will be stretched further leading to their yield and perhaps breakage. Consequently, the first differential of the bending force against bending depth curve will decrease. For unstaked leather, there are relatively large amounts of adhesions between either fibres or fibre bundles inside the sample. These adhesions may be regarded as linkages at different structural levels and as either weak or strong. It is reasonable to assume that in the unstaked leather, there are relatively more weak linkages than that in a staked leather (because in this case they have been broken), which may break at an early stage of tension within the fibre net structure. Kronick *et al* ^[82] studied the softening effect of repeated stretches on leather using the acoustic emission

method and showed that the first stretch was accompanied by the largest number of acoustic pulses, which indicates internal ruptures producing fine cracks (crazes) inside the leather. Such cracks were regarded as within the thick fibre bundles. This cracking corresponds to the slippage/breakage of the adhesion linkages in the proposed model. The amount of acoustic emission accompanying a subsequent stretch is reduced by 90%, and the leather was less stiff after the first extension.

3. 5. 2 An Empirical Equation Describing the Softness of Leather

Based upon the observations of leather behaviour discussed above, an empirical equation which can be used to comprehensively describe the bending behaviour of leather is put forward. Suppose that the three types of bending F - d behaviour can be described by an equation in the form of

$$F = S_e d^\alpha \psi(l, \alpha)$$

where S_e is a constant for a given bending curve and is equivalent to the meaning of the bending stiffness S , and the $\psi(l, \alpha)$ function should approximately make the following statement true, i.e.:

$$F \propto l^x \quad \text{where} \quad x \approx \begin{cases} 3 & (\text{when } \alpha > 1) \\ 2.8 \sim 2.9 & (\text{when } \alpha = 1) \\ 2.2 \sim 2.5 & (\text{when } \alpha < 1) \end{cases}$$

Here the values x (3, 2.8~2.9, 2.2~2.5) were those obtained from the experimental determination of the dependence of F on l (Figure 3.27).

The following expression satisfies the above requirement for the function $\psi(l, \alpha)$:

$$\psi(l, \alpha) = \frac{\alpha}{l^{2\left(1 + \frac{\alpha^3}{1+2\alpha^3}\right)}}$$

Thus, an empirical equation is obtained as follows:

$$F = S_e \cdot \frac{\alpha \cdot d^\alpha}{l^{2\left[1 + \frac{\alpha^3}{1+2\alpha^3}\right]}} \quad (3-31)$$

When an experimental bending curve is given, equation 3-31 can be made to give a best fit by adjusting the two parameters α and S_e . In the basic bending theory (see equation (14) in Appendix III)

$$F = 48S \frac{d}{l^3}$$

where bending stiffness $S = EI$ is a function of the width and thickness of the testing sample

and an intrinsic constant of the testing material, while the remaining part may be regarded as a function of bending depth and the length of the sample. In comparison the S_e value obtained at the best fit of equation (3-31) to a real bending curve may be considered to be equivalent to the bending stiffness of the sample. Unlike S which is a definite function of t , S_e is influenced by the thickness t in a variable way related to the process history of the material and the ratio of the thickness of grain and corium layers as discussed before.

3. 5. 3 Discussion of the Empirical Equation

For any given experimental $F \sim d$ curve, equation (3-31) satisfactorily simulates this curve by the adjustment of the two parameters α and S_e . The experimental bending curve and the calculated curve that gives the best fit to it is illustrated in *Figure 3.28* for series *AI*.

Equation 3-31 was applied to samples in the series of *AI* to *AVII* which were cut from one same side of leather being in the vicinity of each other, and split into different thicknesses. The results are listed in table 3.4.

Sizes of each sample:

width (mm)	length (mm)				
	30	40	50	60	70
25	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}

The result shows that for the same sample with different lengths, the S_e value remains effectively constant, i.e. S_e can be taken as a flexural rigidity of leather material which will not be influenced by sample width or length. For samples with the same process history, the influence of the sample's whole thickness can be eliminated by using the function S_e / t^n where n is the approximate index in the power function describing the relationship of bending force F and the sample thickness t , if the power function is known, and t is the total thickness which includes both grain and corium layer. For the sample discussed above, the value of n is 1 (see section 3.4.2.2)

Figures from table 3.5 indicate that if we consider the values of S_e for samples with different thicknesses, then thick materials have a larger flexural rigidity indicating a less soft material. However, after dividing S_e by t^n (n is 1 in this example), an intrinsic flexural rigidity is obtained, which can be taken as a parameter describing the softness of the leather without the influence of thickness t .

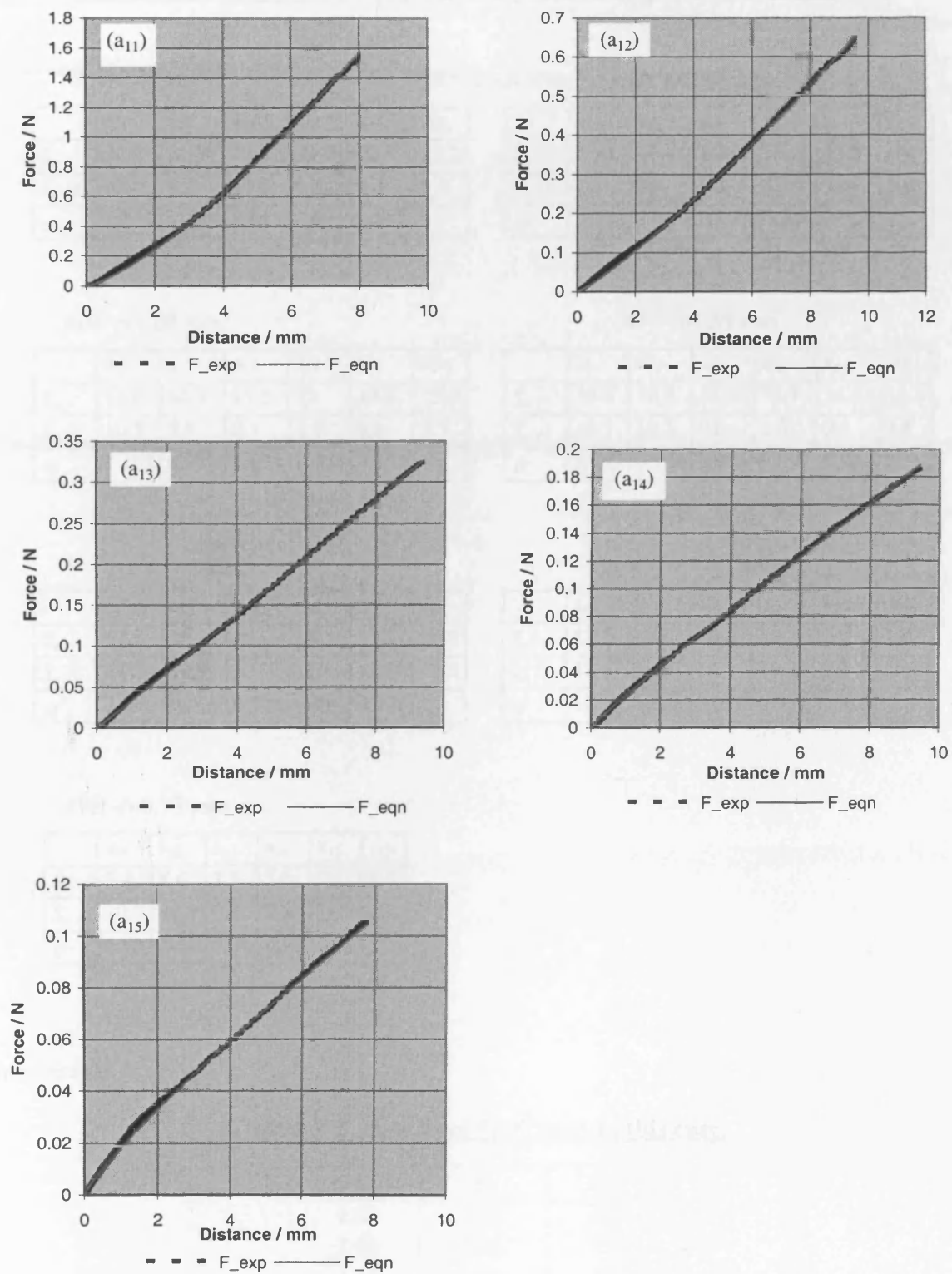


Figure 3. 28 The best fit of the calculated bending curve to the experimental curve.
(Samples are from *AI*)

Table 3. 4 The results for S_e and S_e/t obtained for the samples AI ~ AVII

<i>AI</i> $t=2.44$ mm							<i>AI</i> $t=2.08$ mm						
	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	Av.		a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	Av.
S_e	22.8	21.7	24.4	23.5	22.8	23.2	S_e	16.0	17.4	16.8	16.2	15.8	16.5
S_e/t	9.3	8.9	10.0	9.6	9.3	9.5	S_e/t	7.7	8.4	8.1	7.8	7.6	7.9
α	1.336	1.18	1.015	0.94	0.951		α	1.328	1.05	0.993	0.901	0.904	

<i>AI</i> $t=1.68$ mm							<i>AI</i> $t=1.55$ mm						
	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	Av.		a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	Av.
S_e	17.6	16.7	15.2	15	14.8	15.9	S_e	16.2	16.0	14.9	14.7	14.6	15.2
S_e/t	10.5	9.9	9.1	8.9	8.8	9.5	S_e/t	10.5	10.3	9.6	9.5	9.4	9.8
α	1.102	0.974	0.874	0.852	0.875		α	1.147	0.974	0.925	0.897	0.94	

<i>AV</i> $t=1.25$ mm							<i>AV</i> $t=1.00$ mm						
	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	Av.		a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	Av.
S_e	17.7	16.2	15.9	14.7	15.3	16.9	S_e	12.4	10.6	10.4	10.2	9.9	10.7
S_e/t	14.2	12.9	12.7	11.8	12.2	13.5	S_e/t	12.4	10.6	10.4	10.2	9.9	10.7
α	1.08	0.911	0.868	0.918	0.908		α	1.152	1.008	0.976	0.936	0.918	

<i>AVII</i> $t=0.77$ mm						
	a_{11}	a_{12}	a_{13}	a_{14}	a_{15}	Av.
S_e	8.4	8.6	7.5	7.6	7.7	8.0
S_e/t	10.9	11.2	9.7	9.9	10	10.
α	1.21	1.02	1.04	0.98	0.98	

On average:

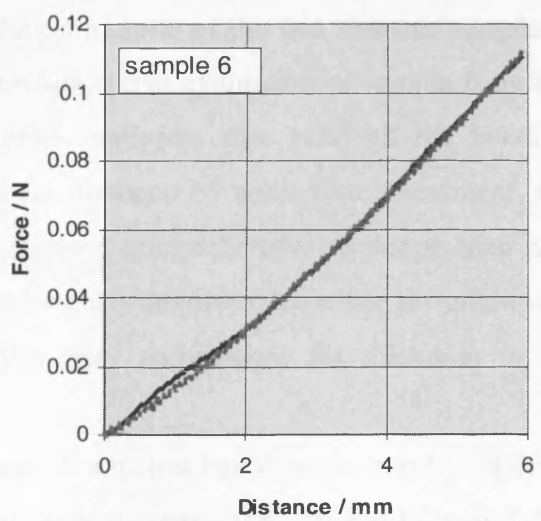
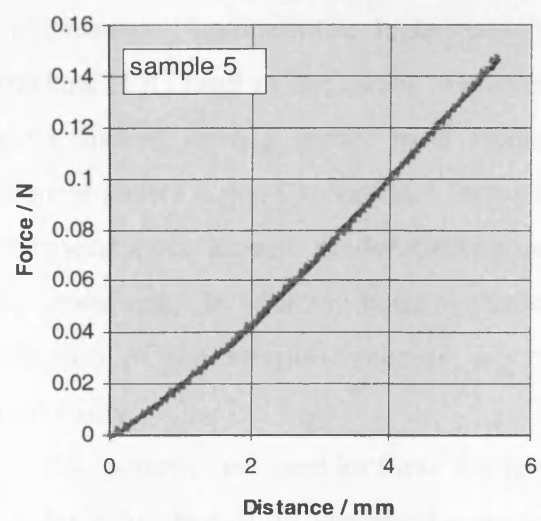
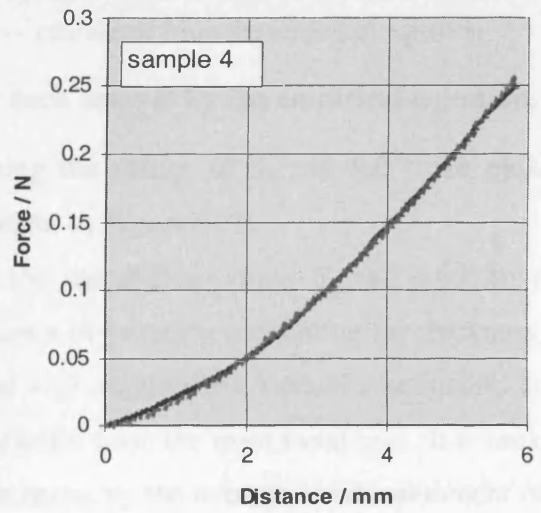
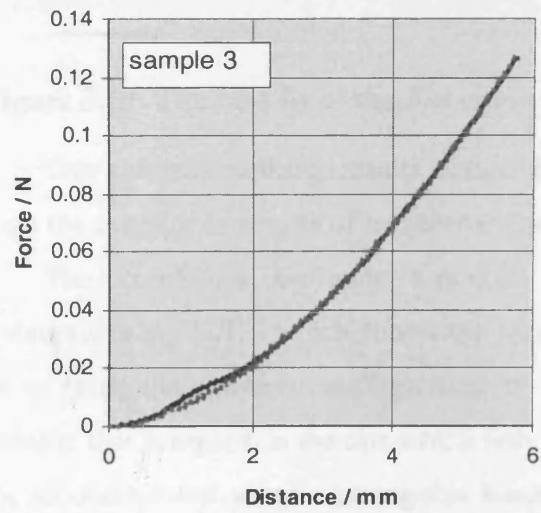
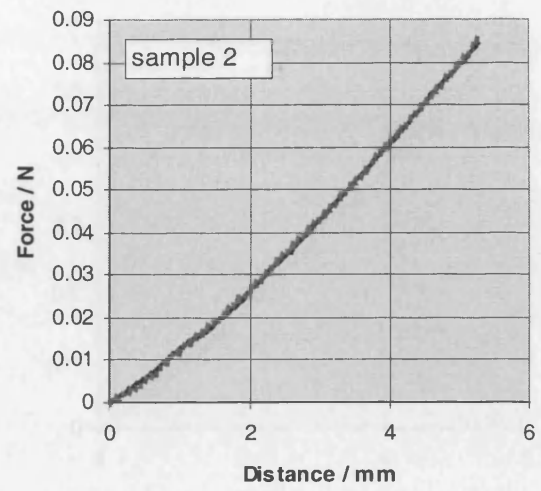
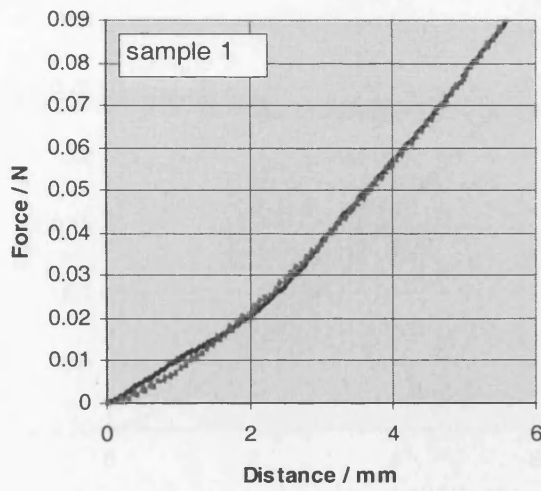
Table 3. 5 Results of S_e/t^n ($n=1$ in this case)

t	S_e	S_e/t
2.44	23.2	9.5
2.08	16.5	7.9
1.68	15.9	9.5
1.55	15.2	9.7
1.25	16.9	13.5
1.00	10.7	10.7
0.77	8.0	10.4

S_e was also calculated for the BLC samples, the softness of which had been evaluated and ranked by a number of experienced tanners^[83]. The best fit between the experimental F - d curve and the empirical equation is shown in *Figure 3.29*. Table 3.6 lists the results and the correlation coefficient value r for these results from the two methods of evaluation.

Table 3.6 The softness order (1~8, 1 is the softest) of BLC samples

	Sample No	S_e	thickness mm	order of softness (before division by $t^{1.5}$)	$S_e/t^{1.5}$	order of softness (after division by $t^{1.5}$)	order of softness (hand)
	1	1.94	1.10	2	1.67	2	2
	2	2.53	0.98	3	2.61	4	5
	3	1.55	1.04	1	1.46	1	1
	4	4.13	1.13	6	3.44	5	3
	5	4.07	1.07	5	3.69	7	6
	6	2.85	1.42	4	1.68	3	7
	7	5.37	1.33	7	3.50	6	4
	8	16.08	1.08	8	14.37	8	8
r				0.62		0.69 0.90 (without sample 6)	



— experimental calculated from the empirical equation

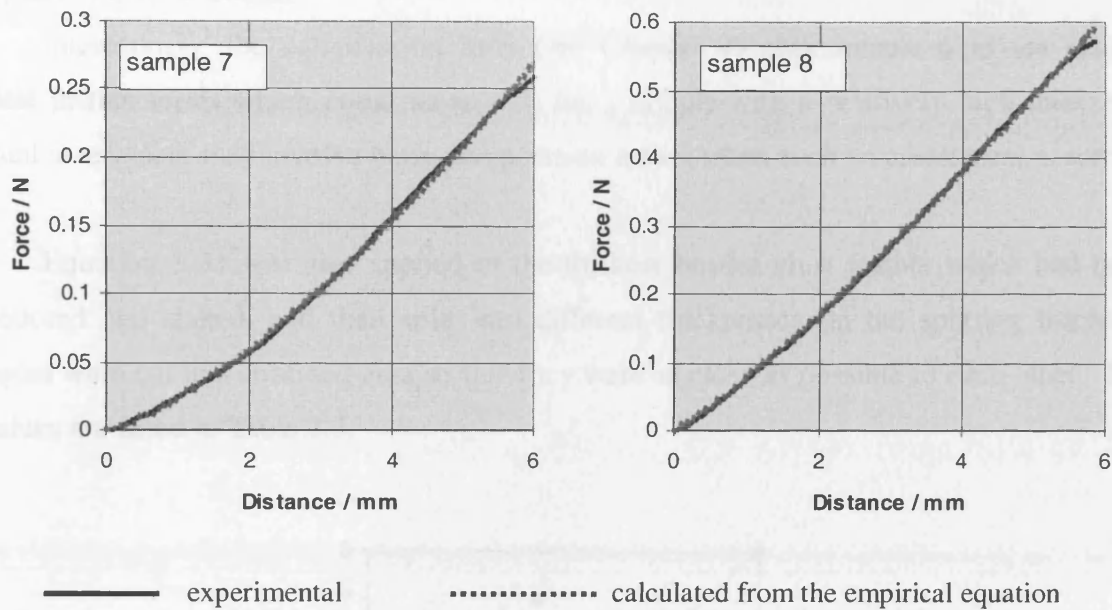


Figure 3.29 The best fit of the F - d curve for each sample by the empirical equation.

The softness ranking results obtained using the values of S_e and $S_e/t^{1.5}$ are plotted against the average of results of subjective assessment in *Figure 3.30*.

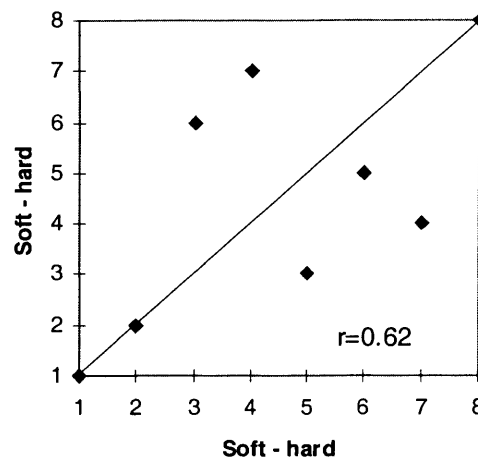
The correlation coefficient r is 0.62 for the calculations using S_e and 0.69 for the calculations using $S_e/t^{1.5}$ which shows the importance of properly accounting for thickness in order to bring the softness ranking closer to what was obtained by manual assessment. It is noticeable that sample 6 is the one which falls markedly from the main trend line. It is ranked as the second hardest sample among this 8-sample series by the average hand assessment of 9 experienced tanners, but the bending curve of this sample (see *Figure 3.31*) shows no clear sign of prominent hardness (i.e. higher bending force) in spite of the fact that this sample is the thickest (1.42 mm) of the series. However, on subjective evaluation of sample 6 by the author it indeed gave a harder hand feeling which indicates that although the bending experiment shows a good accordance with what was obtained by subjective assessment, the latter covers more aspects of deformation and is more comprehensive in scope than any single-aspect test. In addition, hand assessment obviously involves some (as yet unknown) contribution of the sample thickness; i.e. tanners may compensate for thickness in an unknown way.

The power index used for these leathers was 1.5 which is based on the results obtained before for a finished, fully processed commercial leather sample (see sample 6(2) in Table 3.2). This index may not necessarily be exactly the same as that of the BLC leathers, but according to what was found in the bending experiments, this is in general approximately

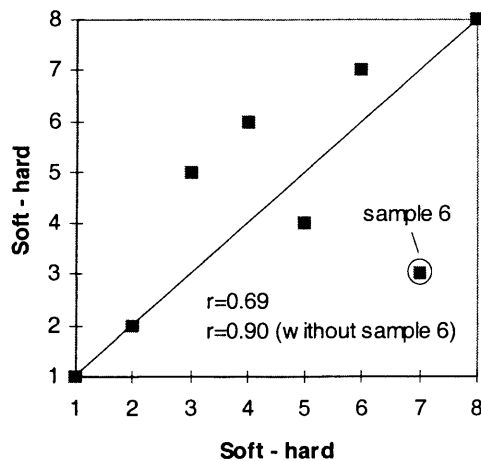
acceptable for such leather.

Interestingly, the compression tests (see *Chapter 4*) rank sample 6 as the second hardest in this series which could mean that for a sample with a relatively high thickness, manual assessment may involve more compression action when such an assessment is carried out.

Equation 3-31 was also applied to the thickest bovine crust leather which had been fatliquored and staked, and then split into different thicknesses on the splitting machine. Samples were cut in a confined area so that they were as close as possible to each other. The S_e values are listed in Table 3.7.



(a)



(b)

Average of hand feeling rankings

Figure 3. 30 The correlation of softness grading between bending results and average manual assessment. (a) S_e results ~ manual. (b) $S_e/t^{1.5}$ results ~ manual.

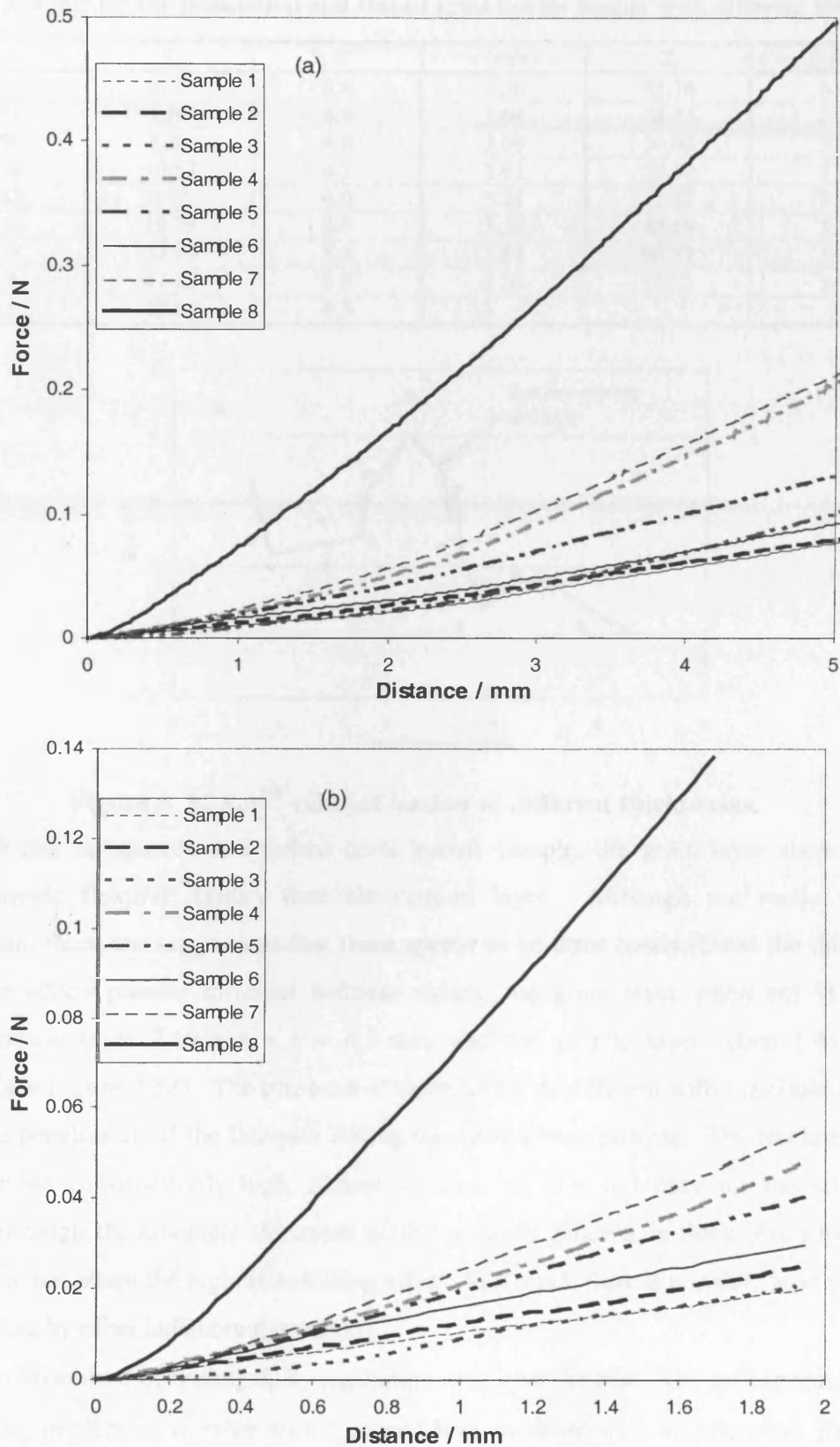
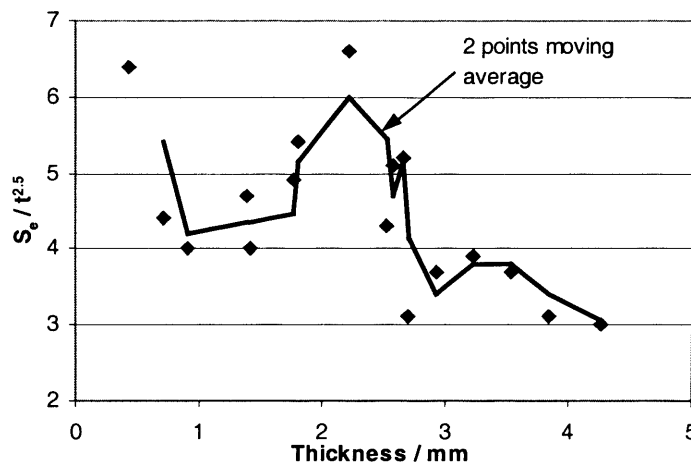


Figure 3.31 Bending behaviour of BLC samples. (a) Whole plot. (b) Initial region.

Table 3.7 S_e value for the fatliquored and staked crust bovine leather with different thicknesses

t (mm)	S_e	$S_e/t^{2.5}$	t (mm)	S_e	$S_e/t^{2.5}$
0.43	0.78	6.4	2.56	53.76	5.1
0.71	1.87	4.4	2.64	58.34	5.2
0.90	3.04	4.0	2.69	36.98	3.1
1.38	10.57	4.7	2.91	53.59	3.7
1.41	9.35	4.0	3.21	71.17	3.9
1.75	19.79	4.9	3.53	85.59	3.7
1.78	22.97	5.4	3.84	90.52	3.1
2.2	47.15	6.6	4.26	111.5	3.0
2.5	42.84	4.3			

**Figure 3.32 $S_e/t^{2.5}$ value of leather at different thicknesses.**

For this fatliquored and staked crust leather sample, the grain layer shows slightly higher intrinsic flexural rigidity than the corium layer. Although not really remarked phenomenon, there are suggestions that there appear to be three bands across the thickness of the sample which possess different softness values: the grain layer when $t < 1.41$ mm, the exterior corium layer $2.69 \text{ mm} < t < 4.3 \text{ mm}$, and the middle layer when $1.41 \text{ mm} < t < 2.6 \text{ mm}$ (see Figure 3.32). The presence of three layers of different softness could be due to incomplete penetration of the fatliquor during the fatliquoring process. The thickness of this leather sample is particularly high, almost 4.5 mm, so it is not easy for the fatliquor to penetrate through the complete thickness of the leather. Since it is thick, even the staking process may not attain the highest softening effect. As a result, there is a middle layer which was not so affected by either fatliquoring or staking.

The procedure of finding S_e by regulating α to give the best fit to an experimental $F-d$ curve can be implemented either with a spreadsheet software such as Microsoft Excel®, or through a tailor-made computer programme. The Newton approaching method was applied during this calculation. The method of Newton approaching and the logic flow of the implementation are shown in Appendix IV.

CHAPTER 4

DEFORMATION IN COMPRESSION

4. 1 Introduction

Among the various kinds of mechanical behaviour, response to compression plays an important role in contributing to the overall characterisation of the deformation of a material. When subjectively judging the softness of leather, compression is also involved in addition to bending and tensile deformation. In some leather testing methods, compressive deformation either contributes significantly to the result, or is indeed the main mode of deformation for characterising the softness.^[84, 85]

For a homogeneous and isotropic material, the compression behaviour (up to a certain strain) is very similar to that obtained from a tensile test, except that there may be different moduli for these two different kinds of deformation. As is well known leather is far from isotropic, and from a microscopic point of view, is composed of overlapping fibres with voids between them. When in compression, the deformation represents the effect on the whole structure or construction which contains both fibres and voids. In other words, compression represents deformation of a heterogeneous structure.

It has been reported^[84] that, in order to describe the softness of light leathers an analysis leading to a parameter called compression index (*CI*) is applicable. Furthermore it has also been reported that the compression behaviour of fabrics is useful for predicting their handle^[86 - 88]. In the case of fabrics an approach involving energy absorption in a compression cycle has been applied. Both of the above approaches (compression index and energy balance) have been used in this study in order to assess which gives the best correlation with the subjective assessment of softness and also to examine the effects of staking. In addition the form of the compressive stress-strain curve of leather is also analysed and discussed with reference to the behaviour of other porous compressible materials.

4. 2 Experimental

4. 2. 1 Instrumentation and materials

Compression testing was carried out using an Instron 1122 universal testing instrument. An initial set force of 0.4 N was applied to the leather sample in the form of a disc with diameter

of 14 mm. The contact area between the cylindrical probe with a diameter of 10.92 mm and the surface of the sample was 93.69 mm^2 . Therefore the initial pressure on the sample is 4.27 KPa. The thickness measured under this pressure was taken as the initial thickness t_0 , which was determined using a micrometer dial gauge to a precision of 0.01 mm. The gauge was installed under the cross head of the Instron machine to accurately measure the displacement of the cylindrical probe relative to the compression table, as shown in *Figure 4.1*.

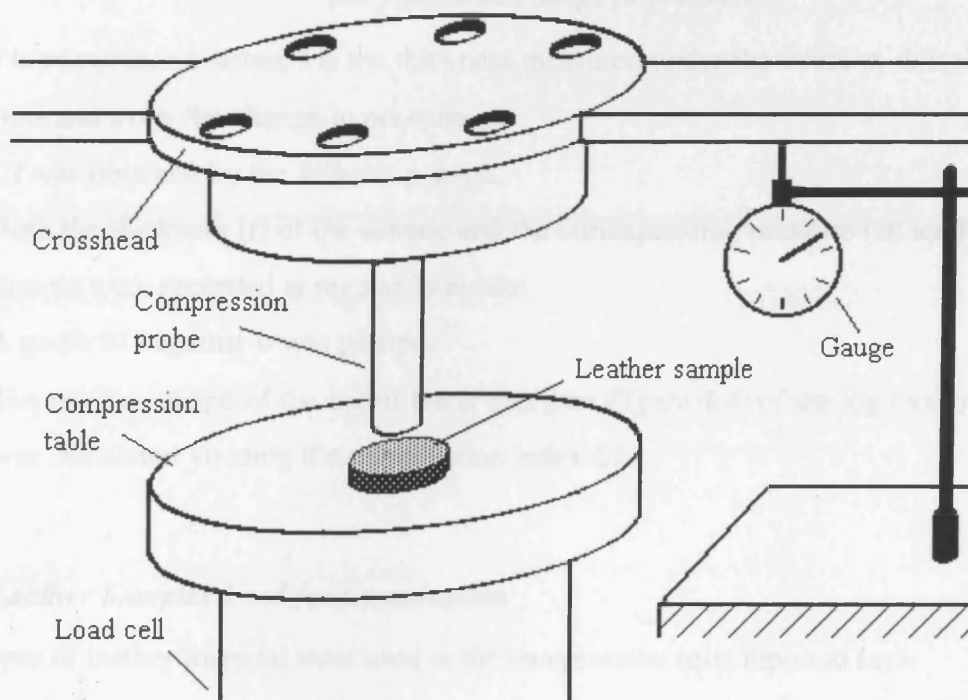


Figure 4.1 The set-up for the compression experiment.

After the initial thickness of the leather sample was determined, the cross head carrying the compression probe was continuously lowered to exert the compression force, while the distance, which was used later to calculate the thickness at any moment, was recorded at regular intervals. The speed of the probe was set as slow as possible, in order to accurately measure the thickness of the sample at a given pressure. The speed chosen was 0.05 mm min^{-1} . The force and the distance the probe had moved were simultaneously recorded automatically by a computer connected to the Instron machine.

Leather samples were conditioned in an atmosphere maintained at $20 \pm 2^\circ\text{C}$ and 65% relative humidity for a period of time greater than one week which was long enough for the samples to reach equilibrium.

4. 2. 2 Calculation of Compression Index

A compression index CI may be defined as^[87]:

$$\begin{aligned}
 CI &= -\frac{dt/t}{d\sigma/\sigma} \\
 &= -\frac{d \ln t}{d \ln \sigma} \\
 &= -\frac{\text{the fractional change in thickness}}{\text{the fractional change in pressure}}
 \end{aligned}$$

where σ is compressive stress, t is the thickness measured under the stress σ , dt is the change in thickness and $d\sigma$ is the change in pressure.

CI was obtained by the following steps:

- i) Both the thickness (t) of the sample and the corresponding pressure (σ) applied on the sample were recorded at regular intervals;
- ii) A graph of t against σ was plotted;
- iii) The negative slope of the initial linear part (see *Figure 4.4*) of the $\log t$ vs $\log \sigma$ curve was calculated yielding the compression index CI .

4. 2. 3 Leather Samples Used for Compression

Three types of leather material were used in the compression tests reported here:

1. Non-fatliquored crust leather comprising two batches of samples. Each batch contained two whole bovine crust wet blue leather hides which were used for non-fatliquored and fatliquored leather samples respectively (see *Chapter 2, 2.1.1*). Each hide in the two batches was divided into two series of samples, with the first series of samples acting as control samples and the second series of samples forming the experimental samples. Both sample series were from the same whole hide but were from the opposite location on each side (i.e. a mirror image across the backbone). Control samples were equilibrated in the conditioning room (see *Chapter 2, section 2.2.1.1*), but had not gone through the staking machine. Experimental samples were conditioned to obtain different moisture contents prior to staking. The first batch covered moisture contents of up to 55% on a dry basis and the second batch covered moisture contents greater than 55%. Experimental samples were kept in the conditioning room for at least a week after they were staked. Sampling locations around the whole hide are shown in *Figure 4.2*.

2. Fatliquored crust leather with the same sample arrangement as described in 1.

3. BLC samples as described in *Chapter 2, 2. 1. 3*. Sampling locations were the same as shown in *Figure 4.2 (b)*.

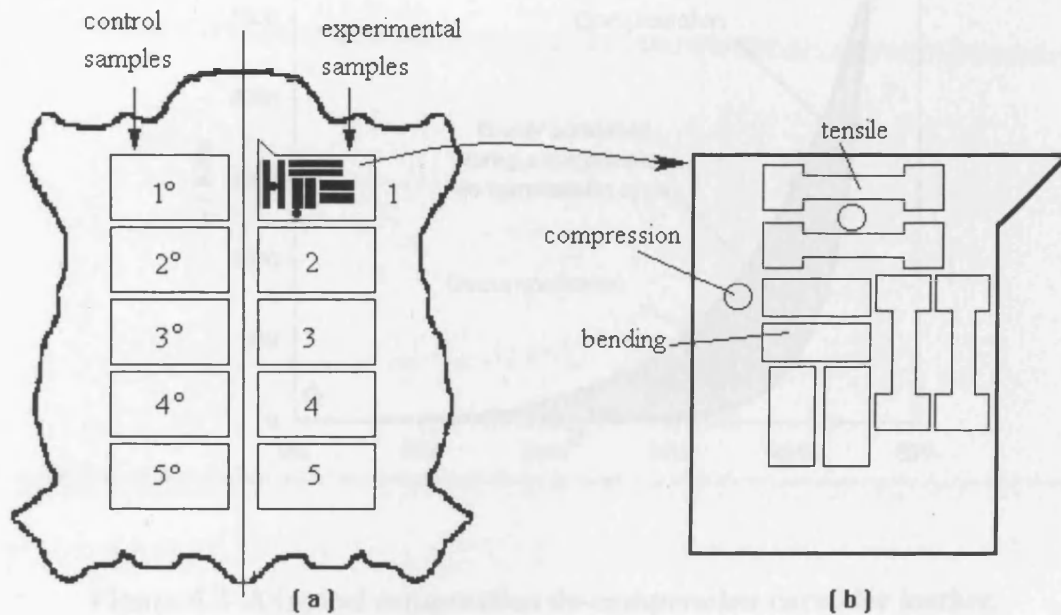


Figure 4. 2 Sampling locations around the whole hide for various tests. (The first batch of fatliquored hide was divided into 5 sampling locations as shown above. All the other batches were divided into 6 sampling locations.)

4. 3 Results of Compression Testing

4. 3. 1 General Characterisation

A typical compression de-compression plot is shown in *Figure 4.3*

where $\varepsilon = (t_0 - t) / t_0$

t_0 — the initial thickness of the sample,

t — thickness of the sample at stress σ .

The energy needed for such a compressive procedure and the energy released during de-compression is obtained from the areas under curve *OA* and curve *AB* respectively. The energy consumed in a whole compression and de-compression cycle is the difference of these two areas, i.e. area *OABO*.

A typical graph of log thickness against log compressive stress is shown in *Figure 4.4*, which gives over the low stress region *AB* a nearly linear relationship. The slope of this linear segment was calculated and taken as the compression index *CI* (see 4.2.2). It should be mentioned that in most cases, the first linear segment is not a strict straight line but a line tending to curve down. So an approximate slope of this segment is taken as the compression index (*CI*) in these cases.

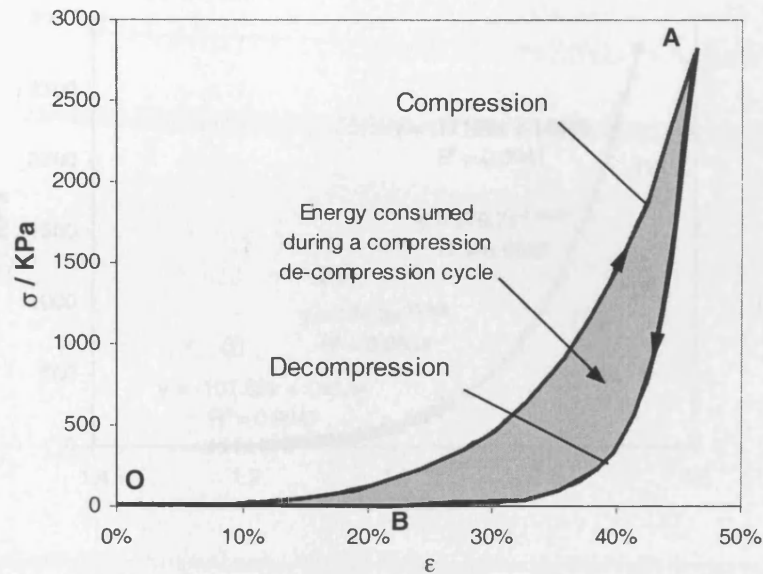


Figure 4.3 A typical compression de-compression curve for leather.

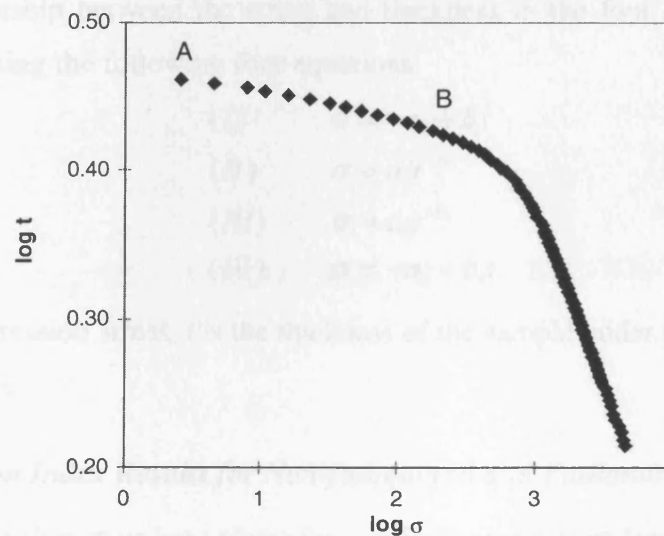


Figure 4.4 The $\log t$ vs $\log \sigma$ plot.

Based on the experimental results of this study, it was found that the compressive behaviour of the fully processed leathers (i.e. BLC samples) could be divided into four regions within the stress — thickness ($\sigma - t$) curve, with linear relationship in the first (I) and last regions (IV), and power relationships in the second (II) and third (III) regions (Figure 4.5). The equations listed in Figure 4.5 describe satisfactorily the curve in each region.

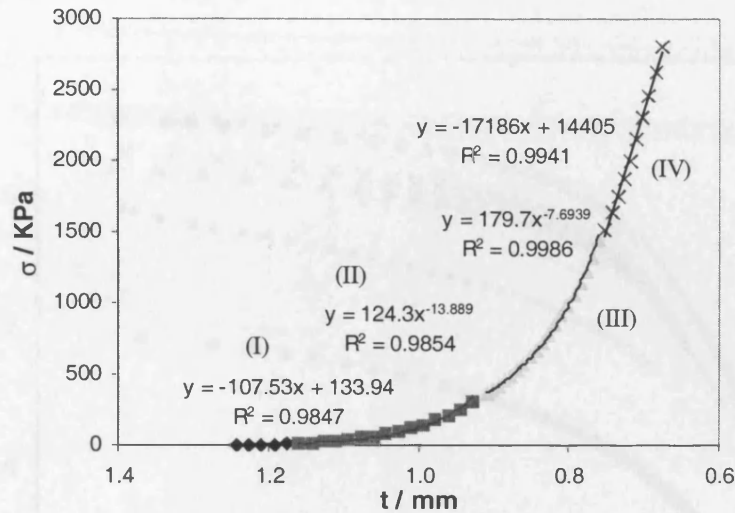


Figure 4.5 A typical compressive stress vs thickness (σ vs t) plot of a fully processed leather (BLC sample No. 1)

The relationship between the stress and thickness in the four regions in this model, can be described using the following four equations:

$$(I) \quad \sigma = -a_1 + b_1 t$$

$$(II) \quad \sigma = a_2 t^{-b_2}$$

$$(III) \quad \sigma = a_3 t^{-b_3}$$

$$(IV) \quad \sigma = -a_4 + b_4 t$$

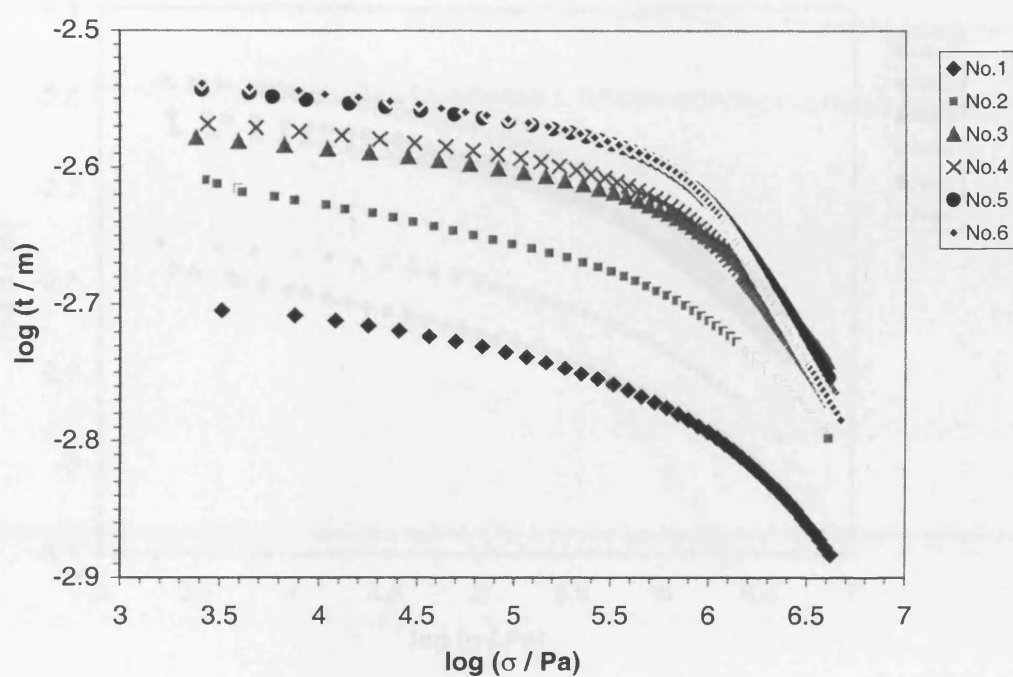
Here σ is the compression stress, t is the thickness of the sample under the stress and a_i , b_i are regression constants.

4.3.2 Compression Index Results for Non-fatliquored and Fatliquored Crust Leather

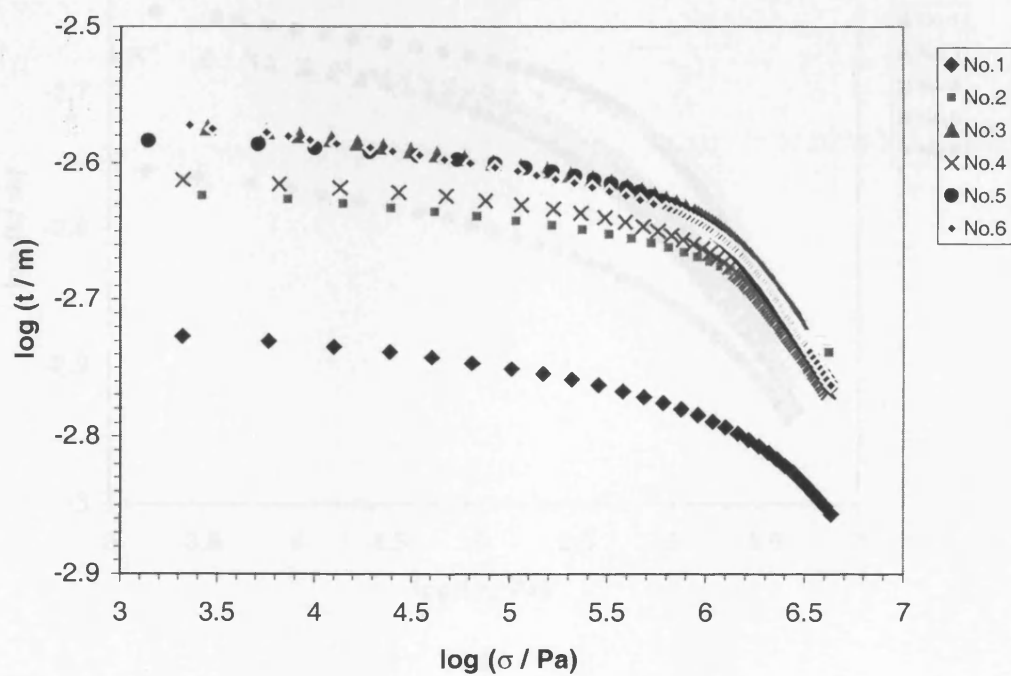
Compression results ($\log \sigma$ vs $\log t$ plots) for non-fatliquored crust leather are summarised in Figures 4.6 (a) to (d). Figures (a) and (b) refer to control samples; Figures (c) and (d) refer to experimental samples.

Compression results ($\log \sigma$ — $\log t$ plots) for fatliquored crust leather are summarised in Figure 4.7 (a) to (d), where (a) and (b) are for control samples and (c) and (d) are for experimental samples.

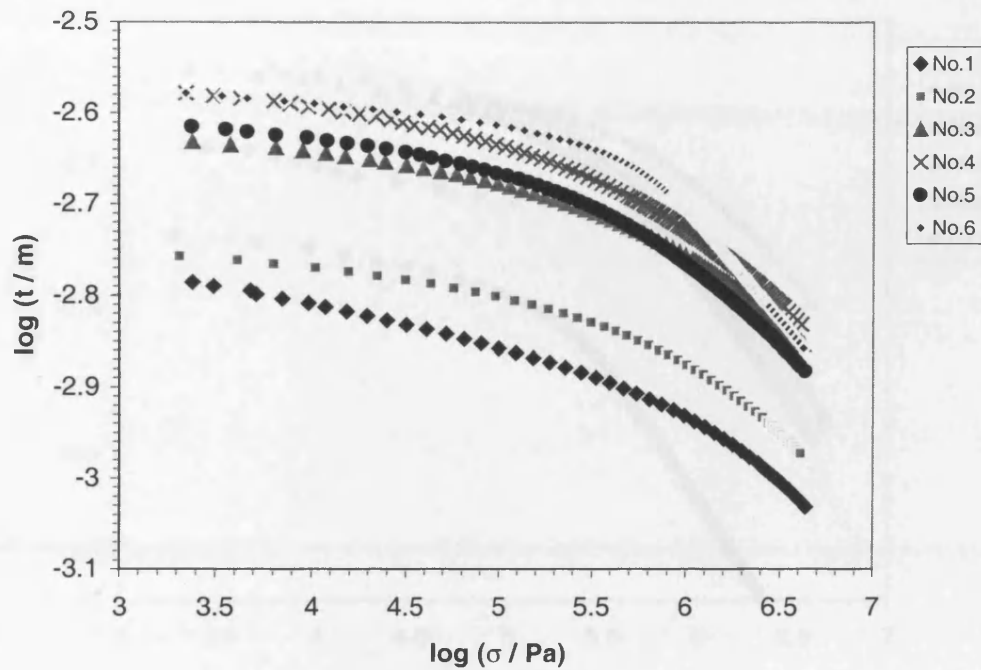
All the parameters relating to the samples and the compression indices calculated from the first linear segment (AB as shown in Figure 4.4) on the logarithm curve are listed in table 4.1



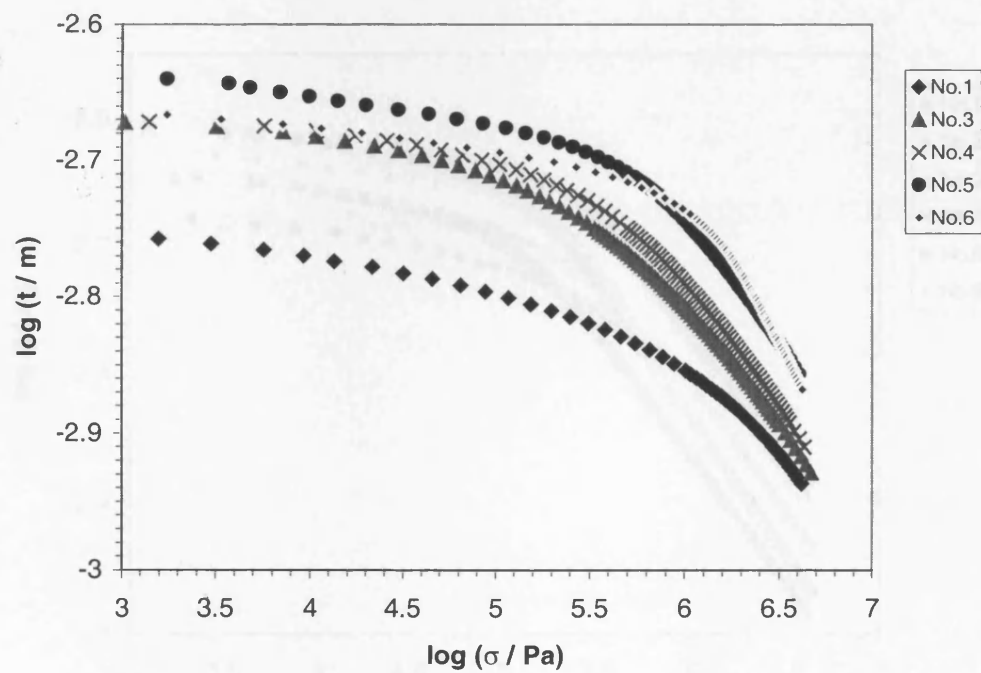
(a)



(b)

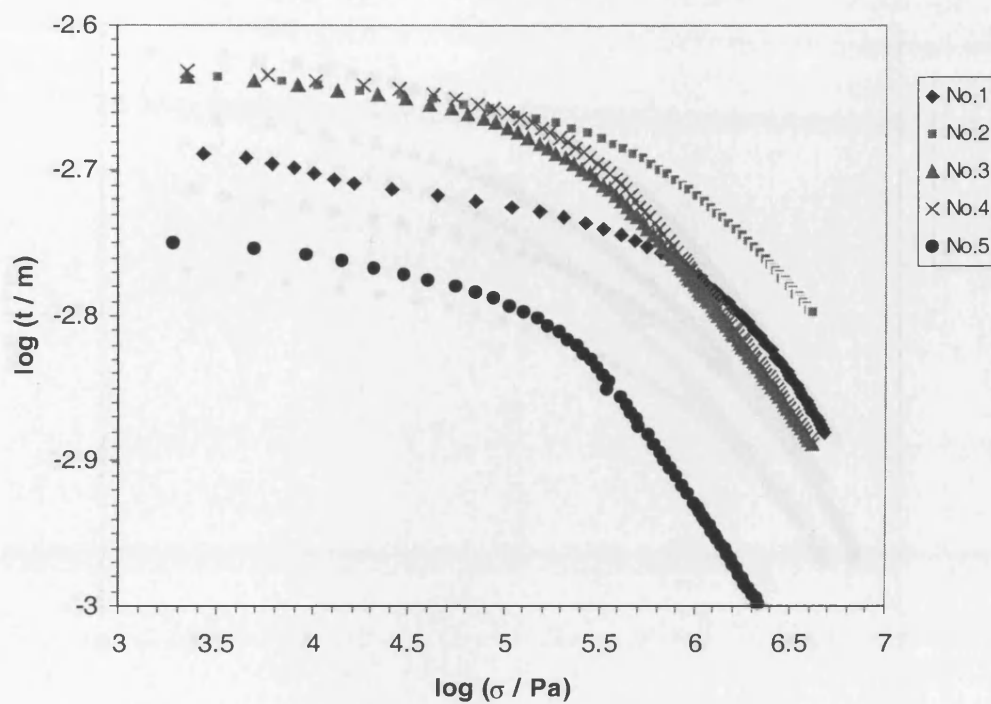


(c)

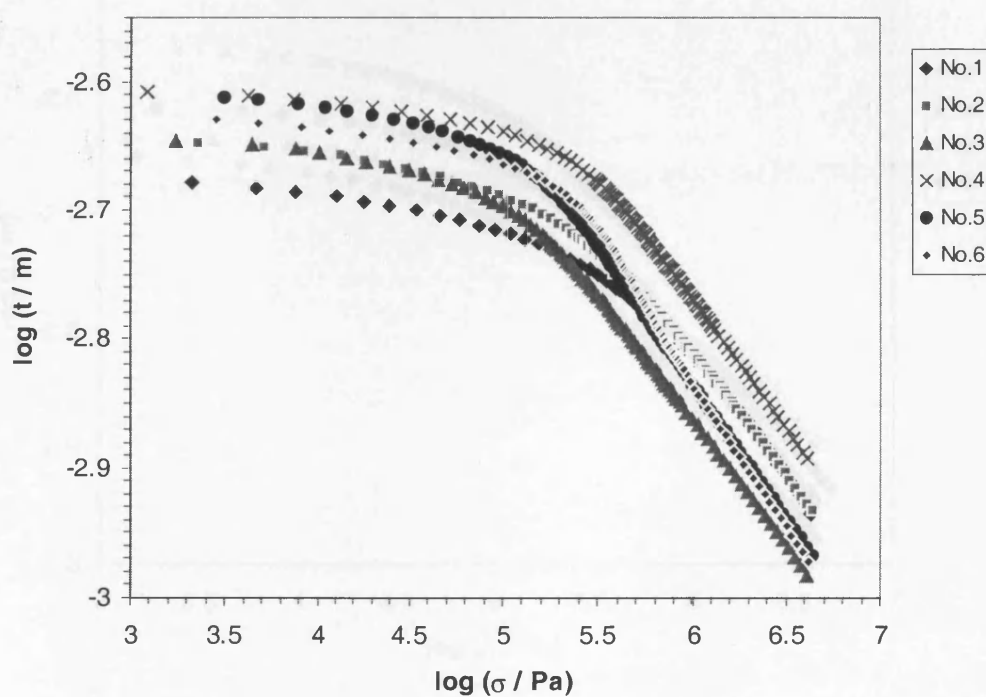


(d)

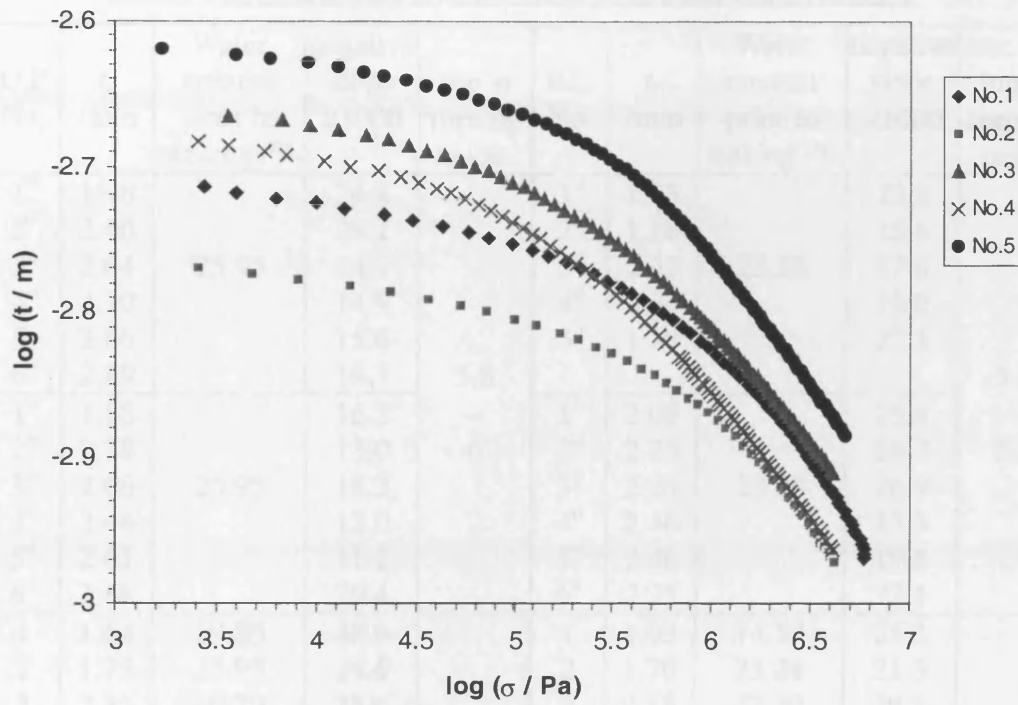
Figure 4.6 The $\log \sigma$ vs $\log t$ plots for unfatigued leather. (a) - control samples, batch (I); (b) - control samples, batch (II); (c) - test samples, batch (I); (d) - experimental samples, batch (II).



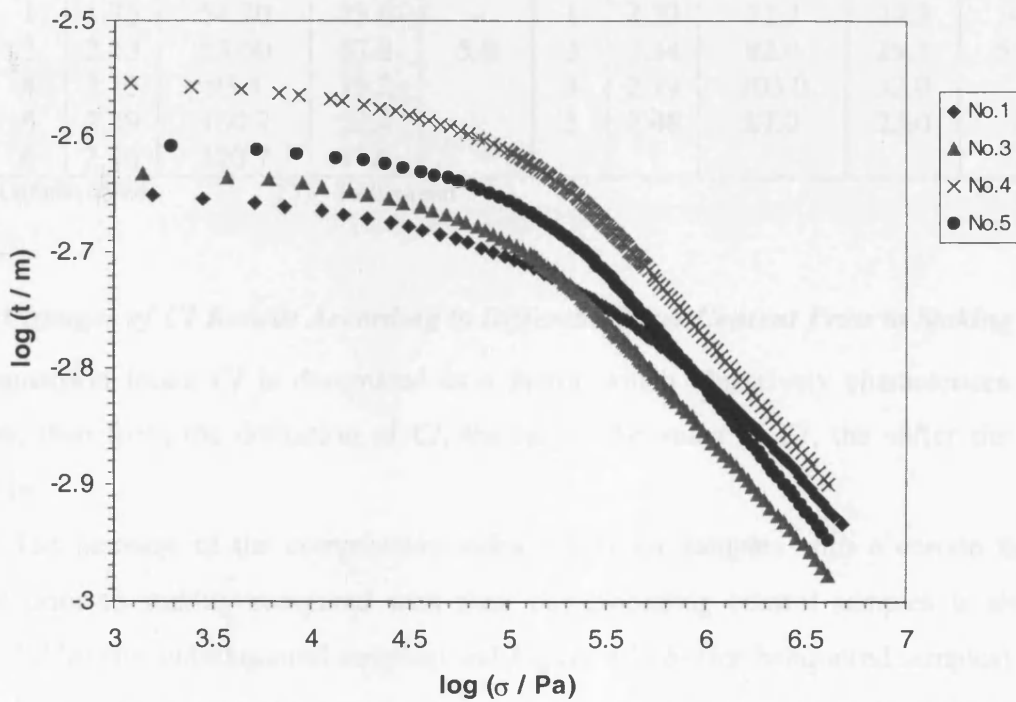
(a)



(b)



(c)



(d)

Figure 4.7 The $\log \sigma$ vs $\log t$ plots for fatliquored leather. (a) - control samples, batch (I); (b) - control samples, batch (II); (c) - test samples, batch (I); (d) - experimental samples, batch (II).

Table 4. 1 Sample parameters and the compression indices

Batch No	U.F No.	t_0 /mm	Water content prior to staking /%	negative slope $\times 1000$	log σ turning point	F.L. No.	t_0 /mm	Water content prior to staking /%	negative slope $\times 1000$	log σ turning point
1	1°	1.98	25.95	24.4	5.8	1°	2.05	23.28	23.8	5.2
	2°	2.46		28.2		2°	1.86		15.6	
	3°	2.64		14.7		3°	2.32		17.8	
	4°	2.70		14.9		4°	2.34		16.0	
	5°	2.86		15.6		5°	1.78		27.1	
	6°	2.89		18.7						
2	1°	1.88	25.95	16.2	~ 6	1°	2.09	23.28	25.6	~ 5.5
	2°	2.38		13.0		2°	2.25		28.7	
	3°	2.66		18.2		3°	2.26		26.9	
	4°	2.44		12.0		4°	2.46		13.3	
	5°	2.61		11.2		5°	2.46		19.8	
	6°	2.68		20.4		6°	2.35		23.1	
1	1	1.64	19.83	48.6	5.5	1	1.93	14.59	25.3	5.0
	2	1.75	25.95	24.6		2	1.70	23.28	21.5	
	3	2.33	30.70	25.6		3	2.18	27.29	29.8	
	4	2.64	37.14	31.2		4	2.08	30.51	25.8	
	5	2.43	54.24	29.2		5	2.40	55	20.5	
	6	2.64	75.40	21.6						
2	1	1.75	54.20	23.6	~ 5.8	1	2.23	52.2	29.3	~ 5.3
	3	2.13	83.60	17.8		3	2.34	82.0	29.3	
	4	2.13	93.4	18.2		4	2.79	103.0	32.0	
	5	2.29	100.7	22.4		5	2.46	87.0	23.0	
	6	2.16	120.7	17.6						

U.F — Unfatigoured.

F.L—Fatigoured

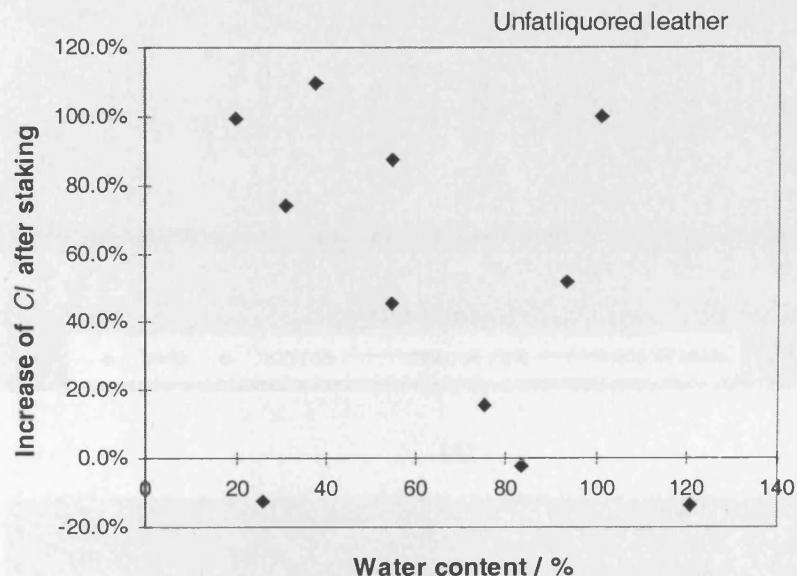
4. 3. 3 Changes of CI Results According to Different Water Content Prior to Staking

If compression index CI is designated as a factor which objectively characterises leather softness, then from the definition of CI , the larger the value of CI , the softer the leather should be.

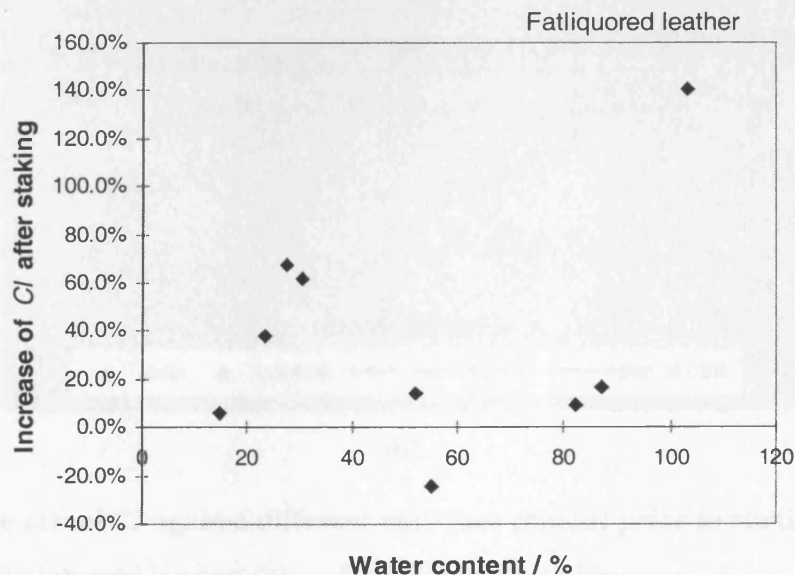
The increase of the compression index (ΔCI) for samples with a certain moisture content prior to staking compared with their corresponding control samples is shown in *Figure 4.8 (a)* (for unfatigoured samples) and *Figure 4.8 (b)* (for fatigoured samples).

Figure 4.9 shows the actual CI against moisture content prior to staking action. *Figure 4.9 (a)* is for unfatigoured leather and *(b)* for fatigoured ones. The mean value of control samples are also drawn in each figure in order to compare the influence of the moisture content on the CI value during the staking action. CI values of control samples were obtained under one single moisture content (see table 4.1)

Mathematical modelling of the type shown in *Figure 4.5* to describe the compression curves of these partially processed leathers changes from sample to sample. The compression curves of all the control samples of (un)fatigued leather and models to describe each of the curves are shown in *Figure 4.10 (a) to (b)* and *Figure 4.12 (a) to (b)*. Results for the experimental samples of (un)fatigued leather are shown in *Figure 4.11 (a) to (b)* and *Figure 4.13 (a) to (b)*.

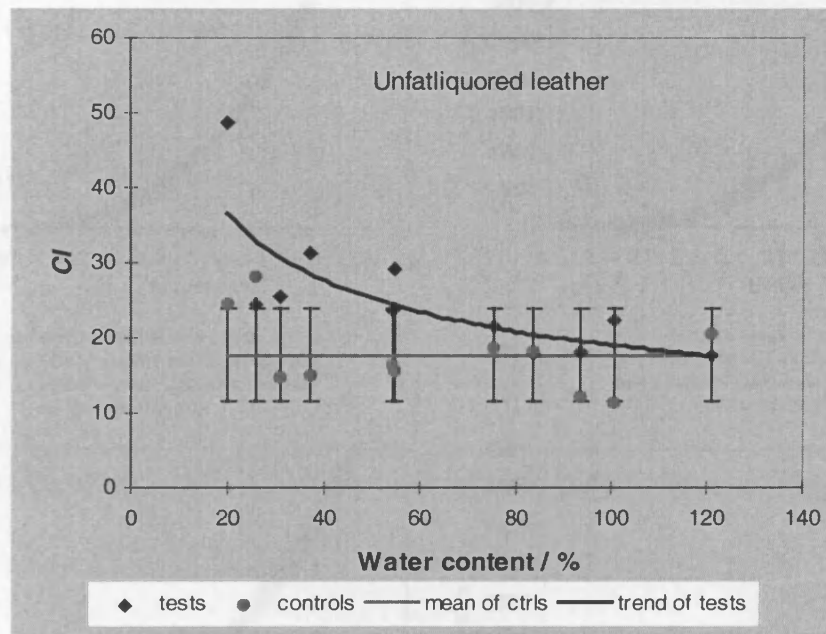


(a)

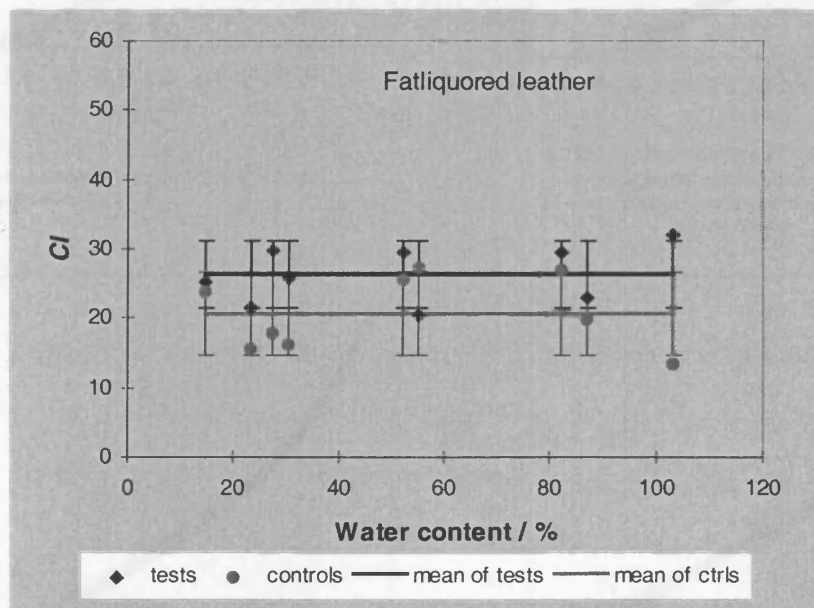


(b)

Figure 4.8 The increase of *CI* for leather with different moisture content prior to staking. (a) — unfatigued leather; (b) — fatigued leather.

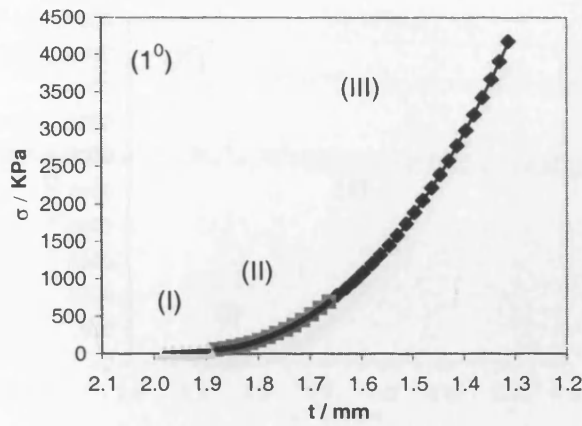


(a)

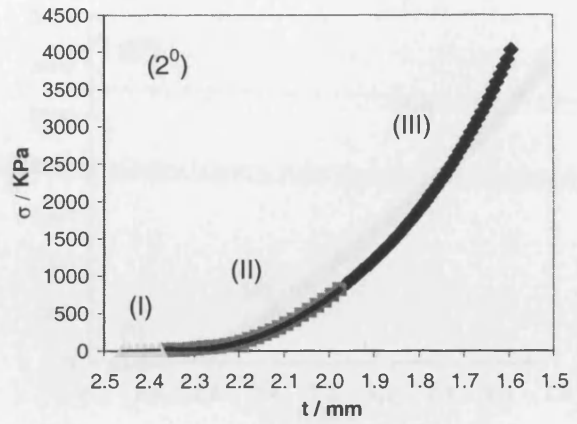


(b)

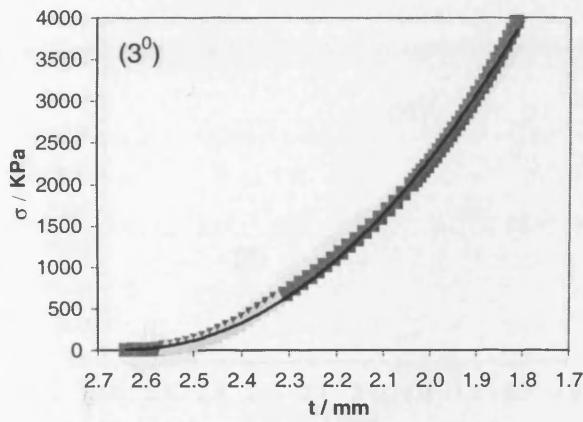
Figure 4.9 The actual *CI* against different moisture content prior to staking. (a) — for unfatigued leather; (b) — for fatigued leather.



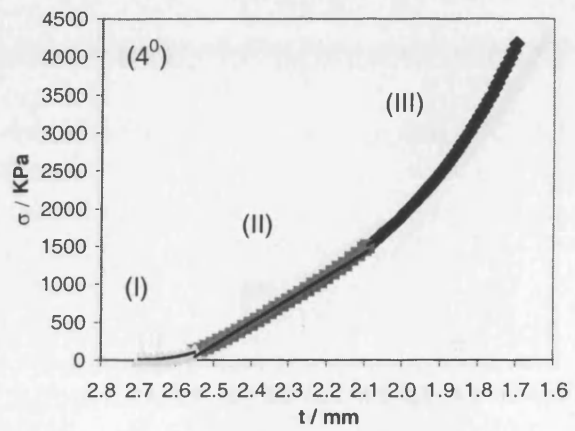
(I) $\sigma = -384.89t + 763.18$ $R^2 = 0.9656$
 (II) $\sigma = 10744t^2 - 40987t + 39136$ $R^2 = 0.9998$
 (III) $\sigma = 15520t^2 - 56007t + 50942$ $R^2 = 0.9999$
 (NF-Ctrl-B1-C01)*



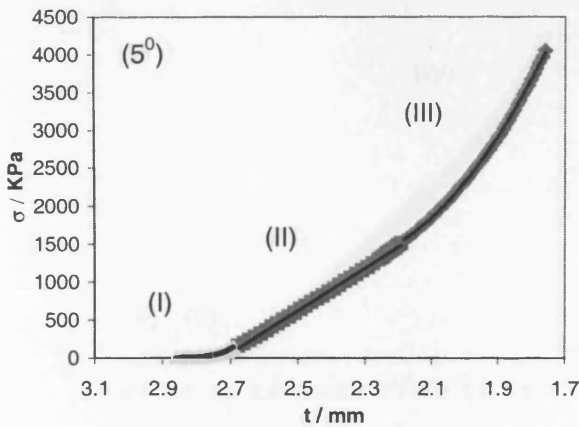
(I) $\sigma = -57.115t + 142.72$ $R^2 = 0.9083$
 (II) $\sigma = 6877t^2 - 31895t + 36998$ $R^2 = 0.9995$
 (III) $\sigma = 11838t^2 - 50422t + 54264$ $R^2 = 0.9998$
 (NF-Ctrl-B1-C02)*



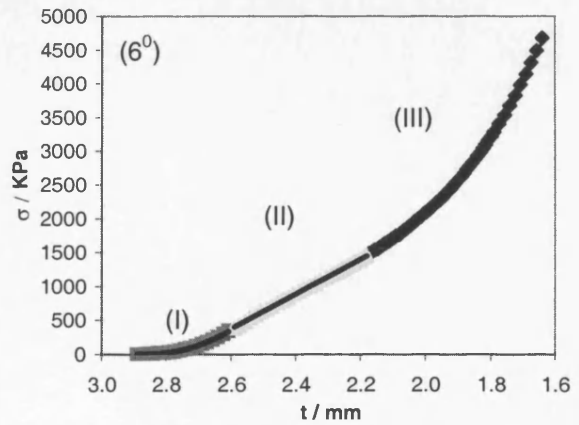
(Whole range) $\sigma = 5695t^2 - 30021t + 39575$ $R^2 = 0.9991$
 (NF-Ctrl-B1-C03)*



(I) $\sigma = -3053.2t + 7823.5$ $R^2 = 0.9959$
 (II) $\sigma = 5212.4t^2 - 28033t + 37694$ $R^2 = 0.9988$
 (III) $\sigma = 8499t^2 - 38938t + 45768$ $R^2 = 0.9998$
 (NF-Ctrl-B1-C04)*



(I) $\sigma = 2E+30t^{65.114}$ $R^2 = 0.9944$
 (II) $\sigma = -2797.1t + 7615.7$ $R^2 = 0.9993$
 (III) $\sigma = 6970.5t^2 - 33298t + 41035$ $R^2 = 0.9998$
 (NF-Ctrl-B1-C05)*



(I) $\sigma = 5488.4t^2 - 31696t + 44374$ $R^2 = 0.9982$
 (II) $\sigma = -2553.4t + 7017.8$ $R^2 = 0.9995$
 (III) $\sigma = 7433.4t^2 - 34108t + 40543$ $R^2 = 0.9992$
 (NF-Ctrl-B1-C06)*

(a) Non-fatigued control samples -- batch 1

* NF -- Non-fatigued; Ctrl -- Control sample; B1(2, 3, ...) -- Batch No.1 (2, 3, ...); C01(2, 3, ...) -- Control sample No. 1(2, 3, ...)

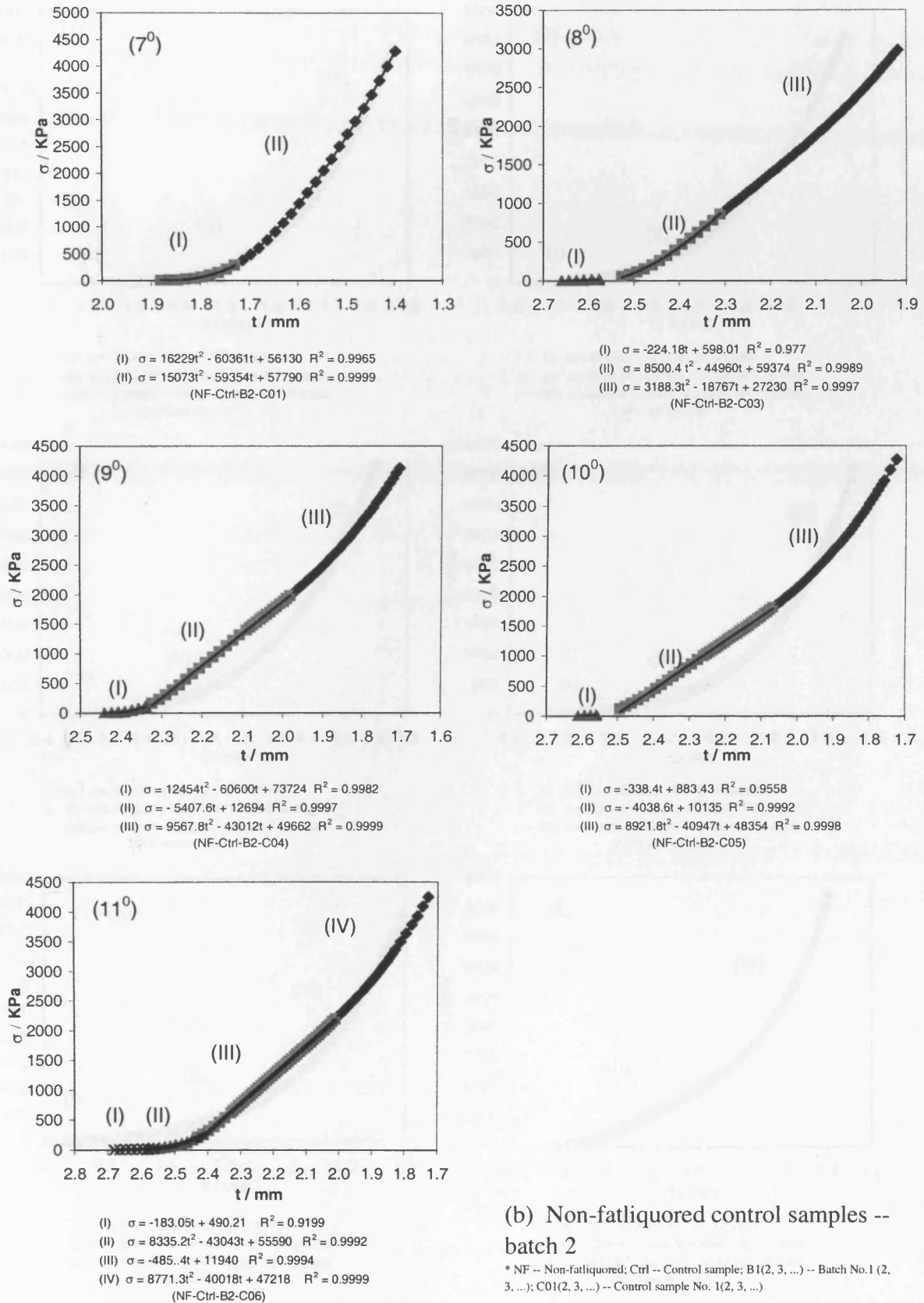
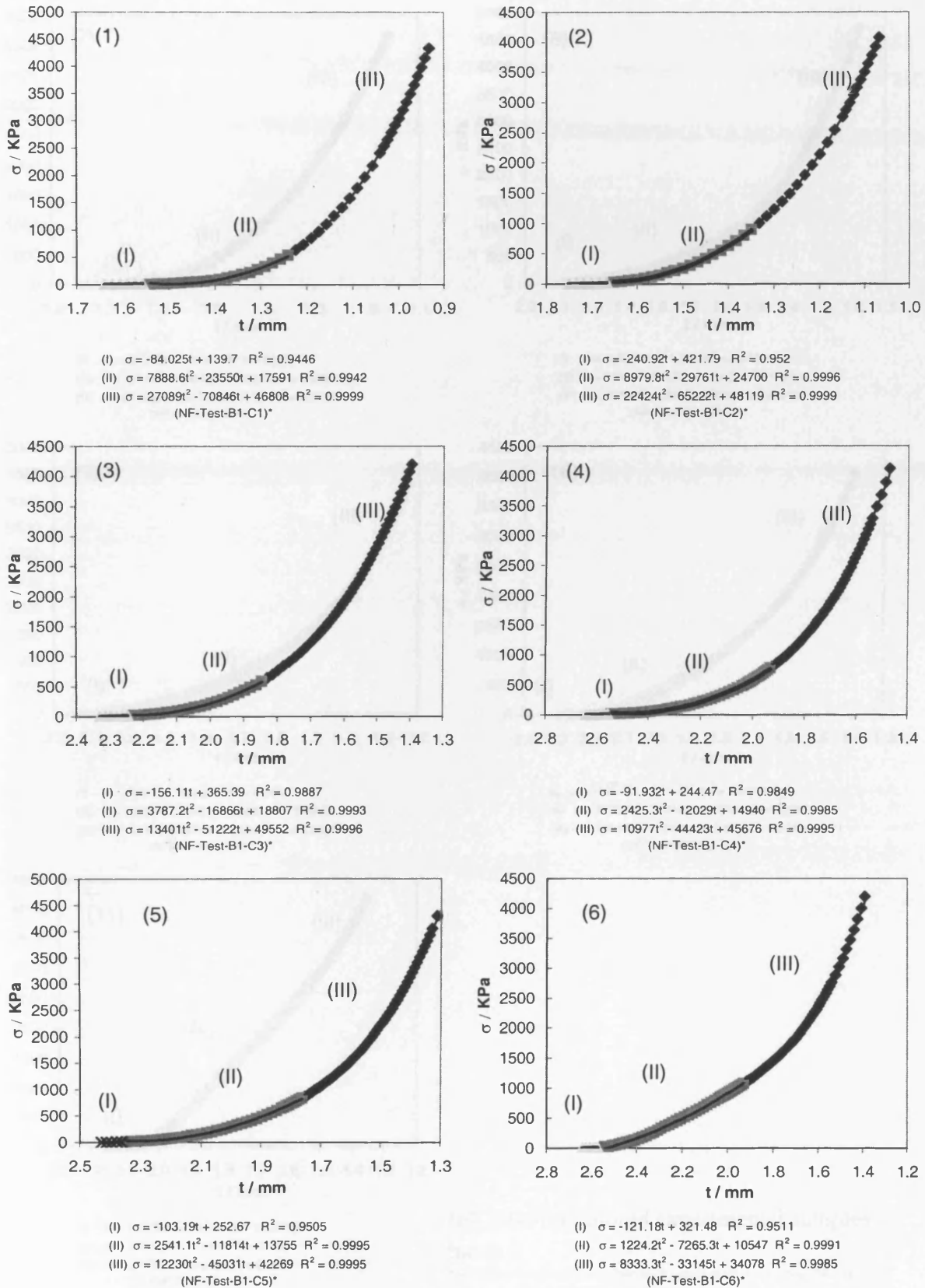


Figure 4. 10 The description of mathematical models for different reigons of non-fatigued leather control samples. (a) batch 1; (b) batch 2



(a) Non-fatigued experimental samples -- batch 1

* NF -- Non-fatigued; Test -- Experimental sample; B1(2, 3, ...) -- Batch No.1 (2, 3, ...); C1(2, 3, ...) -- Experimental sample No. 1(2, 3, ...)

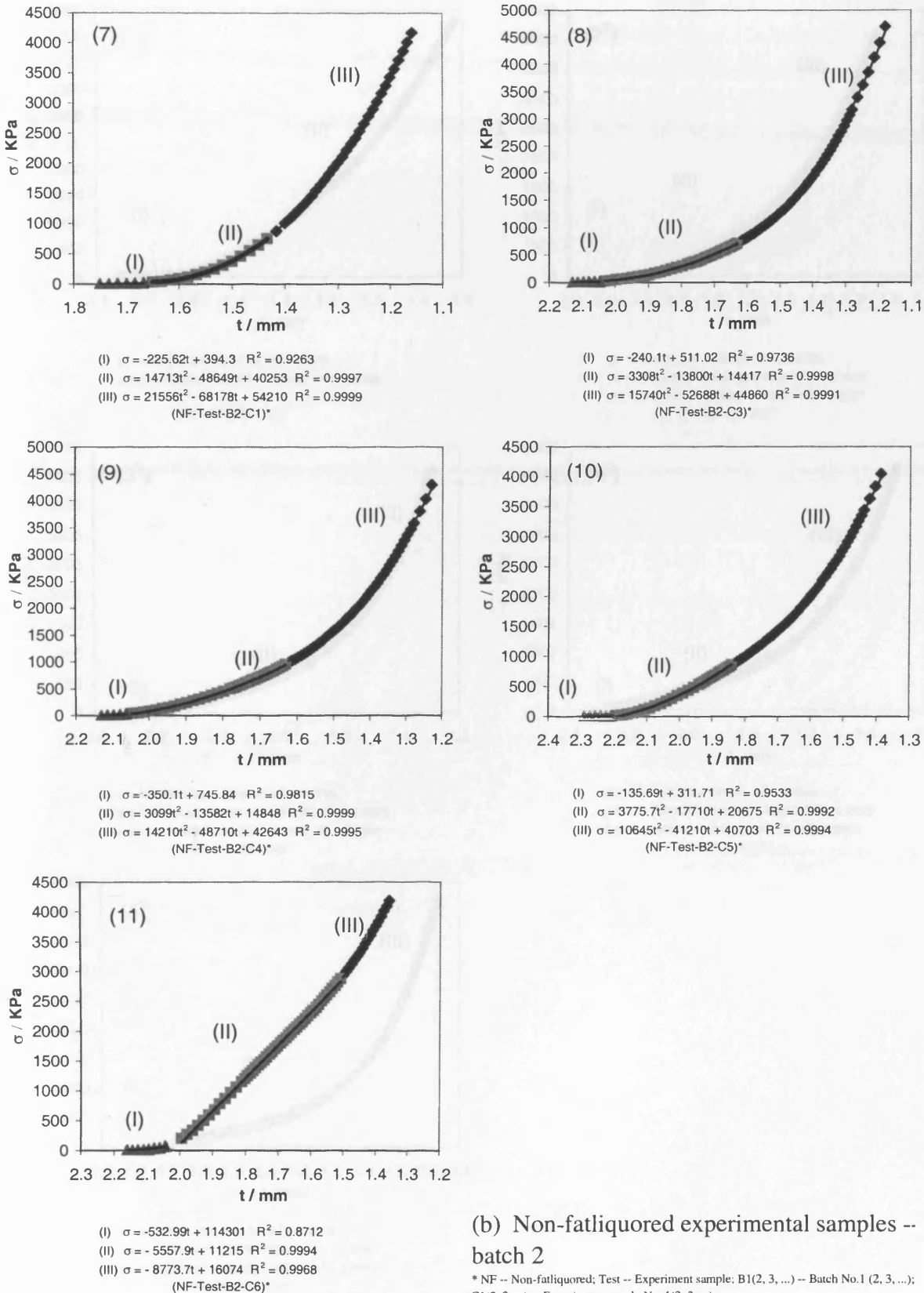
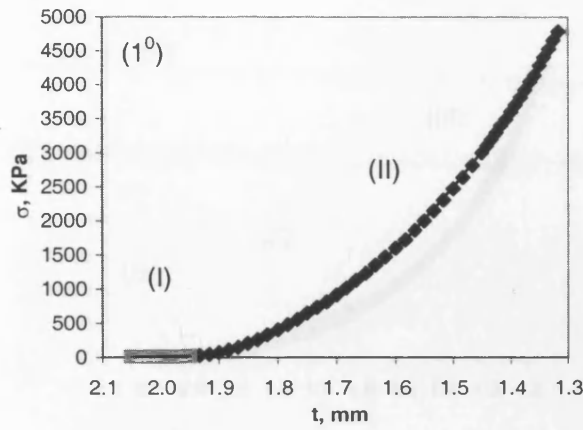


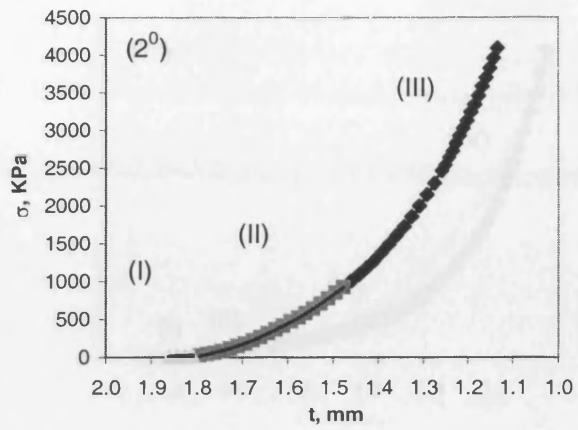
Figure 4.11 The description of mathematical models for different regions of non-fatigued leather experimental samples. (a) batch 1; (b) batch 2



$$(I) \quad \sigma = -134.33t + 277.42 \quad R^2 = 0.978$$

$$(II) \quad \sigma = 10403t^2 - 41381t + 41166 \quad R^2 = 0.9996$$

(FL-Ctrl-B1-C01)*

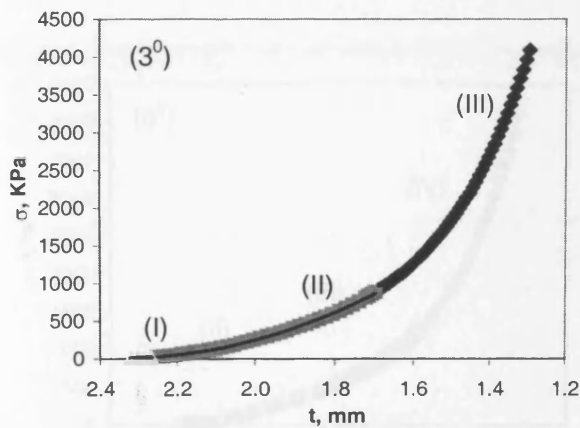


$$(I) \quad \sigma = -285.33t + 533.28 \quad R^2 = 0.9706$$

$$(II) \quad \sigma = 5345.5t^2 - 20343t + 19308 \quad R^2 = 0.9997$$

$$(III) \quad \sigma = 17121t^2 - 53707t + 42960 \quad R^2 = 0.9997$$

(FL-Ctrl-B1-C02)*

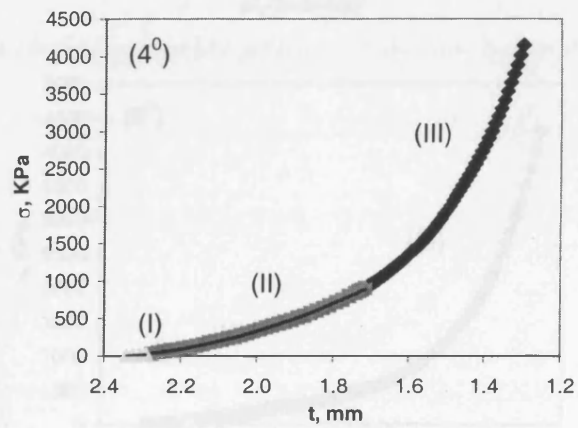


$$(I) \quad \sigma = -225.32t + 524.42 \quad R^2 = 0.9765$$

$$(II) \quad \sigma = 2045.7t^2 - 9621.2t + 11267 \quad R^2 = 0.9995$$

$$(III) \quad \sigma = 15595t^2 - 54323t + 48227 \quad R^2 = 0.9993$$

(FL-Ctrl-B1-C03)*

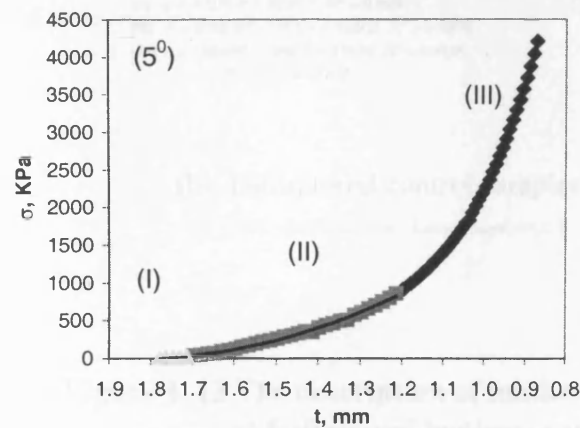


$$(I) \quad \sigma = -318.22t + 745.92 \quad R^2 = 0.9654$$

$$(II) \quad \sigma = 1606.2t^2 - 7938.4t + 9783.6 \quad R^2 = 0.9993$$

$$(III) \quad \sigma = 14851t^2 - 52171t + 46775 \quad R^2 = 0.9991$$

(FL-Ctrl-B1-C04)*



$$(I) \quad \sigma = -285.29t + 508.57 \quad R^2 = 0.9773$$

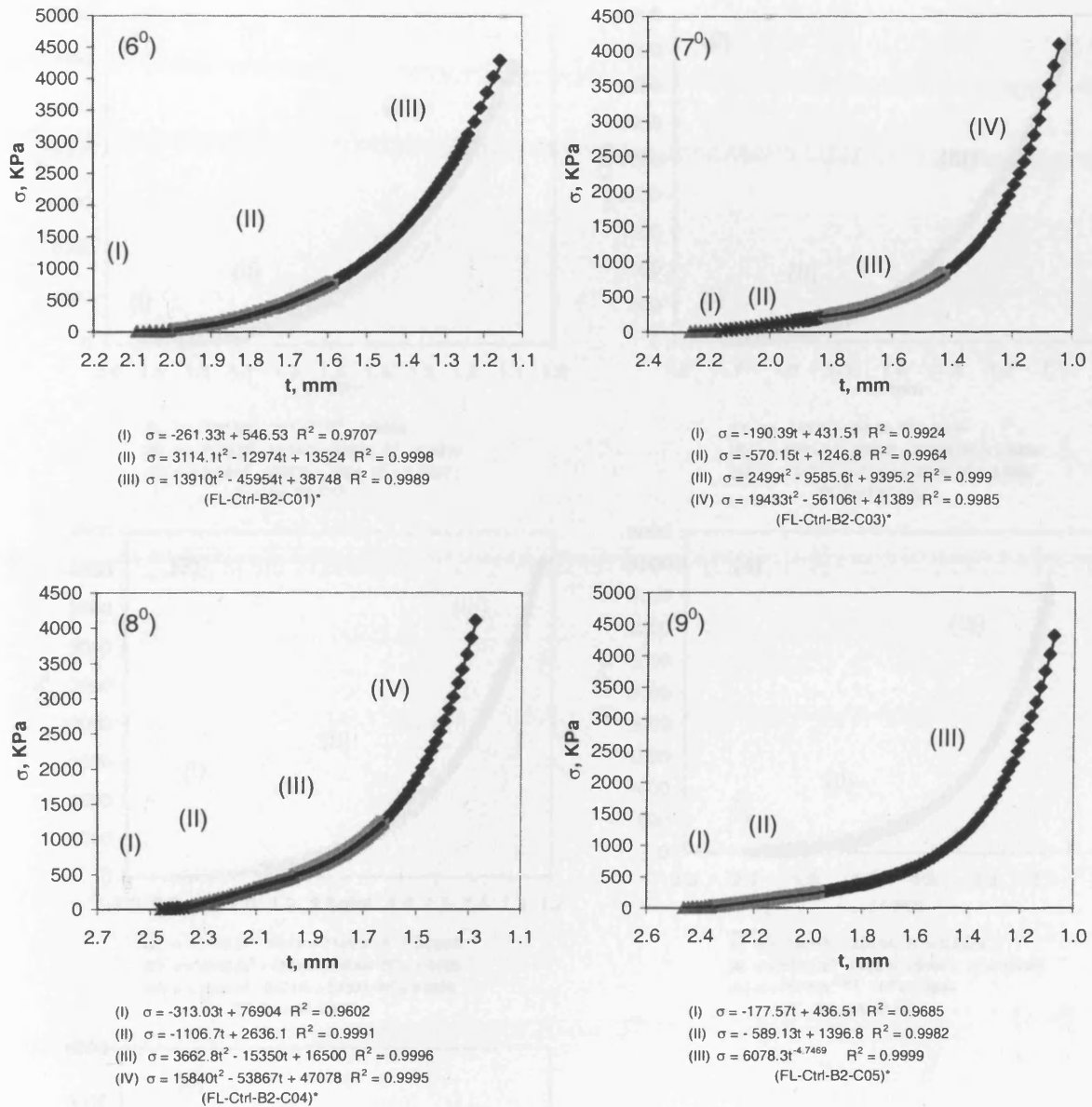
$$(II) \quad \sigma = 2149.4t^2 - 7870t + 7207.8 \quad R^2 = 0.996$$

$$(III) \quad \sigma = 25400t^2 - 62235t + 39090 \quad R^2 = 0.9991$$

(FL-Ctrl-B1-C05)*

(a) Fatliquored control samples -- batch 1

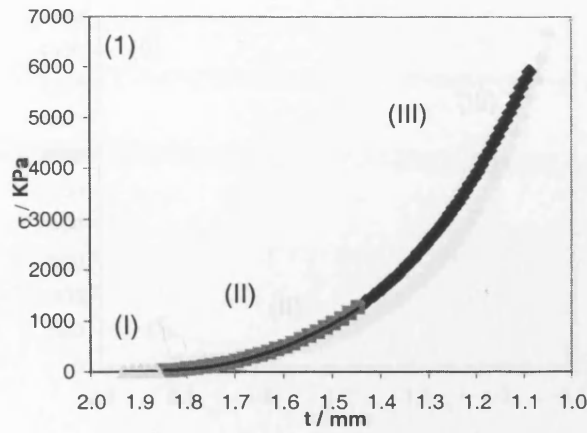
* FL -- Fatliquored; Ctrl -- Control sample; B1(2, 3, ...) -- Batch No.1 (2, 3, ...); C01(2, 3, ...) -- Control sample No. 1(2, 3, ...)



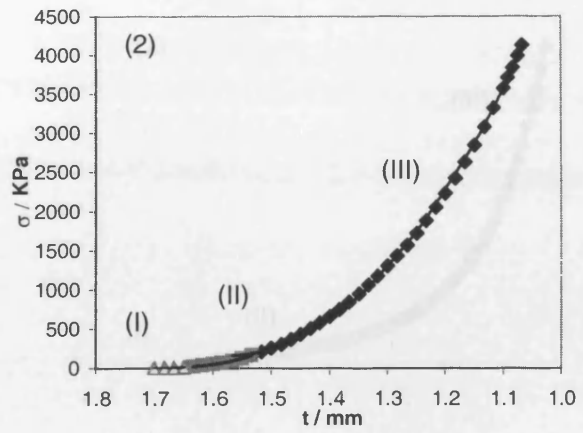
(b) Fatigued control samples -- batch 2

* FL -- Fatigued; Ctrl -- Control sample; B1(2, 3, ...) -- Batch No.1 (2, 3, ...); C01(2, 3, ...) -- Control sample No. 1(2, 3, ...)

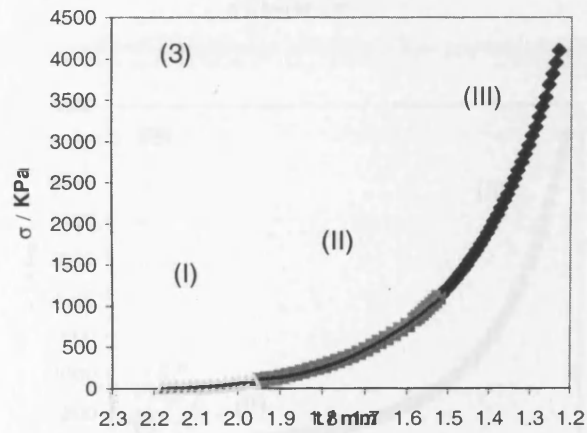
Figure 4. 12 The description of mathematical models for different regions of fatigued leather control samples. (a) batch 1; (b) batch 2



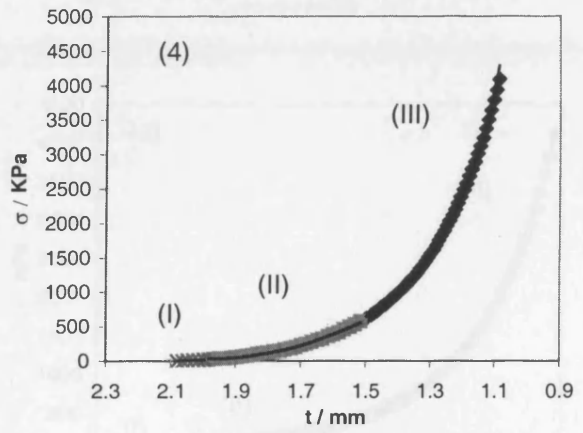
(I) $\sigma = -170.86t + 331.48$ $R^2 = 0.9619$
 (II) $\sigma = 7570.9t^2 - 27947t + 25828$ $R^2 = 0.9995$
 (III) $\sigma = 20589t^2 - 65006t + 5226$ $R^2 = 0.9999$
 (FL-Test-B1-C1)*



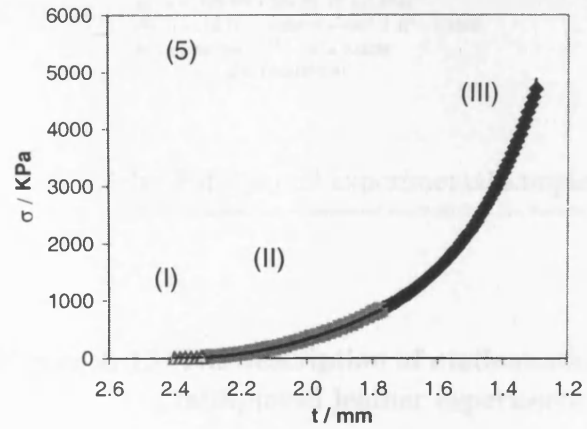
(I) $\sigma = -240.4t + 410.26$ $R^2 = 0.939$
 (II) $\sigma = 8891.1t^2 - 29562t + 24589$ $R^2 = 0.9996$
 (III) $\sigma = 15171t^2 - 47749t + 37736$ $R^2 = 0.9992$
 (FL-Test-B1-C2)*



(I) $\sigma = 1479.2t^2 - 6503t + 7149.8$ $R^2 = 0.9998$
 (II) $\sigma = 4745.9t^2 - 18715t + 18563$ $R^2 = 0.9989$
 (III) $\sigma = 21317t^2 - 68710t + 56331$ $R^2 = 0.9998$
 (FL-Test-B1-C3)*



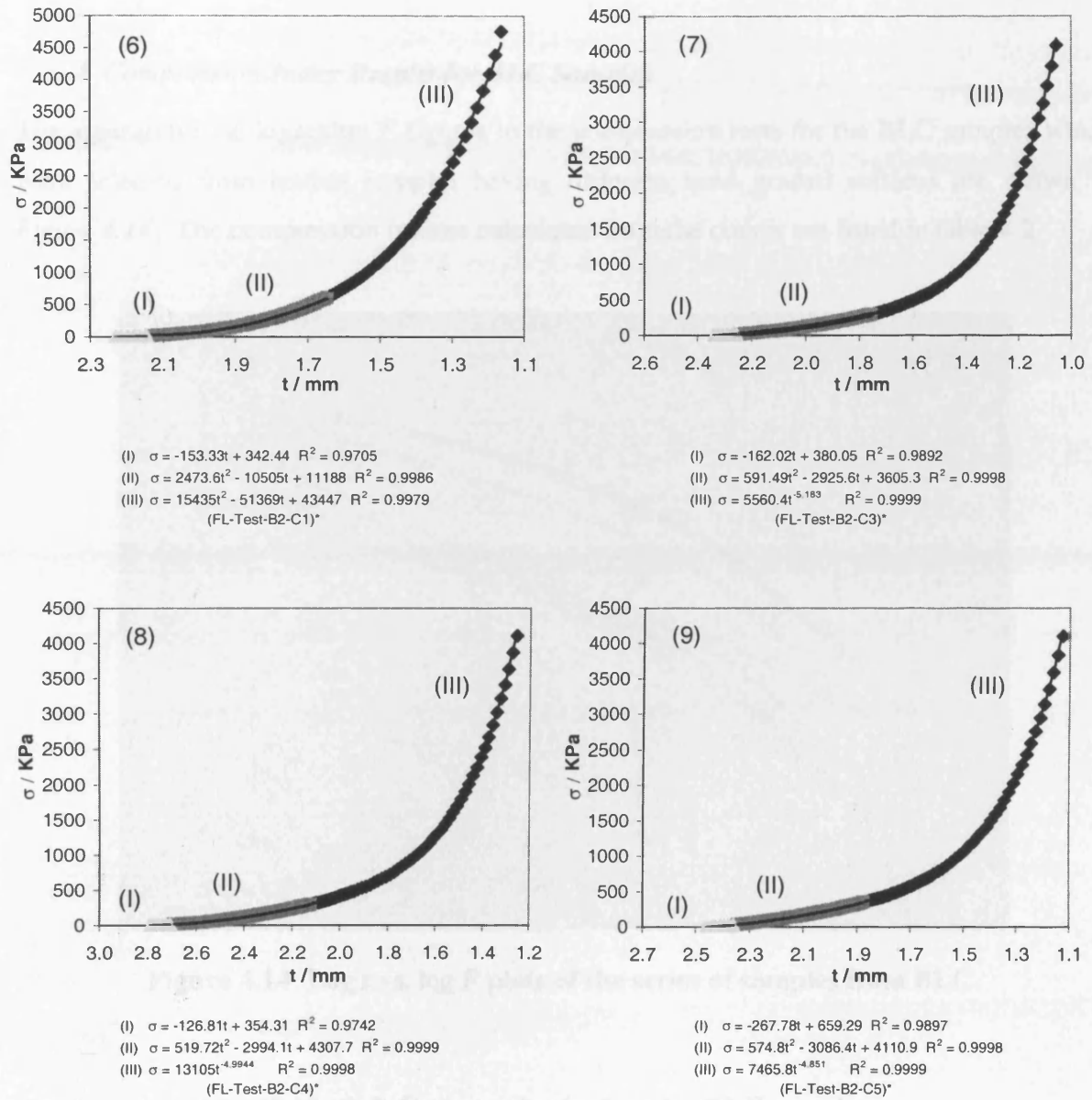
(I) $\sigma = -146.43t + 305.94$ $R^2 = 0.9439$
 (II) $\sigma = 2371.3t^2 - 9408.4t + 9365.4$ $R^2 = 0.9985$
 (III) $\sigma = 7079.3t^{5.918}$ $R^2 = 0.9984$
 (FL-Test-B1-C4)*



(I) $\sigma = -187.09t + 449.75$ $R^2 = 0.9742$
 (II) $\sigma = 2362.3t^2 - 11181t + 13242$ $R^2 = 1$
 (III) $\sigma = 20745t^{5.5237}$ $R^2 = 0.9991$
 (FL-Test-B1-C5)*

(a) Fatigued experimental samples -- batch 1

* FL -- Fatigued; Test -- experimental sample; B1(2, 3, ...) -- Batch No.1 (2, 3, ...); C1(2, 3, ...) -- Experimental sample No. 1(2, 3, ...)



(b) Fatigued experimental samples -- batch 2

* FL -- Fatigued; Test -- experimental sample; B1(2, 3, ...) -- Batch No.1 (2, 3, ...); C1(2, 3, ...) -- experimental sample No. 1(2, 3, ...)

Figure 4.13 The description of mathematical models for different regions of fatigued leather experimental samples. (a) batch 1; (b) batch 2

4.3.4 Compression Index Results for BLC Samples

The logarithm t vs. logarithm F figures in the compression tests for the BLC samples which were selected from leather samples having different hand graded softness are shown in Figure 4.14. The compression indices calculated from the curves are listed in table 4.2

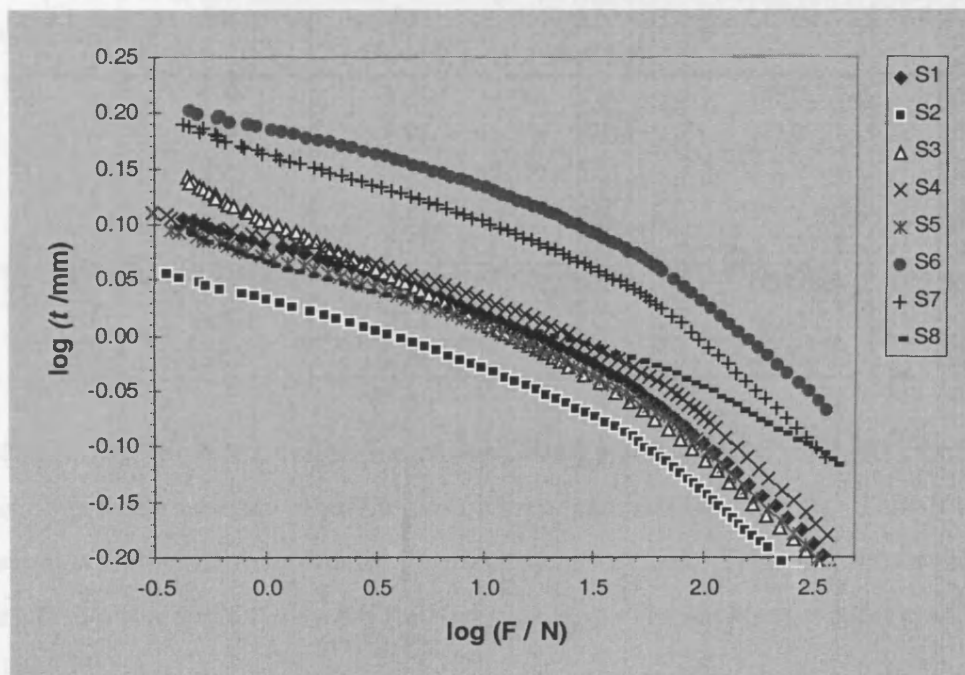


Figure 4.14 Log t vs. log F plots of the series of samples from BLC.

Table 4.2 Compression indices for BLC samples

Sample No.	Compression index (CI)	t_0 (under the initial force 4 N) / mm
1	67.75	1.261
2	65.5	1.104
3	94.5	1.268
4	57.5	1.342
5	67.75	1.232
6	56.75	1.687
7	66.0	1.528
8	55.25	1.247

The forces applied to unit area of the leather sample as a function of relative thickness $t\%$, (i.e. $(t_0 - t)/t_0 \times 100\%$), are shown in Figure 4.15. The de-compression curves, following compression to a relative thickness of 46%, were also recorded and are shown in Figure 4.15

as well. This allows a calculation of the energy consumed when the sample is subjected to such a compressive deformation and the energy released when the sample was decompressed. Furthermore, the loss of energy after the completion of the whole compression procedure and the relative energy loss were also calculated. Results are listed in table 4.3.

Table 4. 3 Energy consumption for BLC samples in compression

Sample No.	E_1 / (J $\times 10^4$)	E_2 / (J $\times 10^4$)	ΔE / (J $\times 10^4$)	$\Delta E/E_1$ / %	t_0 / mm
1	319	115	204	64.0	1.261
2	329	132	198	60.0	1.104
3	79	27	52	65.3	1.268
4	297	105	192	64.7	1.342
5	306	107	200	65.2	1.232
6	450	301	301	66.9	1.687
7	405	277	277	68.4	1.582
8	1367	798	569	41.6	1.247

The results for compression indices and energy consumed during the whole cycle of compression provide a means of ranking or ordering samples for softness. This ordering may be compared with the softness ordering from grading by hand. Table 4.4 shows these results and their correlation coefficient with the hand grading. The rank correlation coefficient r is defined by: ^[89]

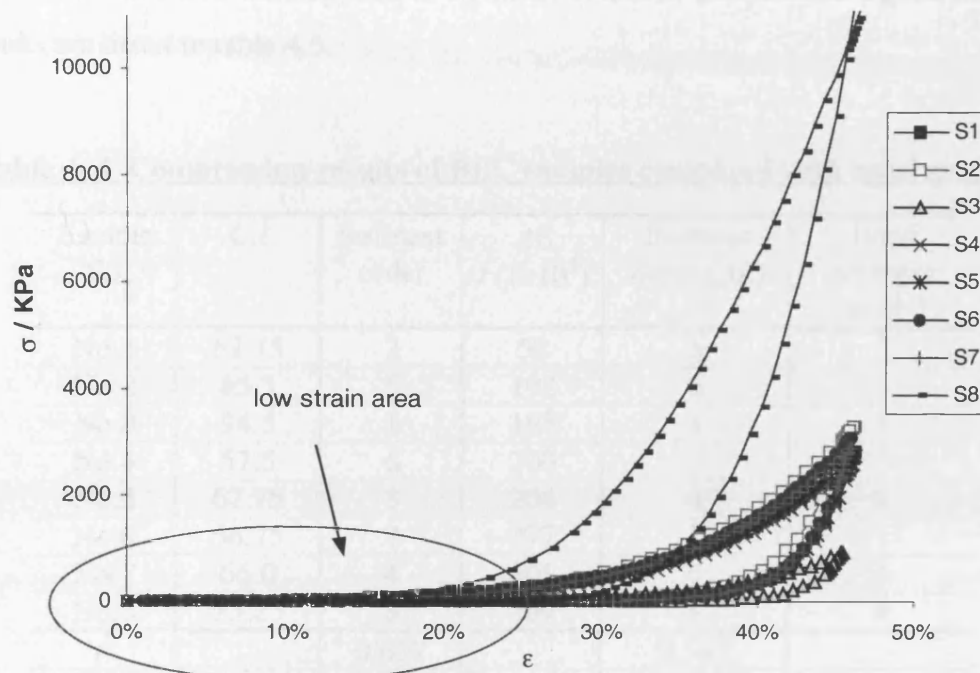
$$r = \frac{n \sum_{i=1}^n x_i y_i - \left(\sum_{i=1}^n x_i \right) \left(\sum_{i=1}^n y_i \right)}{\sqrt{\left[n \sum_{i=1}^n x_i^2 - \left(\sum_{i=1}^n x_i \right)^2 \right] \left[n \sum_{i=1}^n y_i^2 - \left(\sum_{i=1}^n y_i \right)^2 \right]}}$$

where n is the number of samples, x_i and y_i are the i th observation of variables X and Y .

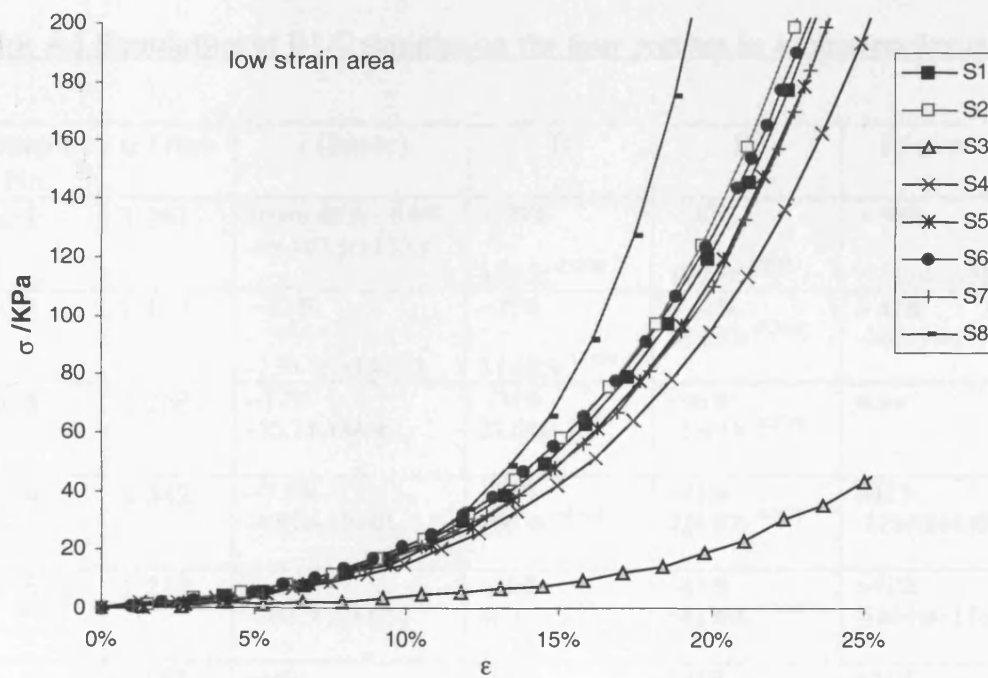
When there are no ties in either the x observations or the y observations, r is reduced to a simpler expression:

$$r = 1 - \frac{6 \sum_{i=1}^n d_i^2}{n(n^2 - 1)} \quad \text{where } d_i = x_i - y_i$$

From the results we can see that compression index shows good accordance with the results graded by hand. Energy consumed during the complete circle of compression also shows a relatively good accordance with hand grading. The degree of agreement with subjective grading from various softness measurements will be compared and discussed in Chapter 5.



(a)



(b)

Figure 4.15 The compression stress ~ strain curves of BLC samples. (a) — whole compressive range; (b) — at low compressive strain area.

Equations (I) ~ (IV) (section 4. 3. I) describing the four regions of the compression stress vs. thickness curve were applied to all the BLC leather samples and a good fit obtained. The results are listed in table 4.5

Table 4. 4 Compression results of BLC samples compared with hand grading

Sample No.	C.I	Softness order	ΔE / (J $\times 10^4$)	Softness order (ΔE)	Hand softness order *
No.1	67.75	2	52	5	2
No.2	65.5	5	192	3	5
No.3	94.5	1	198	1	1
No.4	57.5	6	200	2	3
No.5	67.75	3	204	4	6
No.6	56.75	7	277	7	7
No.7	66.0	4	301	6	4
No.8	55.25	8	569	8	8
r^2		0.617		0.545	
r		0.786		0.738	

* 1 = softest, 8 = hardest

Table 4.5 Simulation of BLC samples on the four regions in a compressive curve

Sample No.	t_0 / mm	I (linear)	II	III	IV (linear)
No. 1	1.261	strain up to ~6.6% $\sigma = -107.5t + 133.9$	~ 29% $124.3t^{-13.889}$	~ 40% $179.7t^{-7.6939}$	> 40% $-16138t + 13638$
No. 2	1.104	~7.5% $-150.18t + 164.31$	~27% $21.685t^{-13.806}$	~ 41% $81.353t^{-7.5133}$	> 41% $-24349t + 17754$
No. 3	1.268	~12% $-35.74t + 44.9$	~34% $22.046t^{-11.641}$	~46% $31.424t^{-9.2769}$	none
No. 4	1.342	~7.5% $-82.1t + 110.01$	~24% $266.4t^{-14.664}$	~41% $224.87t^{-8.3876}$	>41% $-17040t + 14920$
No. 5	1.232	~10% $-202.3t + 241.58$	~26% $88.61t^{-13.24}$	~41% $142.69t^{-7.6125}$	>41% $-18046t + 14696$
No. 6	1.687	~6% $-85.3t + 142.69$	~24% $9910.1t^{-14.673}$	~41% $1881.4t^{-8.2033}$	>41% $-15429t + 17125$
No. 7	1.582	~5% $-63.58t + 100.14$	~26% $3197.7t^{-14.611}$	~41% $1075.3t^{-7.9524}$	>41% $-15388t + 16042$
No. 8	1.247	~7% $-85.36t + 106.13$	~27% $206.77t^{-19.785}$	~38% $503.95t^{-9.5166}$	>38% $-56069t + 48542$

4. 4 Discussion

4. 4. 1 Comparison of the Compressive Behaviour of Leather and Solid Foams

Solid foam materials are similar to leather in some aspects (i.e. they are both compressible porous void filled solids) and their compression behaviour has been well studied^[90, 91]. In fact, Gibson and Ashby implied that fibrous solids (e.g. felt, paper and cotton wool) should show some similarities to a solid foam^[92] and claimed that their mechanical and thermal properties have much in common with those of cellular materials. Theories describing the mechanical behaviours of solid foams may also apply to these fibrous solids. In a cellular solid, the most important structural characteristic is its relative density or porosity. Most mechanical and thermal properties depend mainly on cell shape rather than cell size. When the cells are equiaxial the properties are isotropic. However, the properties vary from isotropic when there are even slight departures in structure from equiaxial.

As is the case for solid foams the compression behaviour of leather is expected to be dependent on both the solid material (in this case the fibres) and their arrangement into a structure which contains voids.

Three typical compressive stress–strain curves representing the compression behaviour of an elastomeric, and elastic-plastic and a brittle foam are shown in *Figure 4.16*^[93]. The whole compressive σ – ϵ curve can be divided into three segments which represent different structural changes: 1) linear elasticity at low stresses which is controlled by cell wall bending and by cell face stretching if the cells are closed, and from which Young's modulus, E^* , can be obtained by calculating the initial slope of the stress - strain curve; 2) a long collapse plateau which is associated with collapse of the cells, i.e. by elastic buckling in elastomeric foams (rubbers, for example); by the formation of plastic hinges in a foam which yields (such as metal); and by brittle crushing in a brittle foam (such as a ceramic); 3) when the cells have almost completely collapsed, further strain compresses the solid itself, giving the final region of rapidly increasing stress.

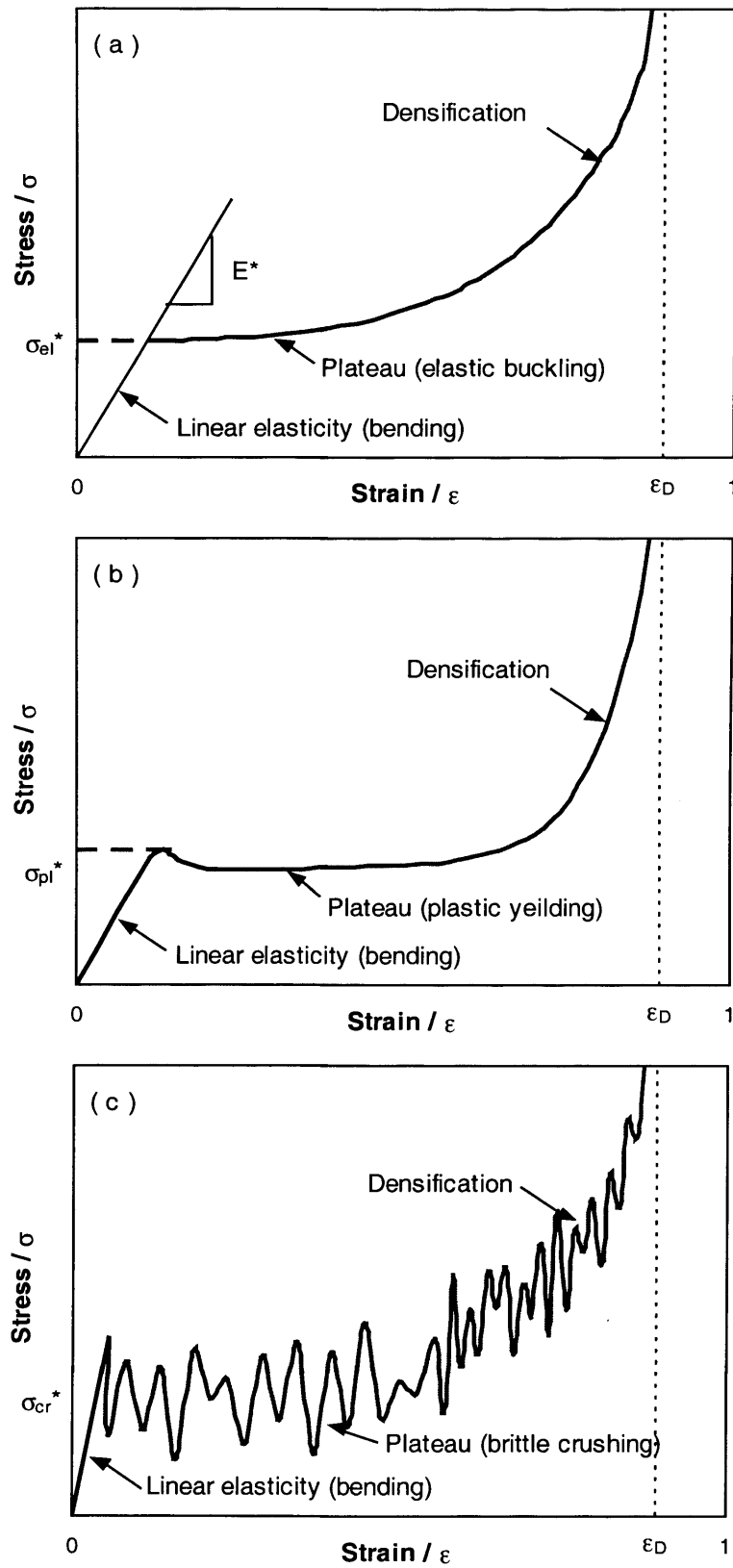


Figure 4.16^[93] **Compressive stress - strain ($\sigma - \epsilon$) curves for foams.** (a) an elastomeric foam; (b) an elastic-plastic foam; (c) an elastic-brittle foam.

According to the typical compressive stress – strain curve of leather (*Figure 4.3*), there is a significant difference between this curve and that of the foam material shown in *Figure 4.16*; i.e. the linear elastic segment in the low stress region for leather is far less prominent than that observed in the foam stress – strain curve. Indeed for leather it is possible that this linear segment does not exist. This pattern is expected, since the fibres and fibre bundles inside leather can not be expected to behave exactly as do the cell walls in a foam material. For a solid foam the linear behaviour of the initial region is mainly due to the bending of these cell walls. The initial deformation mode may not take the same form in leather, or indeed the concept of cell walls or edges may not be reasonable for leather. The linkage points between fibres and fibre bundles will act as hinges when the sample is under compressive force and slippage of these linkage points could happen very easily within the whole hierarchy of the leather structure. If the initial linear elastic segment of the compression stress – strain curve does exist, it will be at very low strains in which most of the fibres or fibre bundles (but not those not in a position forming a right angle with the compressive force) bend before any slippage of linkages within the hierarchy of structure happens. In solid foams there is a distinction between the initial cell wall bending phase and subsequent compression of the void structure (“structural collapse”). But in leather, as the compressive strain increases, it is likely that the bending of the fibres and compression of the inter-fibre void structure (which is analogous to structural collapse as seen in foams) take place simultaneously.

4. 4. 2 A Microstructural Model for the Compression of Leather

Based on a consideration of the $\sigma-t$ compression plot of fully processed leather (*Figure 4.5*), a schematic microstructural model was developed. Leather is an assembly of tightly woven fibres and fibre bundles of different diameters. Between these fibres or fibre bundles are voids. In the initial stage of compression, it is reasonable to assume that firstly, hair-like fibre ends protruding out of the leather surface will come into contact with the compression plate. At the same time the segments of fibres and/or fibre bundles which are at right angles to the grain layer inside the sample will be bent assuming that there is enough space nearby to allow such bending to proceed. This kind of deformation is represented schematically by the change from *a* to *b* in *Figure 4.17* and may be considered to be an elastic region. The stress increases linearly with the decrease of leather thickness to give region (I) as shown in *Figure 4.5*. This region generally reaches up to a point of equivalent stress of 10 KPa. As the force increases further, fibre bundles will be pressed closer together and some movement of the

linkage points between these fibre bundles may occur at the same time. The voids between these fibre bundles become compressed and therefore smaller. This process corresponds to the change from *b* to *c* in *Figure 4.17*. The stress increases in a non-linear way which can be represented as a power function of the thickness as is seen in region (II) of *Figure 4.5*. When the deformation of the fibre bundle network reaches a certain limit, it is reasonable to assume that the fibre structure inside the fibre bundles starts to become re-arranged by further compression and slippage at the linkage points of these fibres could also occur. At this stage, the smaller voids which lie between these fibres will start to close. This suggested mode of deformation is illustrated by the change from *c* to *d* in *Figure 4.17*. Again this is associated with a non-linear region of the stress-thickness relationship which can also be described by a power function (region III in *Figure 4.5*), although with different regression constants from the previous region. Eventually, when there are effectively no voids left, further compression can only occur by deformation of the solid fibres themselves. This final proposed stage is shown schematically by the change from *d* to *e* in *Figure 4.17*. Here the stress is in a linear relationship with the sample thickness as the last region shown on *Figure 4.5* (as would be expected for the compression of a solid material)

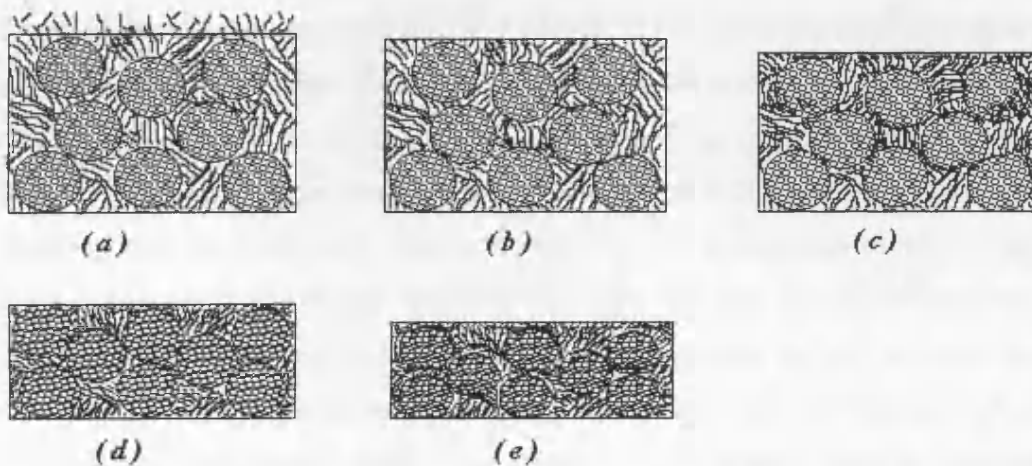


Figure 4.17 Schematic illustration of the proposed stages of compressive deformation of finished leather.

- (a) Initial structure. Hair-like fibres protrude from the flesh surface.
- (b) Hair-like fibres have been bent flat onto the surface. Buckling of vertical fibre bundles
- (c) Voids between fibre bundles have closed up.
- (d) Voids between fibres have closed up.

(e) Solid fibres have become compressed.

This model bears some resemblance to the model of the compression behaviour of fabrics developed by Matsudaira and Qin^[94], but in their model, there are only 3 regions of the $\sigma-t$ curve instead of 4 corresponding respectively to the compression of the sticking-out fibres, the compression of the voids in between the fibres and the compression of the fibres themselves. It is apparent that there is one more compression stage in leather than that in the fabric because multilevel structural hierarchy in leather is more complex.

The model illustrated in *Figure 4.17* implies that there are four distinct stages in the compression of finished leather and a mathematical analysis of the $\sigma-t$ curves suggests that each stage is associated with a distinct mathematical function (either linear or power) linking σ and t . It needs to be mentioned here that this model basically applies only to fully processed leather as mentioned above. For the partially processed leathers, the characteristics of the compressive curve are different and seem to depend on the history of the process as well. In examining the curves for the partially processed leather (see *Figure 4.10* to *Figure 4.13*) we can see that they cannot so readily be separated into the exact four distinct regions, although 2 or 3 compression regions can still usually be identified. In addition the mathematical expressions required to give a best fit to the curve segments are sometimes of polynomial form (e. g. number 3^0 for unfatliquored control sample in *Figure 4.10 (a)*). This observation is perhaps not surprising in terms of complex hierarchical structure of leather. In particular in the partially processed leathers there may be a different void structure and the fibre bundles may be much more resistant to bending due to a greater number of inter-fibre adhesions. The existence of the compressive stages and the associated equations which assume different forms to give a best description of each stage, reflects to some degree the status and changes of the microstructure (inter/intra fibre and fibre bundles) inside leather. In other words, the characteristics of the microstructure of the leather are to be reflected in the compression curve.

4. 4. 3 Compression Analysis of the Experimental Samples

Due to the complexity of leather structure, it is almost impossible to propose one single model to describe all of the compression behaviour of leather. Thus it was not possible to single out one parameter to indicate the observed compression behaviour or softness from the compression $\sigma-t$ curves. However, although it is an approximation, the compression index (*CI*) could still offer a compression parameter which can be used for different leather types.

According to the definition of the compression index:

$$CI = \frac{dt/t}{d\sigma/\sigma}$$

and the CI value can be obtained from the slope of the first approximately linear part of $\log t \sim \log \sigma$ curve. In this logarithm curve, there is a turning point as shown in *Figure 4.6*.

In fact, in most cases the change in leather thickness with increasing applied load is not a simple power relationship although an approximation can be made. The shape, slope and curvature of the compression curves will be dependent on the structure. The structure of leather and its physical properties vary with the manufacturing process. After taking the logarithm of both stress and thickness, an approximately linear relationship was obtained before the turning point. From the results obtained (Table 4.1), we can see that the turning point corresponds to the point where the leather was compressed to approximately 25% of the original thickness. In general, we might assume that softness will not be judged using greater than 25% compressive deformation, so this approximately linear segment in the logarithm graph can be reasonably used to calculate a compression index which may be taken as a measure of hand judged softness of light leathers and thus it can be used for grading leathers objectively.

Another feature of the $\log t - \log \sigma$ curves is that the turning points for leathers with different process history differs from one another. The logarithm values of σ at the turning points are listed in table 4.6.

Table 4. 6 Values of $\log \sigma$ at the turning point

	Unfatliquored	fatliquored
Control samples	5.8~6	5.2~5.5
Experimental samples	5.5~5.8	5.0~5.3

The figures indicate that fatliquored leathers have a lower turning point than the unfatliquored ones, and samples after staking have a lower stress at the turning point than those which have not been through staking. This implies that with fatliquor as a lubricant for the fibres, the fibres and fibre bundles more easily slide internally and relatively to each other and so produce a lower stress at the turning point. For leathers subjected to staking, there is a similar effect. The mechanical vibration has to some degree loosened the structure of leather and thereafter endows the fibres greater mobility when the structure is compressed.

4. 4. 4 Influence of Water Content Prior to Staking on Compression Behaviour

From *Figure 4.8*, it is seen that the influence of water content prior to staking on the softening effect of such a mechanical action in terms of ΔCI is not nearly so evident as for bending. The changes of absolute *CI* values shown in *Figure 4.9* indicate that, for unfatliquored leather, as the water content prior to staking increases, the softening effect obtained from the staking action tends to diminish and no longer exists when water content is above 80%. For fatliquored samples, there is an overall increase of *CI* after staking, but this change of *CI* is not evidently affected by the water content prior to staking. It is assumed that fatliquor played the role of lubricant which, before the mechanical softening action was applied, has assisted the leather to reach its maximum softening limit. So, compared with the lubricant effect of fatliquor, further added water is of little importance in assisting the staking softening. Interactions between water and collagen molecules and how the water molecules affect the softness results obtained from different experimental techniques are discussed in detail in *Chapter 5*.

CHAPTER 5

INFLUENCE OF WATER CONTENT PRIOR TO MECHANICAL ACTION ON THE SOFTNESS OF LEATHER AND COMPARISON OF DIFFERENT SOFTNESS MEASUREMENTS

5.1 Introduction

The substantial constituent of leather is collagen which is a natural polymer comprising various amino acid residues containing many amide groups arranged along the backbone chain of the collagen molecule. It is therefore predictable that leather is prone to absorb water

because the amide groups ($\text{-}\overset{\text{O}}{\parallel}\text{C-NH-}$) have strong polarity and can form hydrogen bonds between the oxygen atoms in the carbonyl groups and hydrogen atoms of water. This hydrophilic property of collagen molecules contributes significantly to the comfort of various leather products which is especially important when leather is used as the raw material of attire, shoes, gloves and upholstery. The interaction between water and polymers and its influence on the properties of such materials has been discussed in several papers^[95 - 99] and many works especially concerned with biological or natural materials^[100 - 110] among which are some related to the topic of leather. The water trapped or held in leather plays a significant role in relation to its processing, mechanical properties^[111 - 115] and other properties such as thermal properties^[116]. It has been stated that collagen is capable of various degrees of water binding which differ in respect of the physical properties of the bound water molecules^[113]. It is also apparent that in protein polymers, one of the main functions of water is to act as a plasticiser^[110]. In fact, this function has long been realised and in practice it has been taken advantage of during leather processing. For example, spraying water on crust leather before being subjected to mechanical action (e. g. staking) is often carried out in the tannery because experience shows that a better softening effect is obtained. Although this technique has been applied in leather manufacture, for many years there has been no quantitative investigation of how the water content prior to staking influences the softening effect on leather in such a mechanical action. If water content does affect the softening result, the optimum water content prior to staking is yet unknown.

In this chapter, the influence of water content prior to staking on the effectiveness of mechanical softening is investigated. Different softness measurements were applied in order

to assess their sensitivity to water content prior to staking, and to allow comparison between these methods of softness evaluation.

5. 2 Experimental

5. 2. 1 Instrumentation and Materials

5. 2. 1. 1 Instrumentation

Staking action was carried out on a Cartigliano model PAL160 staking machine. Further details are given in section 2. 2. 1. 2.

All mechanical deformation measurements used an Instron 1122 Universal Tester.

Differential Scanning Calorimetry (DSC) technique was used to measure the amount of freezable water in wet leather. The model of the DSC apparatus was a Mettler TC10A*.

Humidity cabinets were used for adjusting the water content in the leather by means of a controlled relative humidity atmosphere (see 2. 2. 1. 3).

5. 2. 1. 2 Materials

Three types of leather were involved in the work reported in this chapter:

- (1) 2 whole hides (batch (I) and batch (II))of unfatliquored crust leather prepared by the method described in 2.1.1 and further divided into 2 mirror sections by cutting along the backbone. One half was used as the control sample and the other as the experimental sample which was adjusted to different water contents prior to staking action. It was assumed that samples cut in the same position on opposite sides of the backbone would have virtually the same properties and so the effect of staking could be assessed by comparing the control with the experimental samples.
- (2) 2 whole hides (batch (I) and batch (II)) of fatliquored crust leather prepared by the method described in 2.1.1 with same dividing along the backbone as mentioned above.
- (3) BLC samples as described in 2. 1. 3. (N. B. These samples were not used in the staking trials but provided information on the comparative results of different softness measurements.)

* The author is grateful to BLC The Leather Technology Centre for use of this apparatus.

5. 2. 2 Experimental Design

5. 2. 2. 1 Sampling Method

The sampling method for the unfatigued and fatigued leather mentioned in 5. 2. 1. 2 is illustrated in *Figure 4.2* in *Chapter 4* and *Figure 5.1* as follows. The sample size for all the bending tests was:

$$\text{length } (L) \times \text{width } (w) = 50 \text{ mm} \times 25 \text{ mm}$$

The effective length (l), i.e. the distance between the 2 supporting rollers (see *Figure 2.4*), was set as 30 mm. The size of the dumb-bell shaped sample for all the tensile tests was:

$$\text{length } (L) \times \text{width } (w) = 90 \text{ mm} \times 10 \text{ mm}$$

The effective length (l), i.e. the distance between the 2 grips (see *Figure 2.1*), was 50 mm.

The diameter (D) of the disc-shaped sample for the compression tests was 14 mm, the effective diameter (d), i.e. the diameter of the compressing probe, was 10.92 mm, the effective compressed area was 93.69 mm².

All the size parameters and the codes for the test samples are listed in table 5.1, table 5.2 and table 5.3 for unfatigued, fatigued and BLC samples respectively.

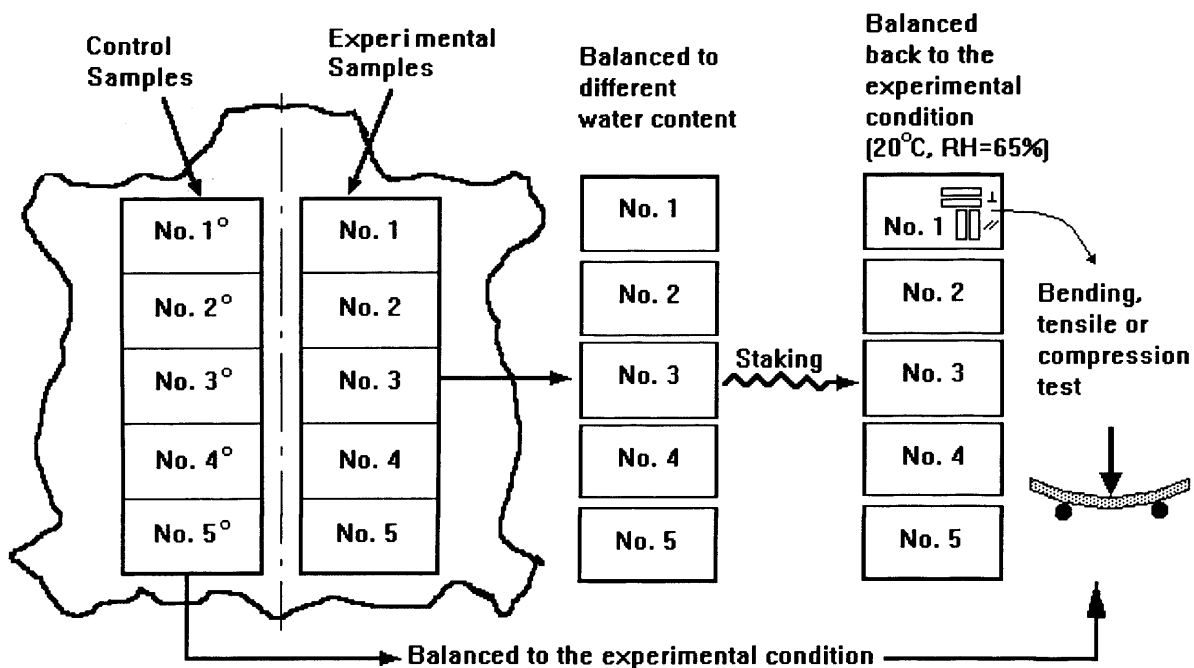


Figure 5. 1 The sampling scheme for water content - staking investigations (5 or 6 pieces)

The code for each sample is arranged in the order of experiment type – status of fatiguor – hide batch number (Roman number) – sample number. The control sample has a “°” symbol at the upper right corner of the sample number. Abbreviations used are:

B — bending test

T — tensile test

C — compression test

UF — unfatliquored crust leather

FL — fatliquored crust leather

H — hide (batch)

° — control sample

For example: B/UF/H(I)/2° means:

Bending test/Unfatliquored/Hide batch (I)/Control sample No.2

and T/FL/H(II)/3 means:

Tensile test/Fatliquored/Hide batch (II)/Experimental sample No.3.

Table 5.1 Sample parameters and codes for unfatliquored leather

Hide batch No.	UF sample No.	Thickness t / mm								Compression
		Bending				Tensile				
		// ₁	// ₂	⊥ ₁	⊥	// ₁	// ₂	⊥ ₁	⊥ ₂	
(I)	1°	2.01	2.09	1.98	2.05	1.85	1.86	1.88	1.93	1.98
	2°	1.84	2.02	2.24	2.33	2.07	2.19	2.28	2.28	2.46
	3°	2.51	2.57	2.63	2.71	2.48	2.43	2.51	2.55	2.64
	4°	2.58	2.36	2.48	2.45	2.67	2.62	2.60	2.61	2.70
	5°	2.67	2.65	2.60	2.63	2.54	2.65	2.46	2.52	2.86
	6°	2.61	2.62	2.67	2.61	2.42	2.48	2.69	2.62	2.89
(II)	1°	1.97	2.06	1.96	2.03	1.89	1.82	1.77	1.82	1.88
	2°	2.44	2.45	2.45	2.45	2.20	2.20	2.34	2.38	2.38
	3°	2.55	2.53	2.59	2.64	2.50	2.49	2.55	2.54	2.66
	4°	2.29	2.41	2.41	2.56	2.24	2.26	2.32	2.35	2.44
	5°	2.57	2.45	2.69	2.70	2.46	2.56	2.56	2.56	2.61
	6°	2.51	2.58	2.70	2.44	2.33	2.38	2.44	2.49	2.68
(I)	1	1.41	1.43	1.56	1.53	1.43	1.44	1.43	1.49	1.64
	2	1.47	1.52	1.58	1.61	1.58	1.61	1.54	1.63	1.75
	3	2.19	2.31	2.22	2.23	2.19	2.23	2.08	2.17	2.33
	4	2.24	2.25	2.50	2.39	2.41	2.50	2.46	2.49	2.64
	5	2.55	2.36	2.31	2.42	2.36	2.33	2.34	2.36	2.43
	6	2.58	2.50	2.54	2.48	2.59	2.69	2.61	2.74	2.64
(II)	1	1.75	1.75	1.63	1.73	1.58	1.63	1.66	1.67	1.75
	3	2.06	2.08	2.16	2.13	2.09	2.02	2.07	2.09	2.13
	4	1.98	2.02	2.05	2.11	2.00	2.08	2.25	2.09	2.13
	5	2.13	2.14	2.15	2.21	1.96	2.05	2.16	2.07	2.29
	6	2.02	1.88	2.05	2.17	2.06	2.03	2.18	2.11	2.16

Table 5.2 Sample parameters and codes for fatliquored leather

Hide batch No.	FL sample No.	Thickness t / mm								Compression
		Bending				Tensile				
		// ₁	// ₂	⊥ ₁	⊥	// ₁	// ₂	⊥ ₁	⊥ ₂	
(I)	1°	1.93	1.86	1.94	1.87	1.98	1.84	1.90	1.89	2.05
	2°	1.69	1.80	1.86	1.93	1.69	1.74	1.73	1.75	1.86
	3°	2.42	2.30	2.36	2.52	2.23	2.21	2.27	2.28	2.32
	4°	2.07	1.27	2.25	2.17	2.00	2.17	2.14	2.11	2.34
	5°	1.81	1.89	1.82	2.01	1.65	1.67	1.98	1.80	1.78
(II)	1°	1.94	1.89	1.88	1.93	1.85	1.88	1.77	1.79	2.09
	2°	2.22	2.19	2.08	2.12	1.91	1.90	1.81	1.93	2.25
	3°	2.05	2.13	2.14	2.14	2.44	2.23	2.20	2.11	2.26
	4°	2.19	2.32	2.30	2.46	2.20	2.21	2.41	2.43	2.46
	5°	2.10	2.26	2.46	2.29	2.25	2.24	2.24	2.28	2.46
	6°	2.26	2.27	2.22	2.23	2.04	2.21	2.32	2.21	2.35
(I)	1	1.70	1.67	1.65	1.67	1.73	1.73	1.76	1.75	1.93
	2	1.49	1.52	1.42	1.49	1.62	1.52	1.48	1.48	1.70
	3	2.04	1.98	1.96	1.79	1.95	1.96	1.99	1.98	2.18
	4	1.84	1.82	1.85	1.87	2.02	1.96	1.97	1.88	2.08
	5	1.97	1.89	2.06	2.15	1.81	1.79	1.80	2.15	2.40
(II)	1	2.17	2.10	2.07	2.05	1.99	1.98	1.89	2.03	2.23
	3	1.99	2.06	2.18	2.28	2.02	2.03	2.14	2.18	2.34
	4	2.48	2.54	2.47	2.53	2.32	2.41	2.40	2.46	2.79
	5	2.02	2.20	2.31	2.26	2.36	2.42	2.22	2.26	2.46
	6									

Table 5.3 Sample parameters and codes for BLC leather samples

No. of samples	Thickness t / mm			
	Bending *	Tensile *		Compression **
		1 [#]	2 [#]	
1	1.103	1.097	1.090	1.261
2	0.980	0.950	0.950	1.104
3	1.040	1.057	1.043	1.268
4	1.130	1.140	1.160	1.342
5	1.067	1.133	1.133	1.232
6	1.423	1.453	1.447	1.687
7	1.330	1.317	1.320	1.582
8	1.078	1.14		1.247

* Thickness of samples in bending and tensile tests were measured under standard thickness tester.

** Thickness of samples in compression tests were measured under an initial force of 0.4 N.

5. 2. 2. 2 Preparing Samples with Different Water Contents Prior to Staking

Samples with different water content were prepared in the way described in 2. 2. 1. 3.

5. 2. 2. 3 Measuring Methods

- (1) Measurement of water content is described in section 2. 2. 1. 3.
- (2) Bending experiment (see section 2. 2. 1. 1— 2)), cross head speed 50 mm min⁻¹, bending length l 30 mm, width w 25 mm, maximum bending depth d 6.5~7 mm, data sampling frequency 10~30 Hz
- (3) Tensile experiment (see section 2. 2. 1. 1— 1)), cross head speed 100 mm min⁻¹, data sampling frequency 10~30 Hz
- (4) Compression experiment (see section 2. 2. 1. 1— 3)), cross head speed 0.05 mm min⁻¹, data sampling rate 5~20 s⁻¹.
- (5) Freezable water measurement — DSC. Temperature reduced from 35°C to -50°C at a speed of 5°C min⁻¹, held 3 minutes at -50°C, and increased back to 35°C at a speed of 3°C min⁻¹. Freezable water on a dry basis was calculated as follows:

$$\text{Freezable water content (dry basis)} = \frac{\sum \Delta H_i}{\Delta H_0} \times \frac{(1 + \eta_d)}{w_{ws}} 100\%$$

where $\sum \Delta H_i$ is the sample's endothermic enthalpy from the DSC curve, J/g, ΔH_0 is the standard fusion enthalpy of pure water, 333.4J/g, η_d is the water content on dry basis, %, and w_{ws} is the weight of wet sample. For deduction of this equation, see *Appendix V*.

5. 3 Results

5. 3. 1 Water

5. 3. 1. 1 Water Content

Water contents for control samples and experimental samples of fatliquored and unfatliquored leather are listed in table 5.4 and table 5.5.

5. 3. 1. 2 Water Content Against Wet and Dry Basis

In addition to fatliquors added purposely during leather processing, leather itself also contains a certain amount of fat although it is intended that most of this fat is removed during the early stage of the leather making process in the tannery. It was necessary to know exactly the amount of fats and other dichloromethane soluble substances in both fatliquored and unfatliquored leather. The fats were assayed according to the standard IUC/4 procedure^[117].

The results are also listed in table 5.4 and table 5.5. The water absorption on different dry bases, i.e. either on a basis of “leather + fat” (referred to as **dry basis** later) or a basis of “leather only” (referred to as **dry leather basis** later), is illustrated in *Figure 5.2* and *Figure 5.3*.

Table 5.4 Water contents of UF for bending, tensile and compression

Unfatliquored leather			
Sample code	R.H% in the cabinet	Water content % (dry leather basis)	Water content % (dry basis (leather + fat))
UF/H(I)/1	50.0	20.19	19.83
UF/H(I)/2	64.0	26.43	25.95
UF/H(I)/3	75.0	31.25	30.70
UF/H(I)/4	85.0	37.88	37.14
UF/H(I)/5	97.0	55.23	54.24
UF/H(I)/6	spreading water		75.40
UF/H(II)/1	97.0		54.24
UF/H(II)/2	—		—
UF/H(II)/3	soaked		83.60
UF/H(II)/4	soaked		93.40
UF/H(II)/5	soaked		100.7
UF/H(II)/6	soaked		120.7

Table 5.5 Water contents of FL for bending, tensile and compression

Fatliquored leather			
Sample code	R.H% in the cabinet	Water content % (dry leather basis)	Water content % (dry basis (leather + fat))
FL/H(I)/1	42.0	16.95	14.59
FL/H(I)/2	64.0	27.03	24.28
FL/H(I)/3	75.0	31.70	27.29
FL/H(I)/4	85.0	35.44	30.51
FL/H(I)/5	100.0	63.88	55.00
FL/H(II)/1	97.0		52.20
FL/H(II)/2	—		—
FL/H(II)/3	soaked		82.00
FL/H(II)/4	soaked		103.0
FL/H(II)/5	soaked		87.00
FL/H(II)/6	—		—

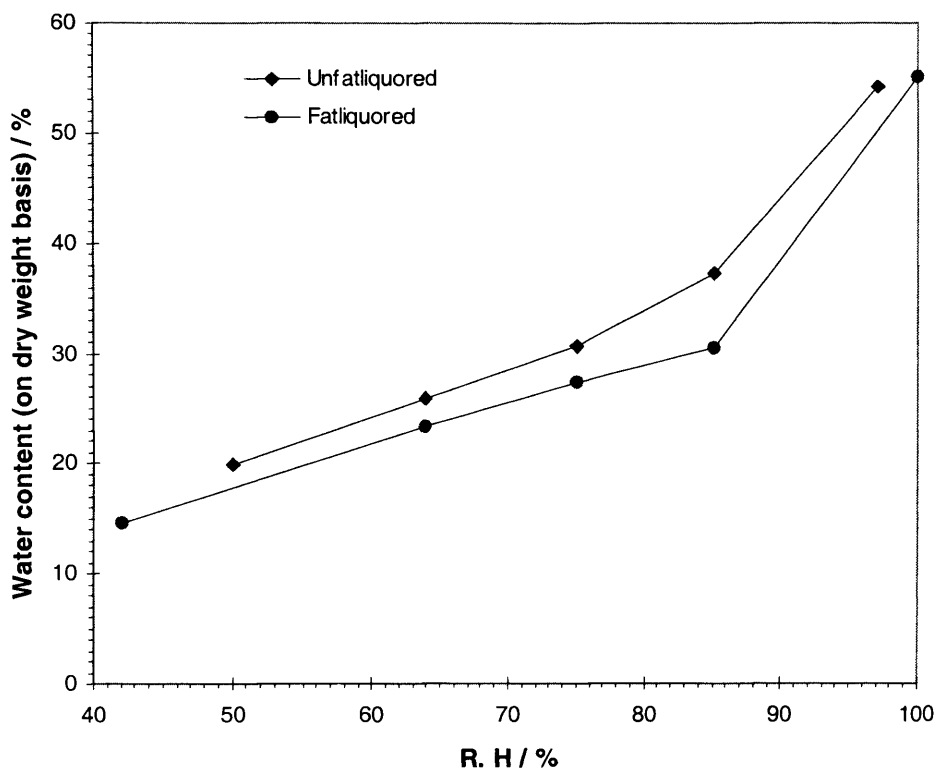


Figure 5. 2 Water content (dry basis) obtained from different relative humidity.

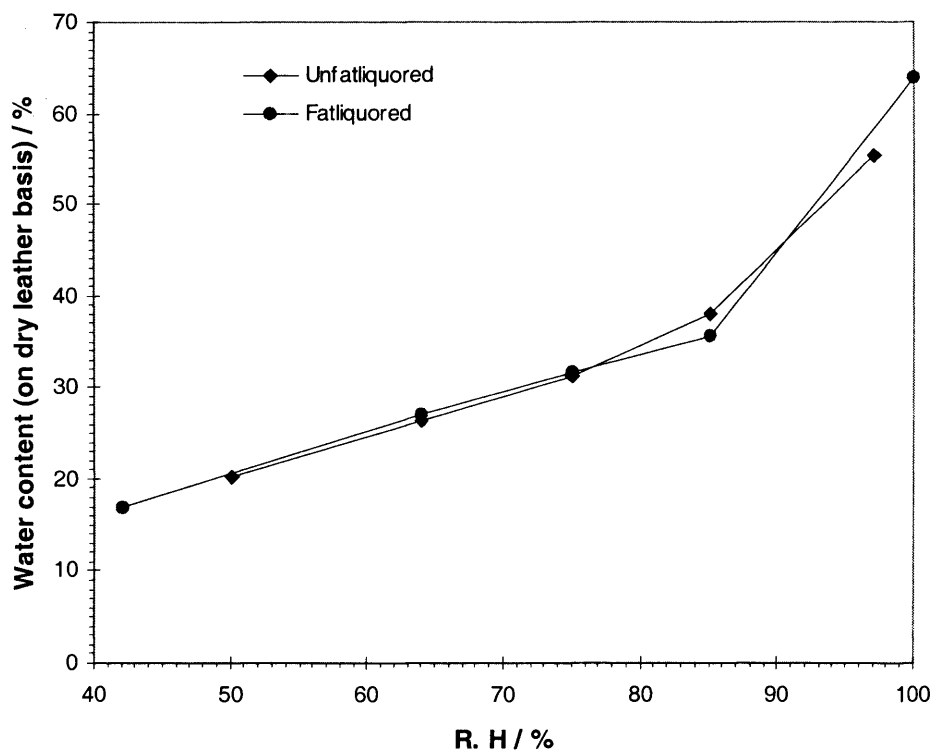


Figure 5. 3 Water content (dry leather basis) obtained from different relative humidity.

5. 3. 1. 3 DSC Results

DSC results for freezable water are given in table 5.6 and original DSC traces shown in *Figure 5.4 (a) and (b)*. The relationship between the amount of freezable water and the total water content is shown by *Figure 5.5*.

Table 5.6 Freezable water content detected by DSC

Unfatliquored, water content % (dry basis)		Fatliquored water content % (dry basis)	
Total	Freezable	Total	Freezable
27	0	44.8	0
54	0	60.4	1.11
66	0.45	70.4	2.02
75	0.92	80.0	2.41
80	2.05		
85	2.32		

5. 3. 2. Unfatliquored Leather

Typical results from different deformation tests are presented below. The examples represent “standard” moisture content (26% on dry basis) material obtained by conditions at 65% RH and 20°C.

5. 3. 2. 1 Bending

Typical bending results from control samples (before staking) and experimental samples (after staking) for unfatliquored leather are given in *Figures 5.6(1) and (2)*, with noticeable differences in both forces required at a given depth, and the shape of the bending curve.

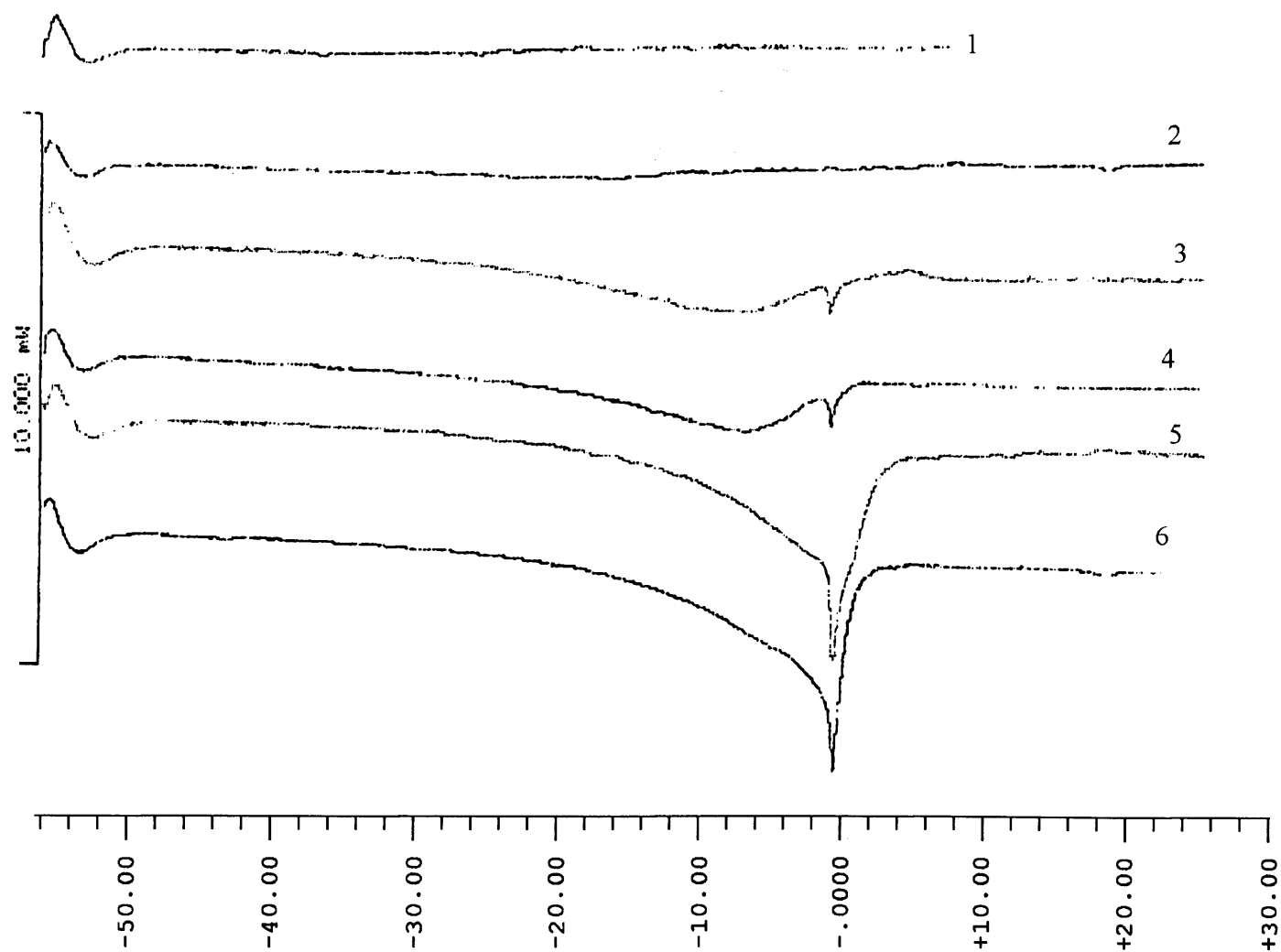
5. 3. 2. 2 Tensile

Typical tensile results (stress-strain curves) for a control sample and an experimental sample are shown in *Figures 5.7(1) and (2)*. A noticeable change in the low strain area is observed where the concave shape at about 5~10% strain in the control sample disappeared after staking.

5. 3. 2. 3 Compression

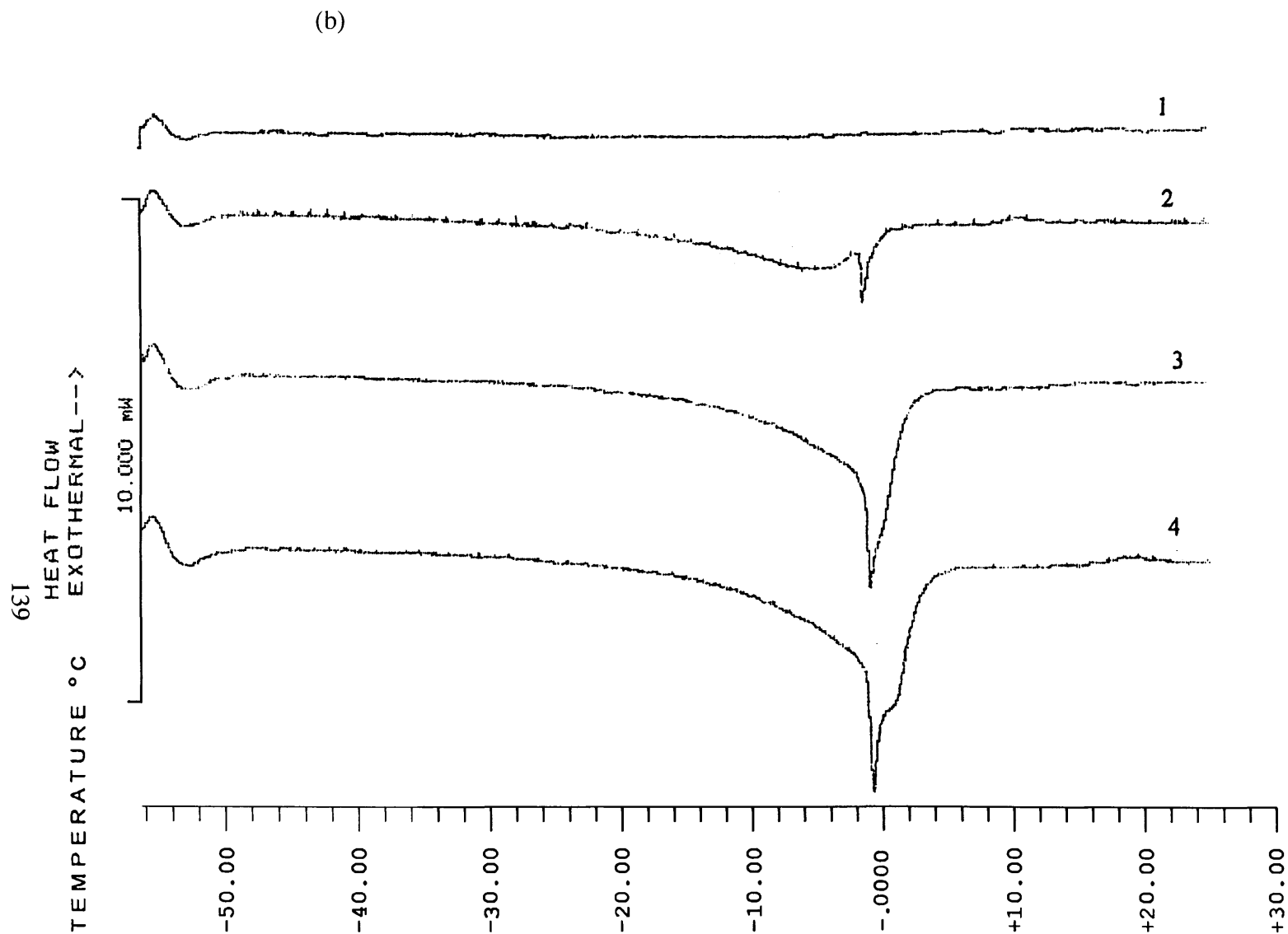
Typical compression results for control samples and experimental sample are shown in *Figure 5.8(1) and (2)*, although all the compression results have been listed in *Chapter 4, Figure 4.10 and Figure 4.11*.

HEAT FLOW
EXOTHERMAL -->
TEMPERATURE °C



No. of curves	Water content, %, (on dry basis)	
	Total	Freezable
1	27	0
2*	54	0
3	66	0.45
4	75	0.92
5	80	2.05
6	85	2.32

* There is a slight bending trend along the whole curve, but this is not taken as the contribution of water.



No. of curves	Water content, %, (on dry basis)	
	Total	Freezable
1	44.8	0
2	60.4	1.11
3	70.4	2.02
4	80.0	2.41

Figure 5. 4 DSC curves of leather samples with different water content. (a) - Unfatliquored samples (b) - Fatliquored samples

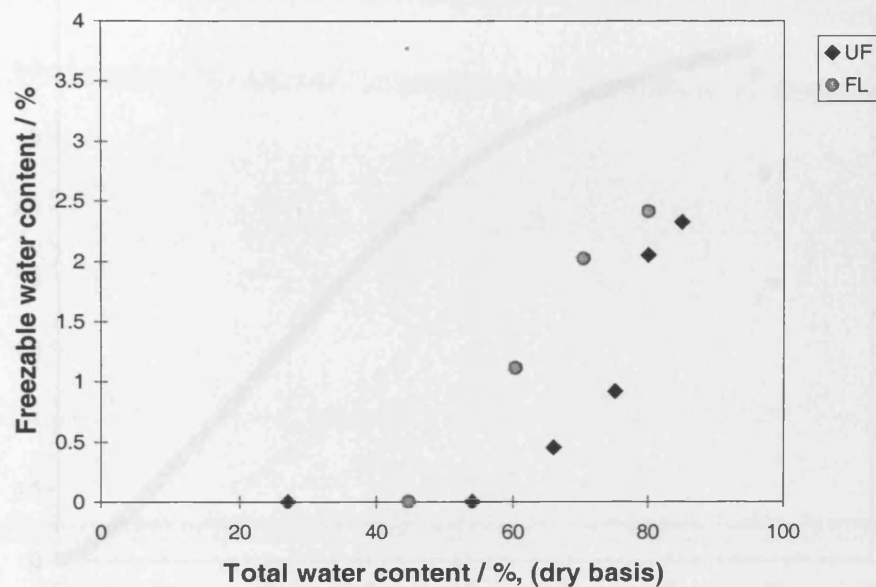


Figure 5. 5 Freezable water detected by DSC against total water content in the leather sample.

5. 3. 3 Fatliquored Leather Samples

Typical results from different deformation tests for fatliquored leather are listed below. (Results are from samples balanced in the conditioning room (20°C, R.H = 65%) and the water content is 26% on a dry basis).

5. 3. 3. 1 Bending

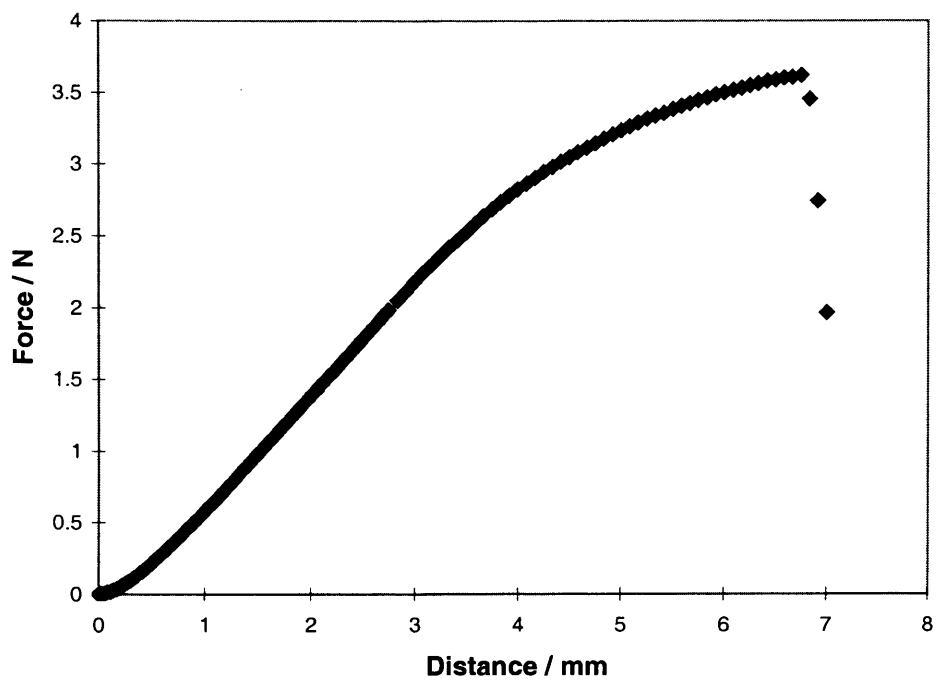
Bending results for fatliquored leather before and after staking (control and experimental samples) are given in *Figure 5.9 (1) and (2)*.

5. 3. 3. 2 Tensile

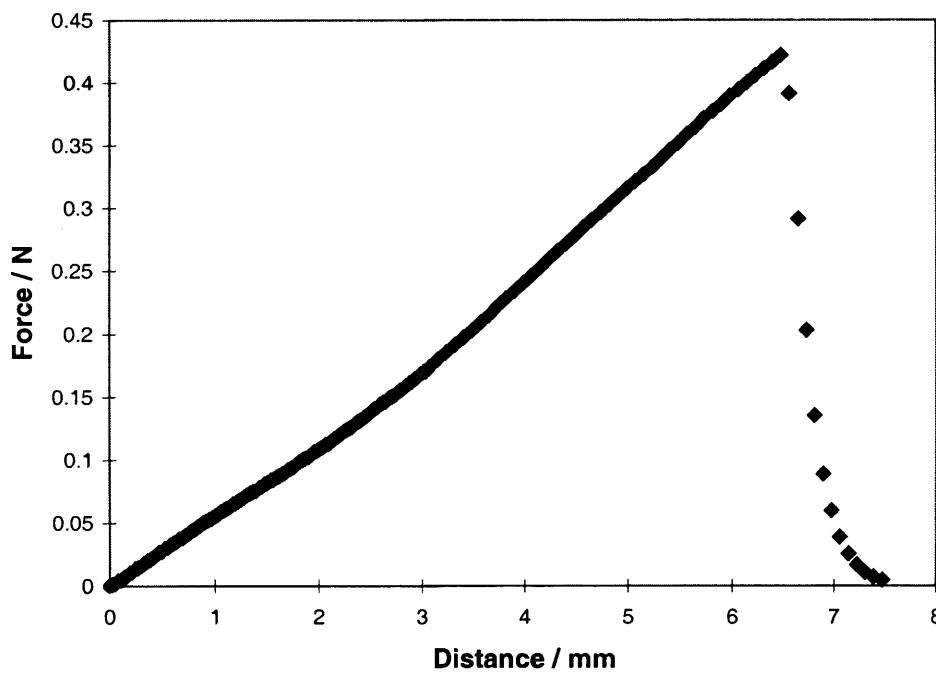
Tensile results for fatliquored leather before and after staking (control and experimental samples) are given in *Figure 5.10 (1) and (2)*.

5. 3. 3. 3 Compression

Compression curves for the fatliquored samples prior to and after staking are shown in *Figure 5.11 (1) and (2)*.

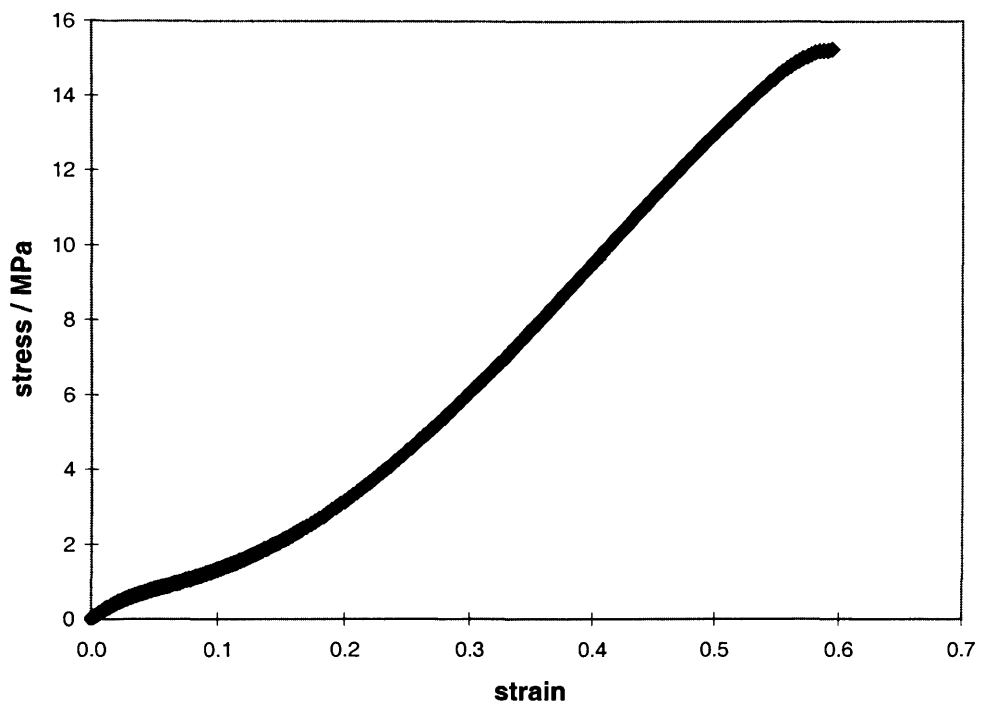


(1)

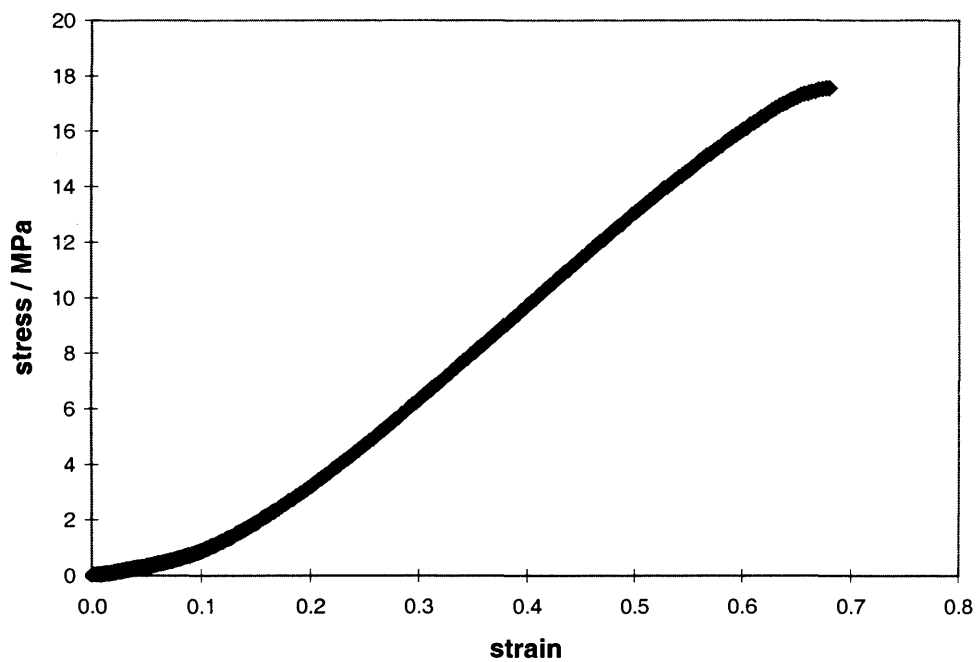


(2)

Figure 5. 6 Bending curves of unfatigued leather before and after staking. (1) - control sample, code B/UF/H1/2⁰//₁ (2) - test sample code B/UF/H1/2//₁



(1)



(2)

Figure 5. 7 Stress-strain curves of unfatigued leather before and after staking. (1) - control sample, code T/UF/H1/2⁰//₁ (2) - test sample code T/UF/H1/2⁰//₁

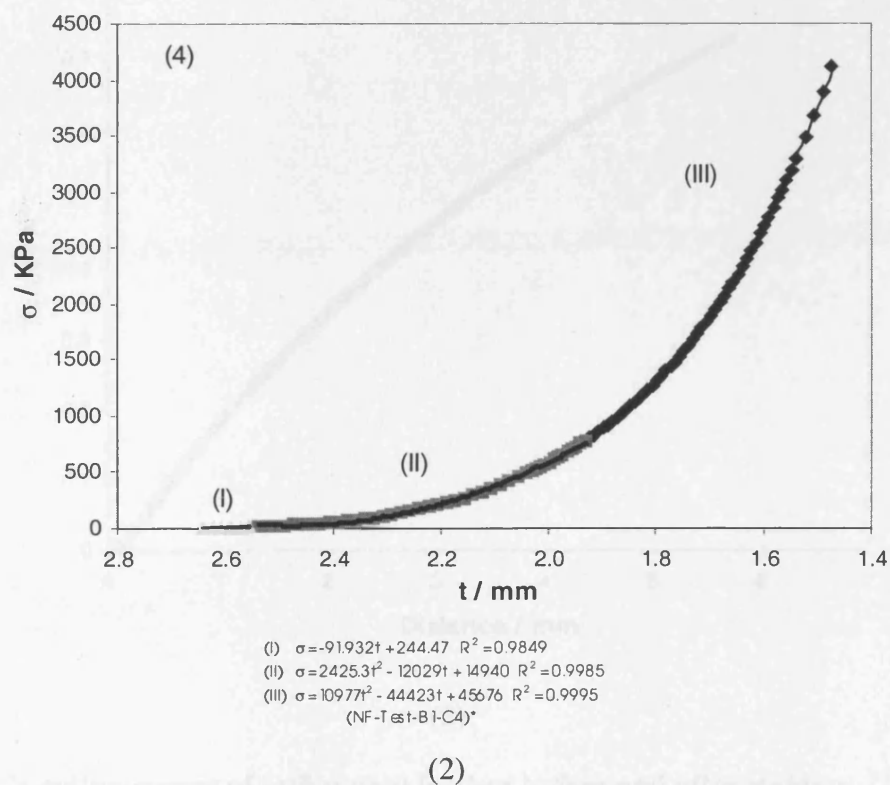
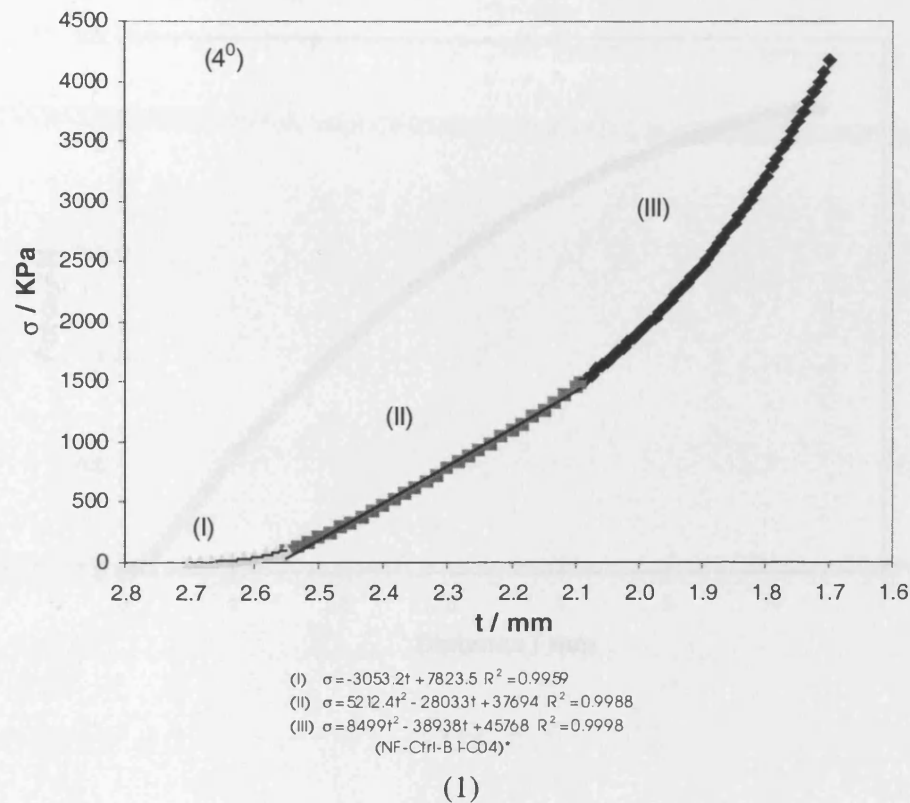
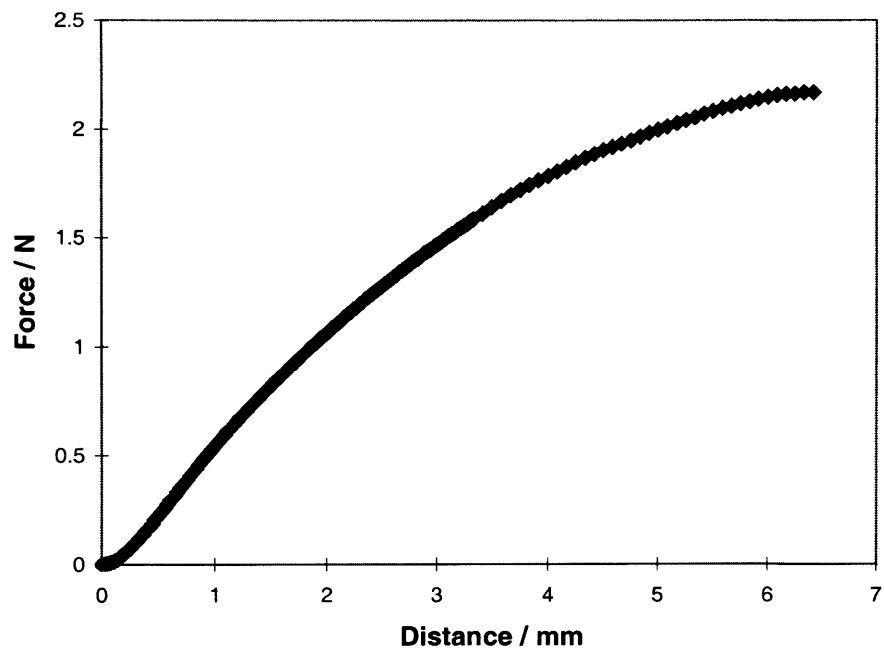
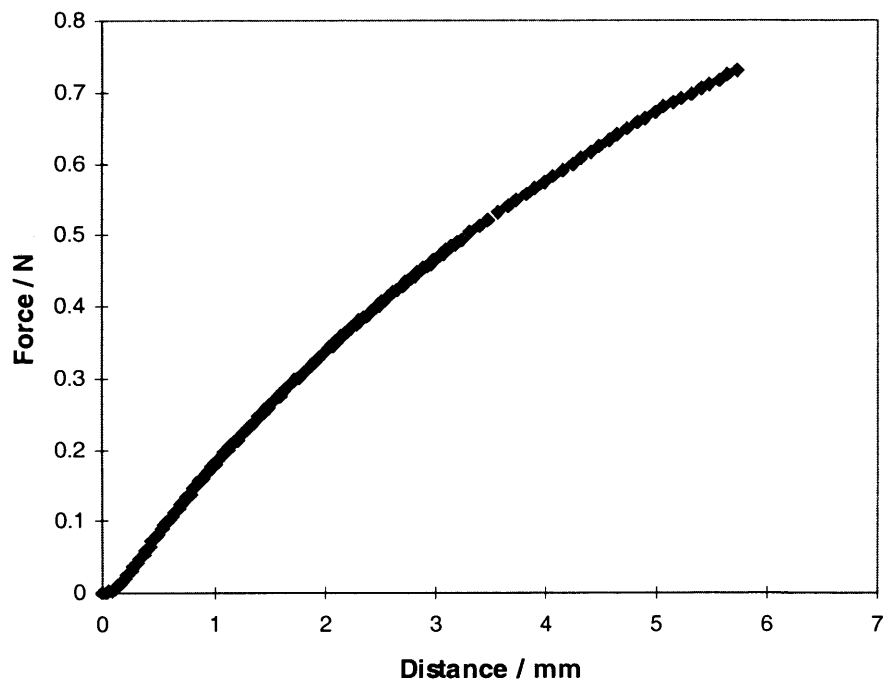


Figure 5. 8 Compression curves of unfatliquored leather before and after staking. (1) - control sample, code C/UF/H1/4⁰ (2) - test sample code C/UF/H1/4

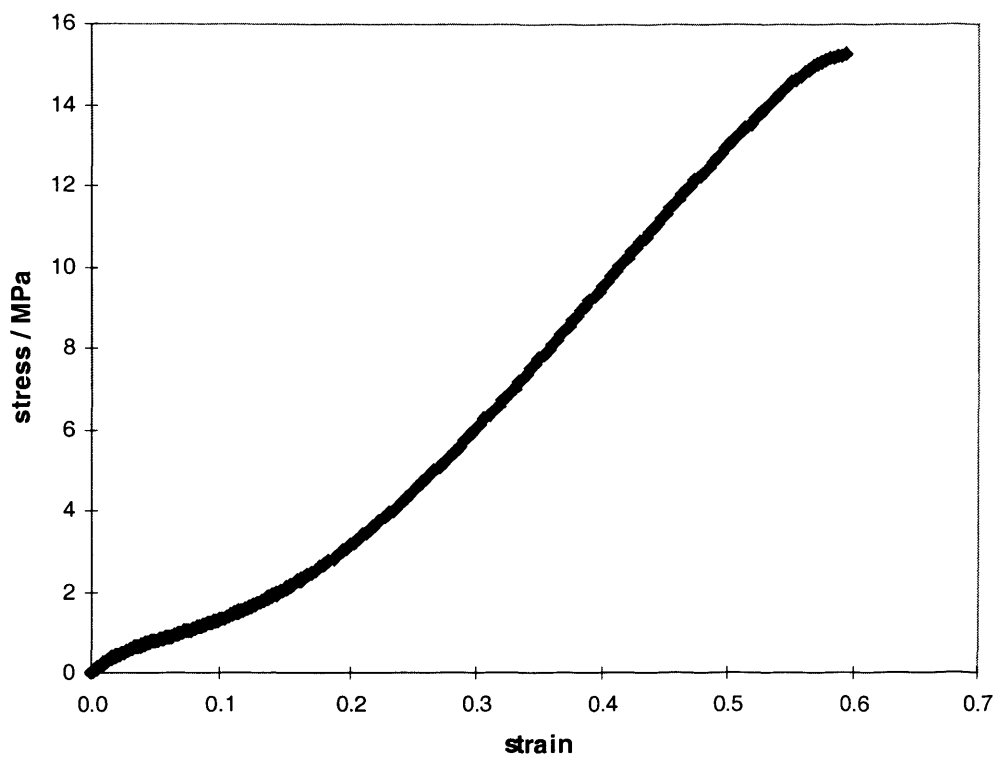


(1)

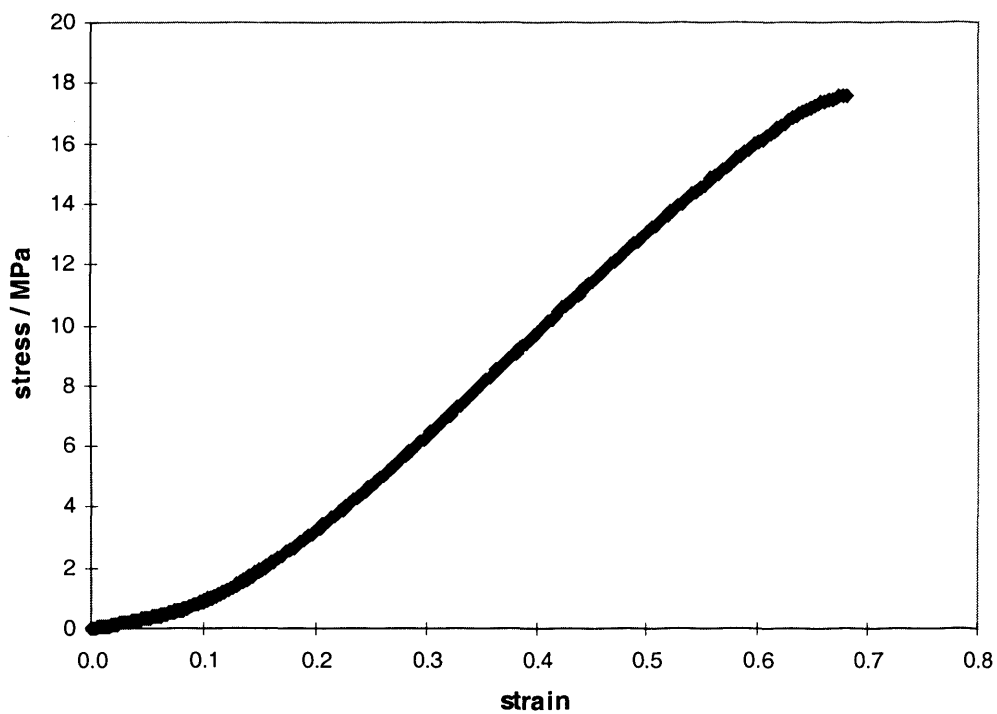


(2)

Figure 5. 9 Bending curves of fatliquored leather before and after staking. (1) - control sample, code B/FL/H1/2⁰//₁ (2) - test sample code B/F/H1/2//₁

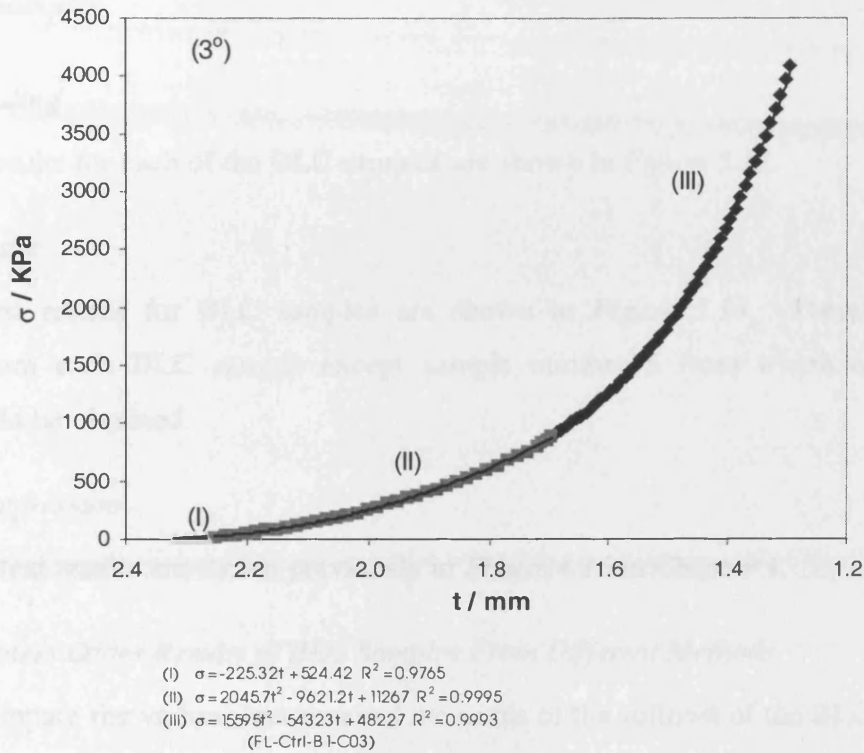


(1)

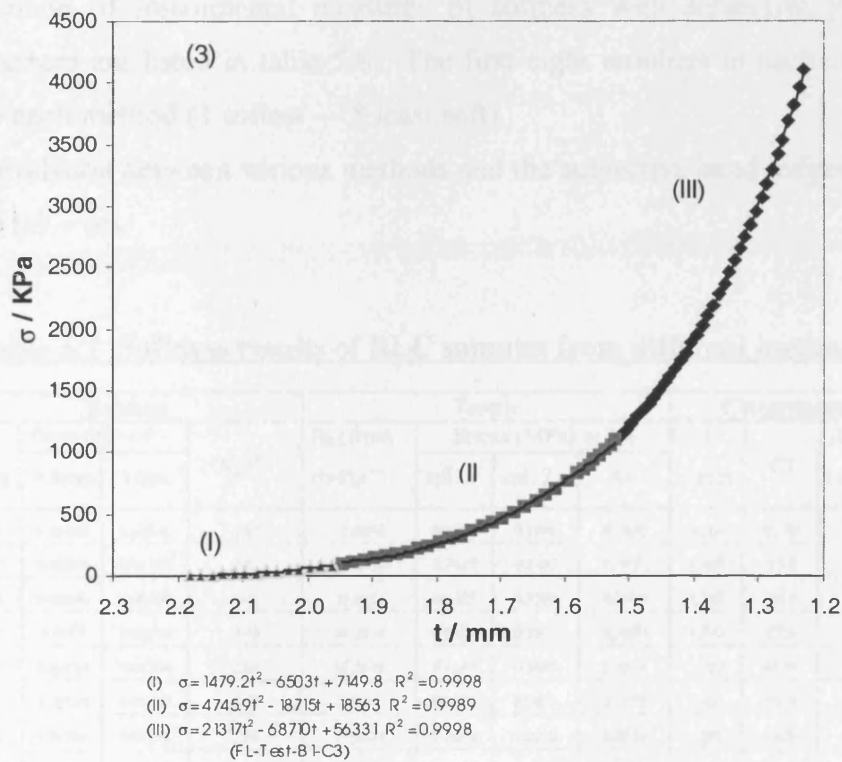


(2)

Figure 5. 10 Stress-strain curves of fatliquored leather before and after staking. (1) - control sample, code T/FL/H1/2⁰//₁ (2) - test sample code T/FL/H1/2//₁



(1)



(2)

Figure 5. 11 Compression curves of fatliquored leather before and after staking. (1) - control sample, code C/FL/H1/3⁰ (2) - test sample code C/FL/H1/3

5. 3. 4 BLC Samples *

5. 3. 4. 1 Bending

Experiment results for each of the BLC samples are shown in *Figure 5.12*.

5. 3. 4. 2 Tensile

All tensile test results for BLC samples are shown in *Figure 5.13*. There were 2 test specimens from each BLC sample except sample number 8 from which only one test specimen could be obtained.

5. 3. 4. 3 Compression

Compression test results are shown previously in *Figure 4.15* in *Chapter 4*.

5. 3. 4. 4 Softness Order Results of BLC Samples From Different Methods

In order to compare the various instrumental measures of the softness of the BLC samples, all results from these methods are listed in table 5.7.

Comparison of instrumental measures of softness with subjective judgements by experienced tanners are listed in table 5.8. The first eight numbers in each column are the rank orders by each method (1 softest — 8 least soft).

The correlation between various methods and the subjective hand judgement is shown in *Figure 5.14 (a) ~ (e)*.

Table 5.7 Softness results of BLC samples from different methods

Sample No.	Bending				Tensile				Compression			Sub- jective judgement [†]
	<i>t</i> / mm	Force (N) at <i>d</i> =		<i>S_e</i> / <i>t</i> ^{1.5}	<i>E</i> ₀ (from $\sigma=E_0\epsilon^n$)	Stress (MPa) at 3%			<i>t</i> / mm	<i>CI</i>	ΔE /(J×10 ⁴)	
		0.5mm	1mm			spl. 1	spl. 2	Av.				
1	1.103	0.00459	0.00945	1.67	13.0858	0.1721	0.1898	0.1810	1.261	67.75	204	2
2	0.980	0.00510	0.01115	2.61	8.1524	0.2437	0.2483	0.2460	1.104	65.5	198	5
3	1.040	0.00246	0.00909	1.46	15.5124	0.3485	0.3503	0.3494	1.268	94.5	52	1
4	1.113	0.0077	0.01866	3.44	47.1014	0.5168	0.5931	0.5550	1.342	57.5	192	3
5	1.067	0.00776	0.01734	3.69	17.2449	0.4264	0.3680	0.3972	1.232	67.75	200	6
6	1.423	1.00754	0.01517	1.68	2.8714	0.0867	0.0803	0.0835	1.687	56.75	301	7
7	1.330	0.00701	0.01681	3.50	87.4022	0.2076	0.2012	0.2044	1.582	66.0	277	4
8	1.078	0.02121	0.05333	14.4	37.6549	0.7175	---	0.7175	1.247	55.25	569	8

* See 2. 1. 3 for the sample source.

[†] 1 to 8 = softest to hardest in the set

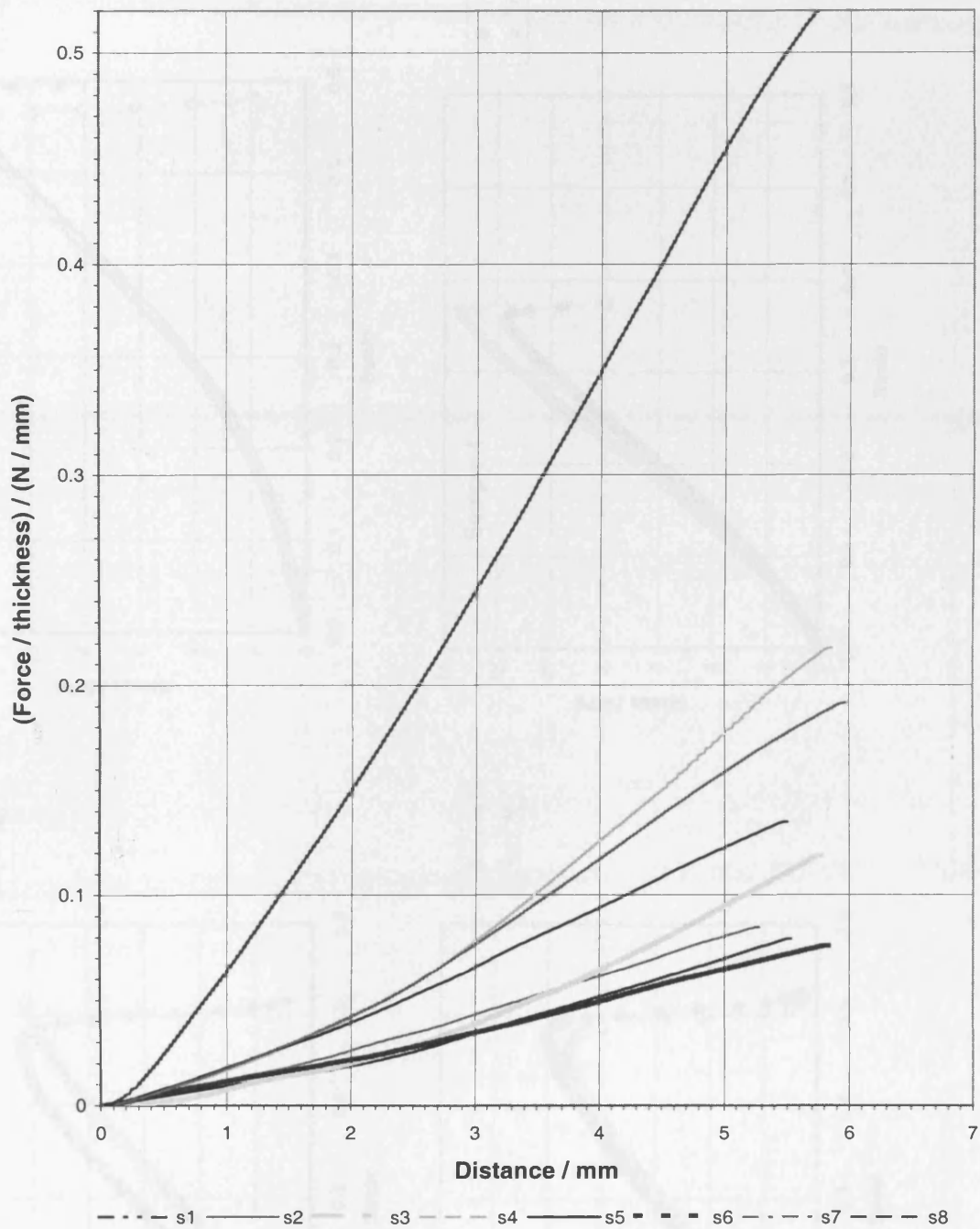
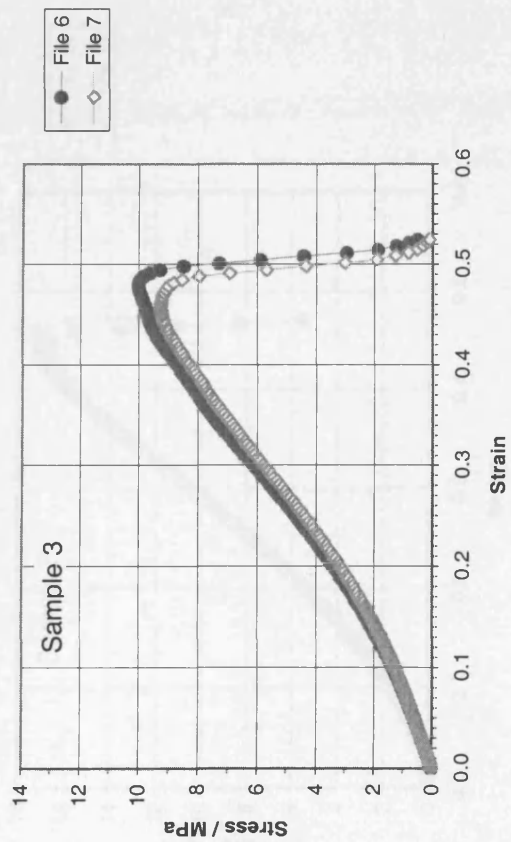
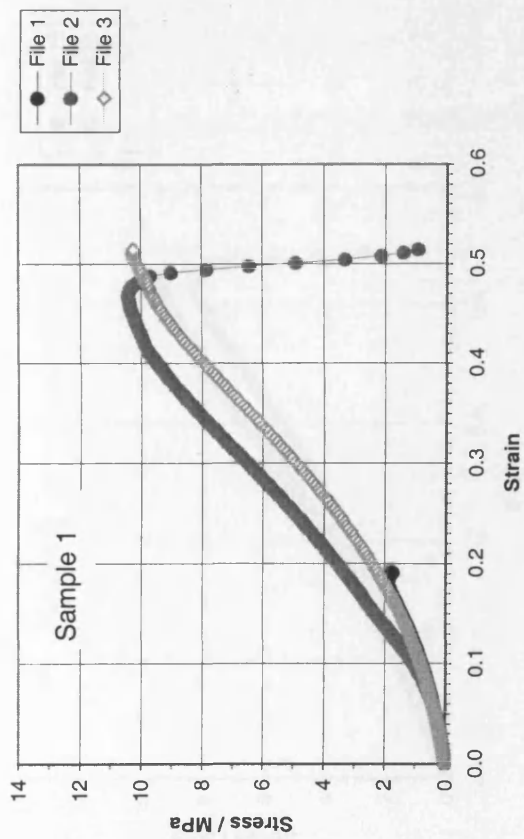
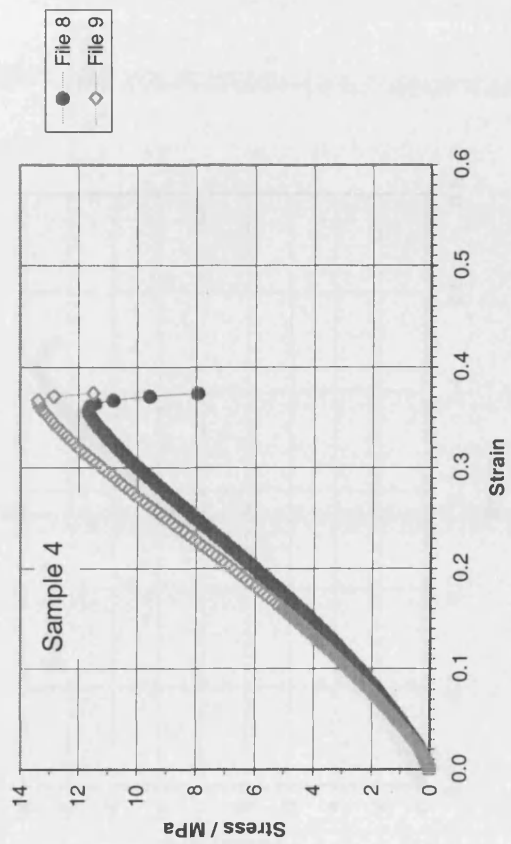
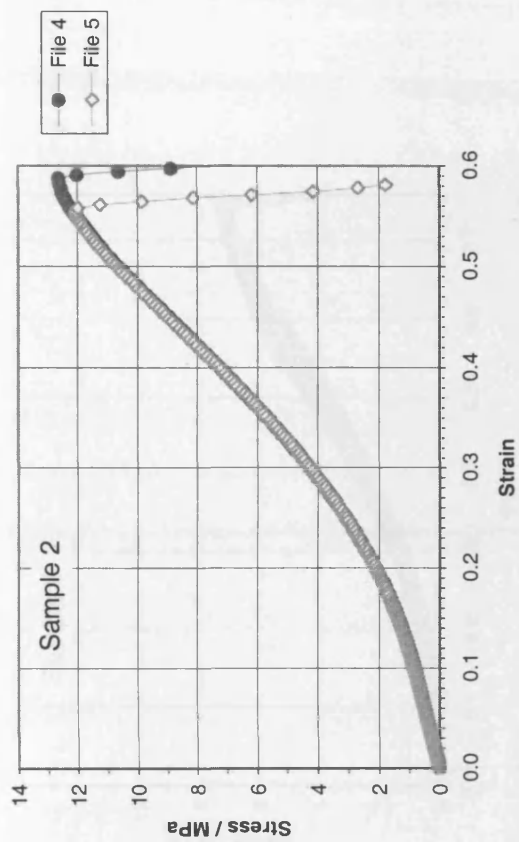


Figure 5. 12 Bending test results of samples from BLC.



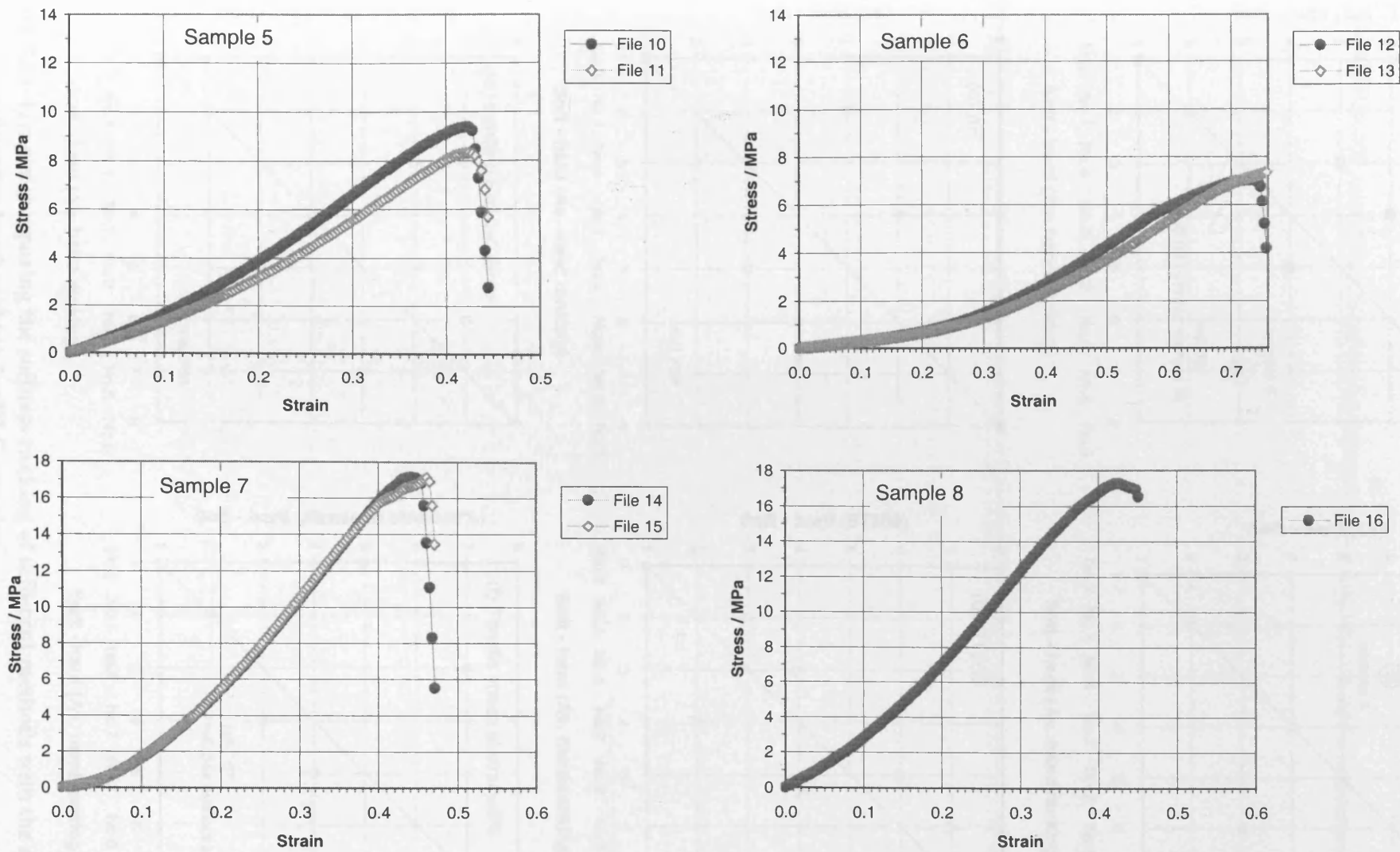


Figure 5. 13 All the tensile test results of BLC samples. Each sample contains 2 testing specimen except sample 8.

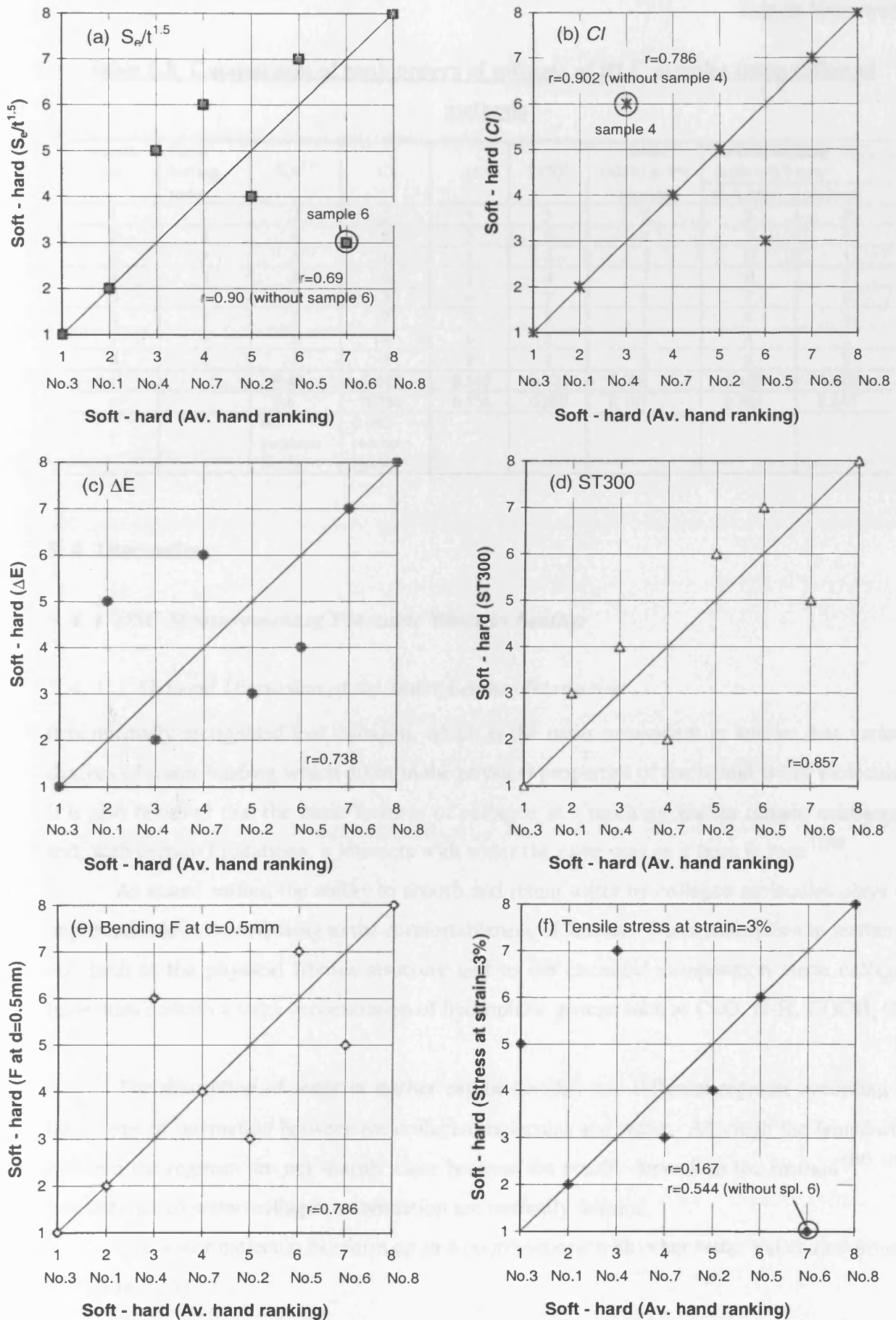


Figure 5.14 Graphs comparing the softness ranking of different methods with the average subjective hand ranking for BLC samples.

Table 5.8 Comparison of rank orders of softness of BLC samples using different methods

Sample No.	Hand feeling order	$S_e/t^{1.5}$	CI	ΔE	ST300	Stress (MPa) at 3% (tensile)	Force at bending depth = 0.5 mm	
							d=0.5mm	d=1mm
1	2	2	2	5	3	2	2	2
2	5	4	5	3	6	4	3	3
3	1	1	1	1	1	5	1	1
4	3	5	6	2	4	7	6	7
5	6	7	3	4	7	6	7	6
6	7	3	7	7	5	1	5	4
7	4	6	4	6	2	3	4	5
8	8	8	8	8	8	8	8	8
r^2		0.48	0.617	0.545	0.735	0.028	0.617	0.413
r		0.6	0.786	0.738	0.857	0.167	0.786	0.643
r		0.9 (without No.6)	0.902 (without No. 4)					

5. 4 Discussion

5. 4. 1 DSC Measurement of Freezable Water in Leather

5. 4. 1. 1 General Discussion of the Water-Leather Interaction

It is normally recognised that collagen, which is the main component in leather, has various degrees of water binding which differ in the physical properties of the bound water molecules. It is also believed that the basic features of collagen in a resulting leather remain unchanged and, with certain limitations, it interacts with water the same way as it does in hide^[113].

As stated earlier, the ability to absorb and retain water by collagen molecules plays an important role in contributing to the comfortableness of leather. Water absorption in leather is due both to the physical fibrous structure and to the chemical composition since collagen molecules contain a large concentration of hydrophilic groups such as C=O, N-H, COOH, OH etc.

The absorption of water in leather can be divided into different regimes according to the degree of interaction between the collagen molecules and water. Although the boundaries between the regimes are not sharply clear because the results depend on the method^[105, 118], five regimes of water-collagen combination are normally defined.

One water molecule can form up to 4 coordinations with other water molecules around it (Figure 5.15)

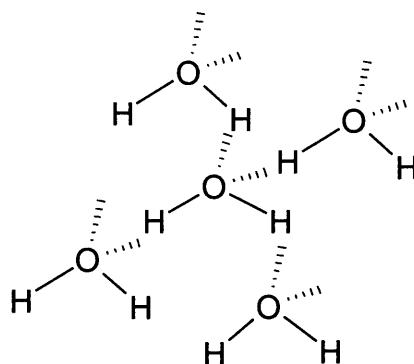


Figure 5.15 Illustration of the 4 coordinations formed around a water molecule.

The first type of water, which is up to 1~2% on a dry collagen basis, is bonded to the collagen triple helix by forming three hydrogen bonds, one of which involves the engagement

with a hydroxyl group on the hydroxyl proline residue ($\left[\text{N} - \text{CH}_2 - \text{CH}(\text{OH}) - \text{C}(=\text{O}) \right]$). This type of

water does not freeze and can not be extracted at room temperature under vacuum.

The second type of water is bound to collagen molecules by two hydrogen bonds. This type of water forms up to 7% moisture content on a dried collagen basis, and forms interchain hydrogen bonds. This water does not freeze either. These molecules correspond to the first type of water molecules that are absorbed after the sample has been kept at room temperature under a vacuum of 10^{-4} Torr. This water does not significantly affect the rigidity modulus of collagen because tropocollagen molecules are rigid rods, and the rigidity of these molecules cannot be greatly increased without the involvement of crosslinking between the rods at this hydration level. However, the appearance of the β peak in the dynamic mechanical spectrum of collagen at this hydration level showed that there is some sort of exchange reaction involving the breaking and re-forming of hydrogen bonds. So this exchange reaction must have happened inside the tropocollagen molecule, i. e, inside the triple helix collagen structure^[105]. Further increase of hydration does not affect the position and amplitude of the β peak indicating a saturation of the water molecules associated with this process.

Beyond this point is the third type of water which ranges between 7~25% on a dry collagen basis. This water is regarded as water located between the triple helices and between

the microfibrils. Water molecules involved in this regime are also bonded to the collagen molecules by forming two hydrogen bonds. There is a large increase in the collagen modulus at low temperature which proves that there is crosslinking between the tropocollagens and microfibrils formed due to the existence of this type of water that forms hydrogen bond linkages between the tropocollagen molecules and between microfibrils. The shifting of the δ peak towards lower temperature in the dynamic mechanical spectrum is due to a further decrease in the intermolecular potential barrier ^[105, 119]. In another explanation the δ peak is interpreted as the association with the oscillations of the proline group, with a decrease of the energy barrier involved in this motion when increasing the hydration level. Such water can freeze below 180°K (-93°C) ^[120] and was described by Berendsen^[121] using a “snake model” (Figure 5.16).

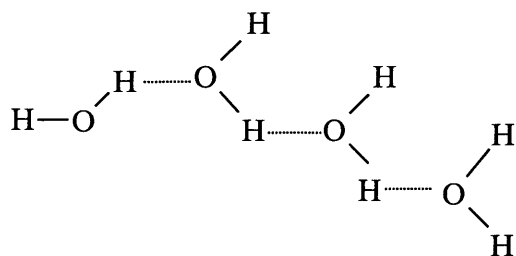


Figure 5.16 “Snake model” of water

Bound water up to an amount of 25~50% on a dry collagen basis is attached to functional groups of side chains and to the peptide bonds. One model explains the fixation of these water molecules between the microfibrils by just one hydrogen bond. Another explanation assigns the fixation of these water molecules inside the hole, length 400 Å, adjacent to the end of tropocollagen. Such water forms an ordered structure around the protein molecules. The γ peak appears around 225 K on the dynamic mechanical spectrum and is associated with the motion of these water molecules ^[105]. The rigidity modulus increases sharply at low temperatures below 180 K but tends to level off at higher ones (above 200 K). From nuclear magnetic resonance (NMR) experiments ^[122] it is concluded that mobile water molecules appear at a concentration of 35% on a dry collagen basis. Such water freezes at about 265 K (-7°C). The latent heat of fusion in this region also shows some differences from bulk water ^[113]. When water concentration reaches 46% (dry collagen basis), there is an abrupt decrease in the sonic velocity – water content plot which led to the conclusion that above this percentage free water molecules exist ^[123].

Above 50% moisture on dry collagen basis water molecules are located between the microfibrils. These water molecules take part in rapid proton exchange with bulk water and the freezing point is 7°C lower than that of the bulk water. The water can be removed mechanically. The rigidity modulus decreases drastically (above 0°C) because water molecules in this status act as a plasticiser ^[113].

5. 4. 1. 2 Analysis of the Experimental Results Obtained from DSC

The DSC results (*Figure 5.4 (a) and (b)* and table 5.6) show that the freezable water content in the leather detectable by the DSC experiment increases from zero at water content about 56% for unfatliquored leather and around 50% for fatliquored leather. In both cases, the DSC detectable freezable water is composed of two types which are manifested in the DSC spectrum by two endothermic peaks (*Figure 5.4 (a) and (b)*). The sharp peak at about 0°C must represent the melting of water having similar properties to bulk water. Before this sharp endothermic peak, there is another endothermic peak which has a broader and less prominent shape with a maximum value at about -5.5°C. This feature is present for samples having water contents of 66% and 75% for the unfatliquored sample (*Figure 5.4(a)*) and a water content of 60.4% for the fatliquored sample (*Figure 5.4 (b)*). As the water content increases this broader endothermic peak is overlapped by an increasingly prominent sharp (0°C) peak and eventually they completely merge to become apparently one peak when the water concentration is high enough (70~80%).

It is reasonable to assume that the freezable water detected by DSC can be divided into two different water states which interact with collagen molecules in a different manner. In general, five states of water exist according to the way water interacts with collagen molecules. In the first two states, water interacts with the collagen molecules by forming three hydrogen bonds and two hydrogen bonds respectively inside the triple helical collagen molecules. Therefore, the water molecules do not have the abilities to form ice structures, in which all four co-ordination bonds have to be engaged.

The third state of water appearing at concentrations of 7~25% has been shown to be freezable at 180°K (-93°C) as discussed earlier. This state could not be identified using DSC in this work.

It is recognised that for water present in a concentration of 35% to somewhere between 50% ~ 200%, some fraction of water is freezable at about -7°C. Sasaki ^[122] called the water fraction present just above 35% as mobile water, which is water in a state of being

fixed between collagen filaments by just one hydrogen bond thus allowing the water molecule to rotate. This high degree of freedom produces a characteristic response in NMR signal ^[122]. There are also differences in the latent heat of fusion of water in this range ^[113]. The amount of water participating in this regime has been shown to be a function of total water content and of extent of crosslinking ^[103].

There is another concept related to the water state with the hydration degree in the range mentioned above in that we can distinguish weakly bound water (life time 10^{-10} sec) which is slightly different from free water (lifetime 10^{-11} sec) ^[113]. Using sonic velocity measurement, Cusack and Lees ^[123] found that below 46% moisture (dry collagen basis) most of the changes in sonic velocity can be attributed to a change in the effective mass of collagen molecules as water is increasingly absorbed. Above 46% there is an abrupt decrease in sonic velocity that cannot be explained by added mass and must be the result of the presence of free water and its effect on the various molecular elastic restraints. However in Cusack's paper no distinction is made between weakly bound water and free water. Bienkiewicz ^[113] suggested that the method used in Cusack's work did not allow such a difference to be detected.

Comparing the DSC results shown in *Figure 5.4 (a)* and *(b)* and referring to the plot of *Figure 5.5*, similarities and differences are noted in the thermal behaviour between the unfatliquored and fatliquored leather samples. In a certain range of hydration, both samples gave an almost identical result (line No.3 in *Figure 5.4(a)* and line No.2 in *(b)*): both contain two endothermic peaks. The first one has a rather broad shape located at -9.4°C in the unfatliquored sample and at -6.4°C in the fatliquored sample respectively. The second peak has a sharper shape and appeared at -1.6°C and -1.5°C in these two types of leather samples respectively. There are also differences. First, the hydration level of fatliquored leather where the freezable water can first be detected by this method comes earlier than the unfatliquored leather, or in other words, DSC detectable freezing water in the fatliquored sample causes the trace to leave the abscissa at a lower temperature than that observed for the unfatliquored one (see *Figure 5.5*). Second, in the unfatliquored sample, the sharp peak temperature shifted slightly towards higher temperature as the water content increased while in the fatliquored leather it remained the same. Third, when water concentration reached 70% in the fatliquored leather, another endothermic shoulder peak located at 0°C appeared which is absent in the unfatliquored case.

The DSC results for unfatliquored and fatliquored leather samples are summarised in table 5.9.

Table 5.9 DSC results for (un)fatliquored leather samples

No. of curve	water content (%)	unfatliquored				No. of curve	water content (%)	fatliquored				
		no peak	broad peak	sharp peak	other			no peak	broad peak	sharp peak	shoulder peak	other
1	27	✓				1	44.8	✓				
2	54	✓			bending slightly downwards	2	60.4		-6.4°C	-1.5°C		
3	66		-9.4°C	-1.6°C		3	70.4			-1.6°C	emerged at 0°C	2 peaks merged
4	75		-7.5°C	-1.4°C		4	80.0			-1.6°C	shown at 0°C	
5	80			-1.5°C	2 peaks merged							
6	85			-1.2°C	2 peaks merged							

Figure 5.5 shows that the freezable water detected by DSC experiments on fatliquored leather occurs at lower total moisture content compared with the unfatliquored leather, even after considering the presence of the oil component in the fatliquored leather, i.e. by shifting the fatliquored plot 3~4% rightwards. The amount of shift is determined according to Figure 5.2.

This suggests that there is a stronger water-collagen interaction in the unfatliquored leather than in the fatliquored one. Without fatliquor, water trapped inside the collagen fibrils can make contact with and interact with the adjacent collagen molecules in a more efficient way. This is the case especially for water molecules which interact with the collagen molecules by forming a hydrogen bond. The amount of water which directly interacts with collagen molecules will affect the amount of free water which in turn influences the shape and position of the peaks on the DSC traces. In the fatliquored leather samples, the presence of the fatliquor diminishes the direct water-collagen interaction effect and correspondingly makes the formation of small aqueous domains possible. Thus it is easier to form water clusters which show a melting peak in the DSC.

That the influence of water on unfatliquored leather tends to be stronger than on fatliquored leather should also be reflected in other mechanical properties. Specifically the influence of the degree of mechanical action on leather softness as a function of water content on fatliquored leather is predicted to be more dramatic than that on unfatliquored leather — this is the case as we can see later in this chapter.

The sharp peak at about -1.5°C should be due to the so called “free water” according to Bienkiewicz, although it is said that the freezing point is 7 K lower than that of the bulk water. Whereas in these DSC results it was found to be only 1.5 K lower than the bulk water. Pineri^[105] did not name this type of water and described it as water molecules which form

clusters large enough to behave as ice. The appearance of the α peak on the mechanical dynamic spectrum^[105] of collagen at -3°C is in good accordance with what is observed in the DSC results here.

Interestingly in the unfatliquored sample, the location of this sharp peak shifts slowly towards higher temperature as the water content increases, whereas in the fatliquored sample the location remains the same. This pattern indicates that in the unfatliquored sample, the amount of this free water may approach a rather high level before the appearance of real bulk water. The increase of water content gradually weakens the interaction between the free water and collagen molecules or, in other words, promotes more water molecules in the free water to exchange with the bulk water. A longer and more ordered water chain will form at this stage. The location of the sharp peak in the fatliquored sample remains the same because the fatliquor between the fibrils act as a shield between free water and the collagen. Although this free water interacts with collagen molecules to a certain degree, the fatliquor encourages the formation of small aqueous domains. It is difficult for further increased water to blend in evenly with this free water between the fibrils and re-dissipate again. Therefore, further added water tends to form relatively isolated water clusters, i.e. bulk water, for which the freezing temperature is the same as bulk water. The shoulder shown on the DSC spectrum for the fatliquored leather indicates the presence of this bulk water.

5. 4. 2 Influence of Water Content Prior to Staking on Leather Softness

5. 4. 2. 1 Softness Change Measured by Bending

Table 5.10 and table 5.11 list the bending measurement results for both unfatliquored and fatliquored leather. Both the parameter $S_e^{\dagger}$ and the actual force at bending depth $d = 2\text{ mm}$ are used to represent the softness measured by test. For each sample code, there were 2 parallel samples. The result listed is the average data of these 2 samples.

The samples were cut from a different location on the leather hide (see *Figure 5.1*), hence the intrinsic softness of the sample may change across the whole side. Thus a relative decrease of force at a certain depth or relative decrease of S_e/t^n is used to reflect the influence of water content prior to staking on the softening effect of such a mechanical action. The relative decrease is calculated as:

[†] S_e — bending stiffness derived from empirical equation (3-31), see 3. 5. 2 in *Chapter 3*.

$$\text{Relative decrease of parameter (\%)} = \frac{\Delta \text{parameter}}{\text{parameter}_0} \times 100$$

where the *parameter* means either bending force at a certain depth (*F*) or S_e/t^n .

$$\Delta \text{parameter} = \text{parameter}_0 - \text{parameter}_1$$

The subscripts “₀” and “₁” stand for control and test sample respectively.

Table 5.10 S_e and force at $d=2$ mm results for B/UF/H(I) & (II)

test sample code	water content prior to staking / %	force at $d=2$ mm / N	S_e	S_e/t^n ($n=2.5$)	control sample code	water content prior to staking / %	force at $d=2$ mm / N	S_e	S_e/t^n ($n=3.4$)
UF/H(I)1 _∥	19.83	0.1153	10.99	6.50	UF/H(I)1° _∥	25.95	1.5095	117.2	19.98
UF/H(I)2 _∥	25.95	0.0719	6.66	3.64	UF/H(I)2° _∥		0.8891	83.64	17.00
UF/H(I)3 _∥	30.70	0.1453	13.77	4.07	UF/H(I)3° _∥		2.0378	158.8	16.92
UF/H(I)4 _∥	37.14	0.1469	13.99	4.06	UF/H(I)4° _∥		1.4934	101.1	12.88
UF/H(I)5 _∥	54.24	0.1495	13.92	3.56	UF/H(I)5° _∥		1.1050	90.17	8.61
UF/H(I)6 _∥	75.40	0.1382	12.49	3.09	UF/H(I)6° _∥		1.3234	91.66	9.12
UF/H(II)1 _∥	54.24	0.5779	55.49	23.97	UF/H(II)1° _∥		2.9040	260.2	47.94
UF/H(II)3 _∥	83.60	0.4251	40.48	13.61	UF/H(II)3° _∥		1.2703	123.0	13.11
UF/H(II)4 _∥	93.40	0.5979	47.27	16.65	UF/H(II)4° _∥		1.3685	129.2	16.88
UF/H(II)5 _∥	100.7	0.4615	44.21	14.15	UF/H(II)5° _∥		0.7678	73.07	8.00
UF/H(II)6 _∥	120.7	0.4012	37.15	13.58	UF/H(II)6° _∥		0.9486	88.67	9.43
UF/H(I)1 _⊥	19.83	0.2467	23.73	12.37	UF/H(I)1° _⊥	25.95	2.6347	207.3	38.47
UF/H(I)2 _⊥	25.95	0.1312	12.83	6.37	UF/H(I)2° _⊥		1.5501	150.6	17.00
UF/H(I)3 _⊥	30.70	0.1718	16.37	4.93	UF/H(I)3° _⊥		3.6376	249.4	16.92
UF/H(I)4 _⊥	37.14	0.1235	11.35	2.96	UF/H(I)4° _⊥		1.0333	82.61	12.88
UF/H(I)5 _⊥	54.24	0.1368	12.86	3.56	UF/H(I)5° _⊥		1.3804	100.3	8.61
UF/H(I)6 _⊥	75.40	0.2208	21.08	5.30	UF/H(I)6° _⊥		1.2555	92.73	9.12
UF/H(II)1 _⊥	54.24	0.5594	53.56	24.50	UF/H(II)1° _⊥		2.2333	210.2	40.04
UF/H(II)3 _⊥	83.60	0.4372	42.98	13.68	UF/H(II)3° _⊥		1.3551	124.9	12.40
UF/H(II)4 _⊥	93.40	0.6009	54.43	18.27	UF/H(II)4° _⊥		1.3504	131.4	14.89
UF/H(II)5 _⊥	100.7	0.6606	61.72	19.08	UF/H(II)5° _⊥		1.3800	136.4	12.63
UF/H(II)6 _⊥	120.7	0.9893	99.55	32.29	UF/H(II)6° _⊥		0.9711	88.14	9.05

Figure 5.17 and Figure 5.18 show the relative decrease of these parameters as the water content increases in the sample prior to staking. Figure 5.17 shows the results for unfatliquored leather and the Figure 5.18 the results for fatliquored.

Parameter *F* is used here only as a reference result because it is a parameter that does not exclude the influence of the sample thickness. The quantity S_e/t^n is preferred because it

basically excludes the influence of sample thickness. In other words, this property can be regarded as a parameter which represents the intrinsic softness of the test sample.

Table 5.11 S_e and force at $d=2$ mm results for B/FL/H(I) & (II)

test sample code	water content prior to staking / %	force at $d=2$ mm / N	S_e	S_e/t^n ($n=2.69$)	control sample code	water content prior to staking / %	force at $d=2$ mm / N	S_e	S_e/t^n ($n=3.4$)
FL/H(I)1	14.59	0.3945	30.53	13.96	FL/H(I)1°	24.28	1.4611	100.2	21.77
FL/H(I)2	24.28	0.2108	16.76	9.08	FL/H(I)2°		0.7238	53.77	14.05
FL/H(I)3	27.29	0.2965	21.66	7.60	FL/H(I)3°		0.7932	63.90	8.06
FL/H(I)4	30.51	0.1554	12.86	5.20	FL/H(I)4°		0.6059	48.48	8.02
FL/H(I)5	55.00	0.1988	17.30	6.43	FL/H(I)5°		0.3705	35.10	8.05
FL/H(II)1	52.20	0.3019	26.92	8.64	FL/H(II)1°		0.5028	44.85	9.44
FL/H(II)3	82.00	0.1045	8.82	3.06	FL/H(II)3°		0.1602	14.90	2.52
FL/H(II)4	103.0	0.1548	11.59	2.91	FL/H(II)4°		0.1503	14.49	2.09
FL/H(II)5	87.00	0.0831	7.20	2.32	FL/H(II)5°		0.1201	11.14	1.72
FL/H(I)1 _⊥	14.59	0.2152	18.19	8.52	FL/H(I)1° _⊥	24.28	1.0552	72.43	15.56
FL/H(I)2 _⊥	24.28	0.2148	17.45	9.94	FL/H(I)2° _⊥		0.7909	55.27	11.89
FL/H(I)3 _⊥	27.29	0.1560	11.73	4.55	FL/H(I)3° _⊥		0.6037	47.46	5.59
FL/H(I)4 _⊥	30.51	0.0892	7.52	2.97	FL/H(I)4° _⊥		0.2527	20.20	3.01
FL/H(I)5 _⊥	55.00	0.1554	12.89	4.22	FL/H(I)5° _⊥		0.2762	23.73	5.00
FL/H(II)1 _⊥	52.20	0.1895	16.59	5.61	FL/H(II)1° _⊥		0.2526	23.86	5.06
FL/H(II)3 _⊥	82.00	0.0856	7.70	2.31	FL/H(II)3° _⊥		0.1090	10.05	1.62
FL/H(II)4 _⊥	103.0	0.1238	9.97	2.53	FL/H(II)4° _⊥		0.0925	8.54	1.07
FL/H(II)5 _⊥	87.00	0.1018	9.05	2.63	FL/H(II)5° _⊥		0.1304	11.58	1.46

For the unfatigued leather, a water content at about 30% prior to staking produces a maximum influence on the $\Delta S_e/t^n$ plot. After this point, further increase of water content decreases the softening effect of such a mechanical action. When the water content reaches up to 80~90%, the softening effect of staking disappears.

For the fatigued leather, no peak value of water content within the water range of this experiment design produces a best softening effect of staking. The lowest water content in this study range is 15%, which endowed the fatigued leather the highest softening effect in this experimental series. As the water content increases, the softening effect tends to decrease to disappear when water content approaches 80%.

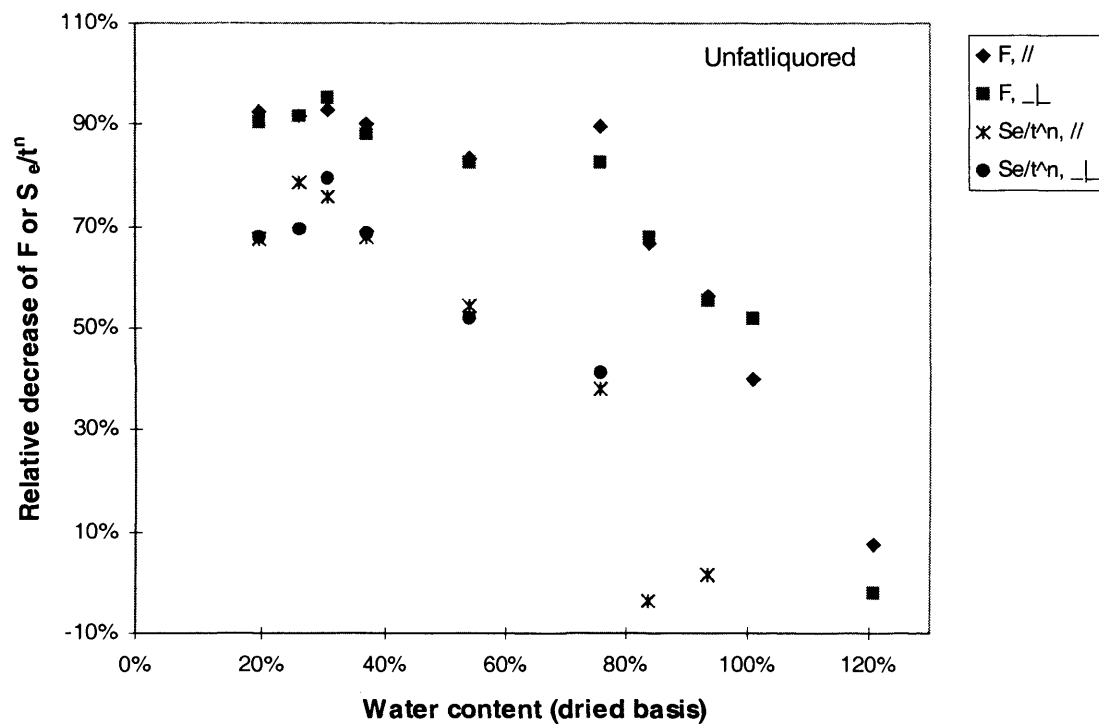


Figure 5. 17 The relative decrease of bending force (at $d=2$ mm) and S_e/t^n after staking at different water content (dried basis). Unfatigured samples

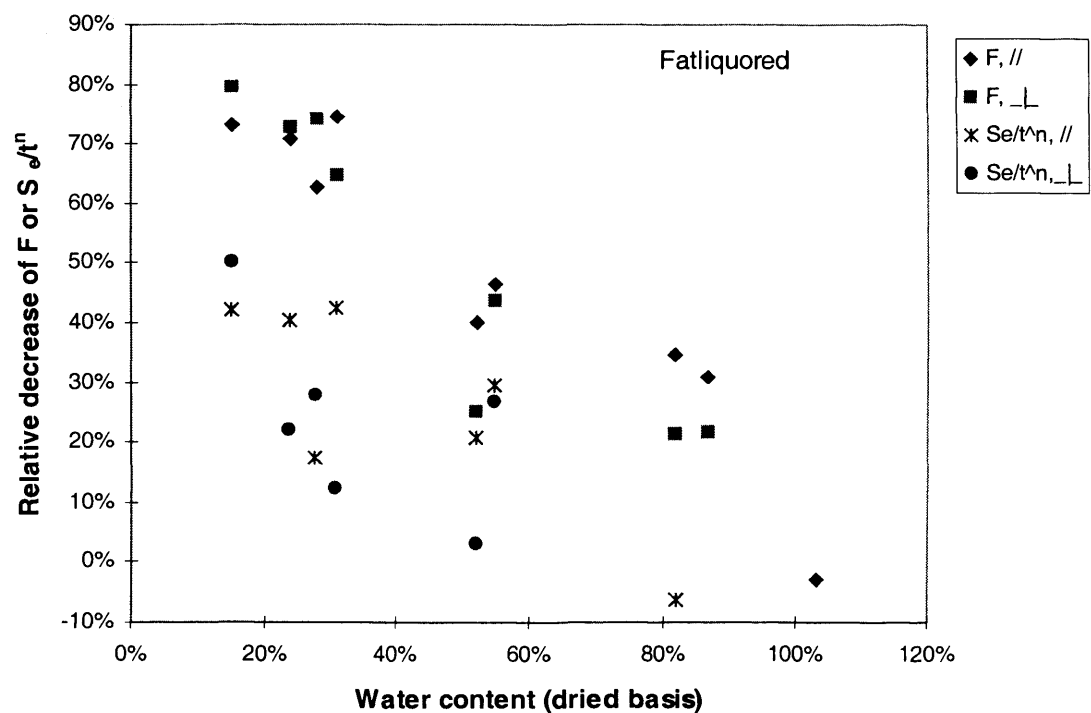


Figure 5. 18 The relative decrease of bending force (at $d=2$ mm) and S_e/t^n after staking at different water content (dried basis). Fatigured samples

The unfatliquored sample shows a stronger influence of water content on the softening effect of staking than the fatliquored one. The existence of fatliquor before staking has softened the leather to some degree and further mechanical action only adds the physical softening effect onto the leather to extend its softness. Without fatliquor, leather assumes a considerably stiff form which is much more easily altered by applying mechanical action. The presence of water within a certain limit plays the role of a plasticiser in the unfatliquored leather. Participation of more water increases the plasticising effect and reaches a maximum when the third and fourth type of water start to coexist (see 5. 4. 1. 1). At this stage, most water molecules are filled inside the tropocollagen and between microfibrils. Some water fills the voids adjacent to the end of tropocollagen. However, in the fatliquored leather, fatliquor molecules already play the role of lubricant or plasticiser. So the effect of water as a plasticiser is not as apparent as in the fatliquored sample. On the contrary, water molecules are forced to penetrate into the fatliquor-leather system during the vigorous staking process, which may well reduce the lubricant effect of the fatliquor and thus the softening effect on the leather.

After the softening effect of staking reaches zero, further hydration of leather (by soaking the leather in water and balancing back to the water content required) prior to staking causes an increase of S_e/t'' (i.e. the relative decrease of S_e becomes negative). An apparent hardening effect of staking on leather occurs. Why is this? The leather used in the experiment was toggle dried at the last stage of preparation, before cutting into test samples. Such a drying method would inevitably apply a certain strain to the leather on the toggle frame. Wright and Attenburrow's work^[124] showed that drying under strain fixes a particular fibre network configuration and that this configuration is to a considerable extent maintained even after a lengthy soak in water. The hardening effect of staking on such soaked leather indicates that the fibre network configuration built up during the drying procedure under strain can be destroyed when the wet leather is subjected to mechanical action. Such an action assists water molecules to penetrate into the finer structure of the leather more evenly. When dried again without any constraint, the adhesions between the microfibrils and fibre bundles re-form and become even more tightly packed due to the evaporation of more evenly distributed water.

5. 4. 2. 2 Tensile Behaviour

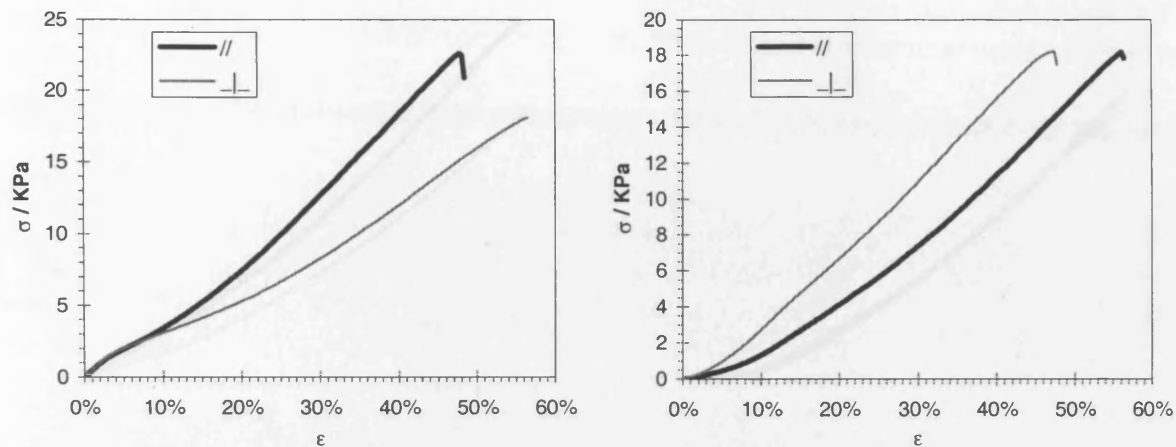
Generally speaking, the main difference in tensile behaviour between the control samples (without staking) and experimental samples (after staking, and with different water content

prior to staking) is shown mainly at the low strain region. This is clearly seen from *Figure 5.7* (1) and (2) for unfatliquored and *Figure 5.10* (1) and (2) for the fatliquored leather. *Figure 5.19* and *Figure 5.20* show the tensile stress-strain behaviour of the different control and experimental samples of unfatliquored and fatliquored leather. Figures in the left column are control samples which did not go through staking process; those in the right column are the experimental samples which contained different water content prior to staking.

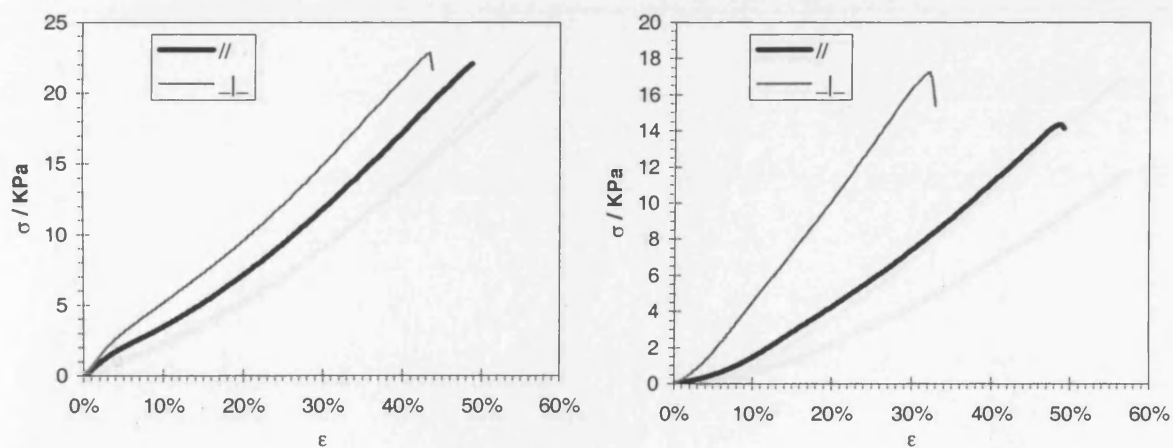
Leathers measured directly from drying and without further mechanical softening treatment show very prominent characteristics in the low strain region on the $\sigma - \epsilon$ curve. Instead of producing a *J* curve as for fully finished leather, there is a reverse *S* shape up to a strain of 10%. There is a linear stress increasing region before the strain reaches about 8% and afterwards there is a well recognised critical point from where the curve becomes the normal *J* shape. Such shape changes have also been reported by Kronick et al.^[49]

When the water content prior to staking is within a certain range, the reverse *S* shape shown by the stress-strain curve disappears and reverts to the normal *J* curve after the sample undergoes staking. To a great degree, adhesions (mainly physical adhesions) exist between the fibres and fibre bundles before the mechanical softening action. The formation of these adhesions is closely related to the evaporation of the water during the drying process. In his model Bienkiewicz showed how the water molecules find their positions between the collagen molecules during the drying procedure^[113]. Collagen molecules have a large number of polar side chains and because of their electric charges these can be treated as dipoles. The first step of aggregation is removal of free and weakly-bound water via interaction of dipoles, located in the perpendicular position and spaced by one or two nonpolar residues. Those water molecules that can take part in the interaction with collagen molecules will rearrange in a more ordered way in the space between dipoles, which strengthens the adhesion between the collagen molecules.

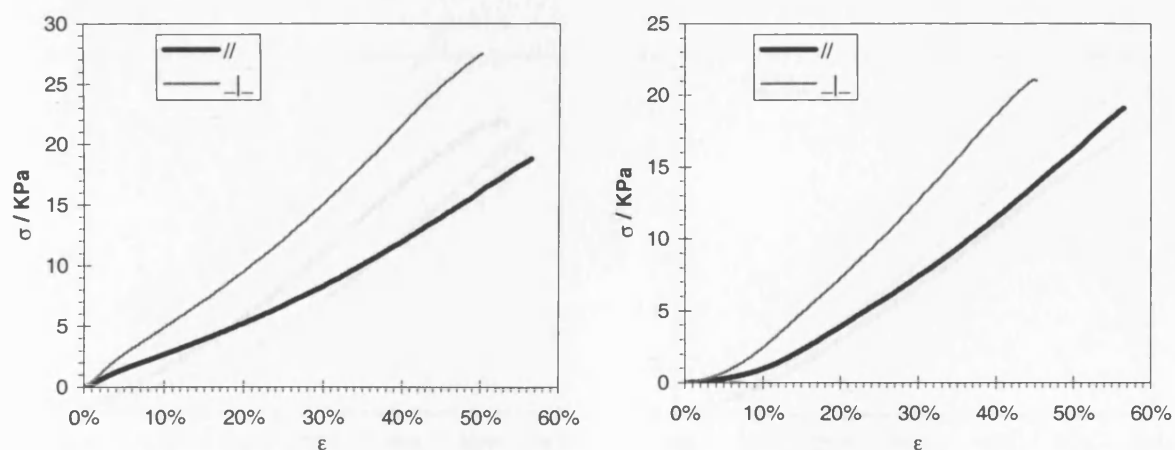
It is because of the adhesion between the collagen molecules, and subsequently between fibres and fibre bundles, that the leather sample behaves effectively as a whole unit without sub-divided structural levels especially at the low range of strain when in tension. So in this low strain area, stress-strain curves of leather in such a status assume a quasi-linear appearance, similar to many other materials such as metals or some polymers. The modulus in this region normally is 4~7 times higher than that of staked leather (with 20~30% water content). However, such physical adhesions are easily disrupted. In other words, when a certain level of mechanical force is applied, adhesions break to some degree. In the tannery,



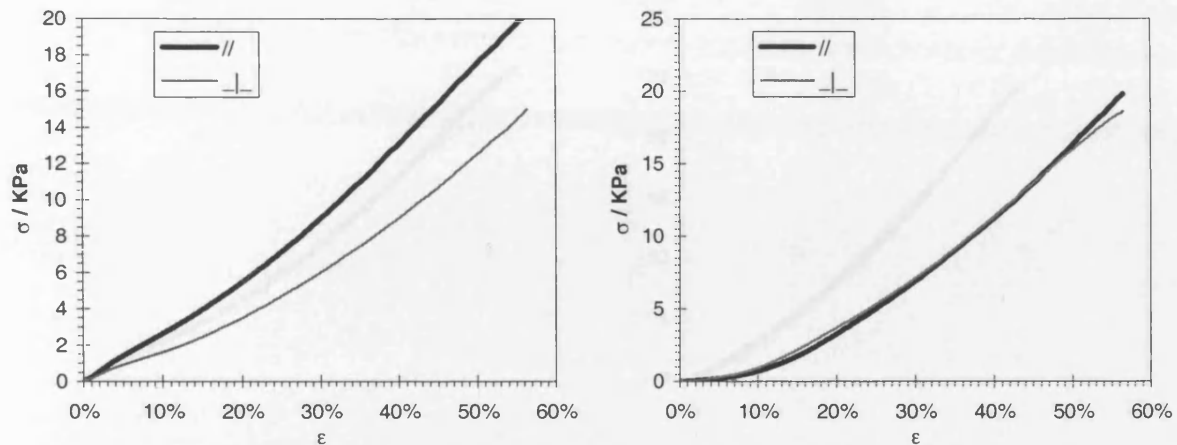
(a) Left -- control samples; Right -- test samples whose water content prior to staking is 19.83%



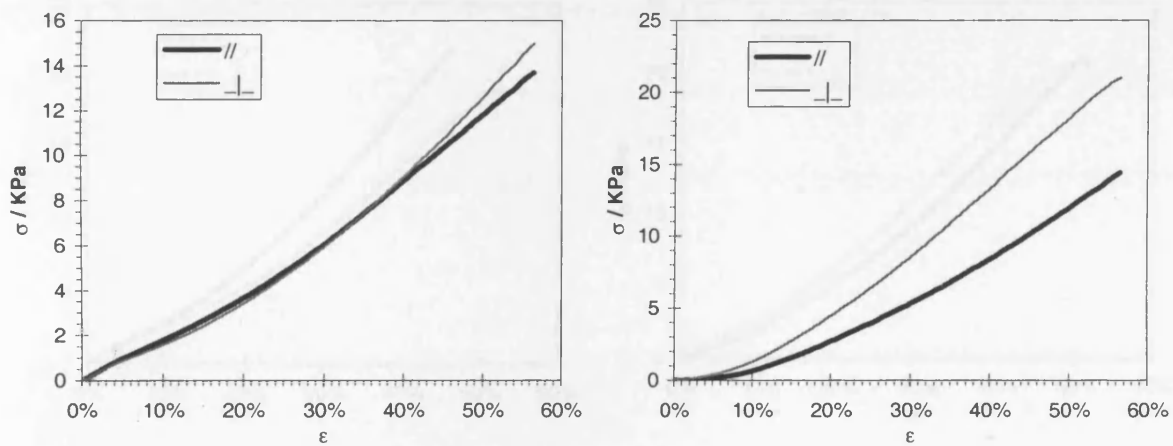
(b) Left -- control samples; Right -- test samples whose water content prior to staking is 25.95%.



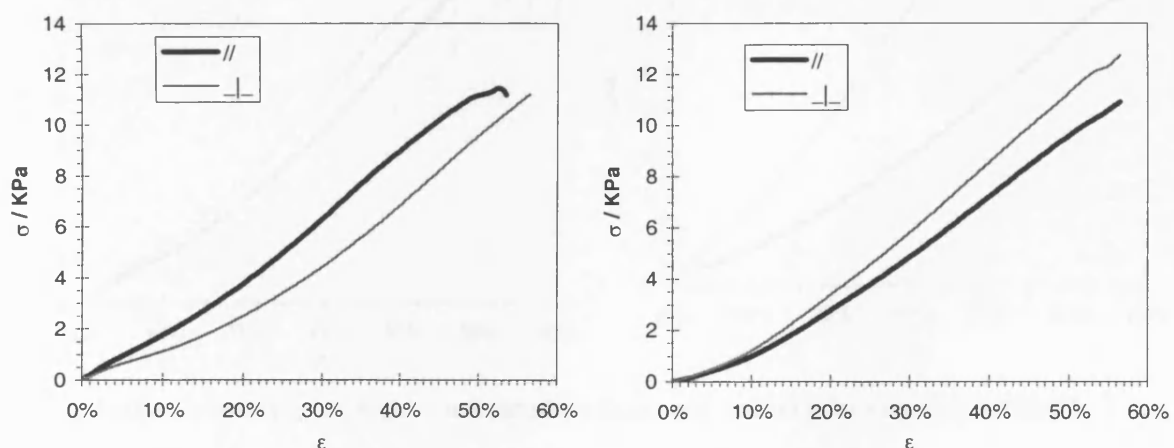
(c) Left -- control samples; Right -- test samples whose water content prior to staking is 30.7%



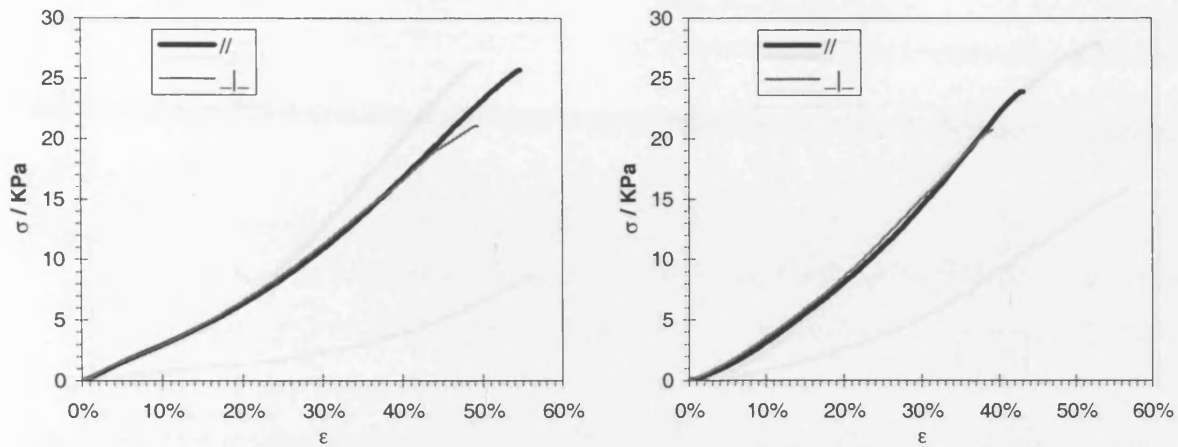
(d) Left -- control samples; Right -- test samples whose water content prior to staking is 37.14%



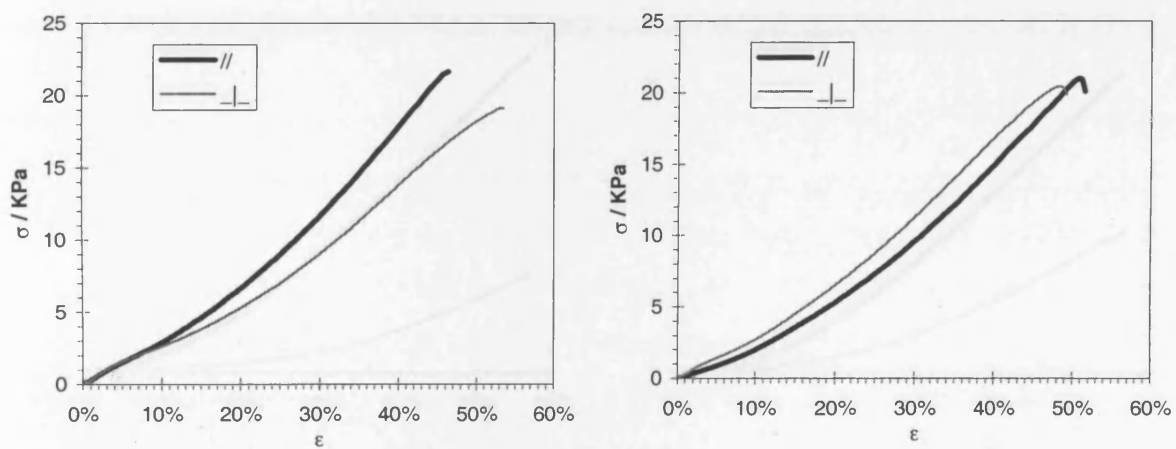
(e) Left -- control samples; Right -- test samples whose water content prior to staking is 54.24%.



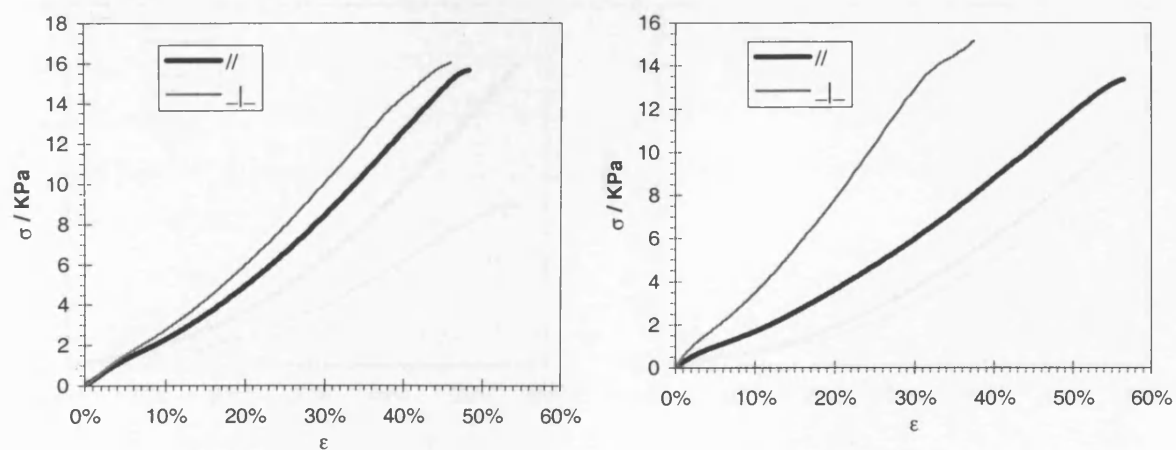
(f) Left -- control samples; Right -- test samples whose water content prior to staking is 75.4%.



(g) Left -- control samples; Right -- test samples whose water content prior to staking is 83.6%

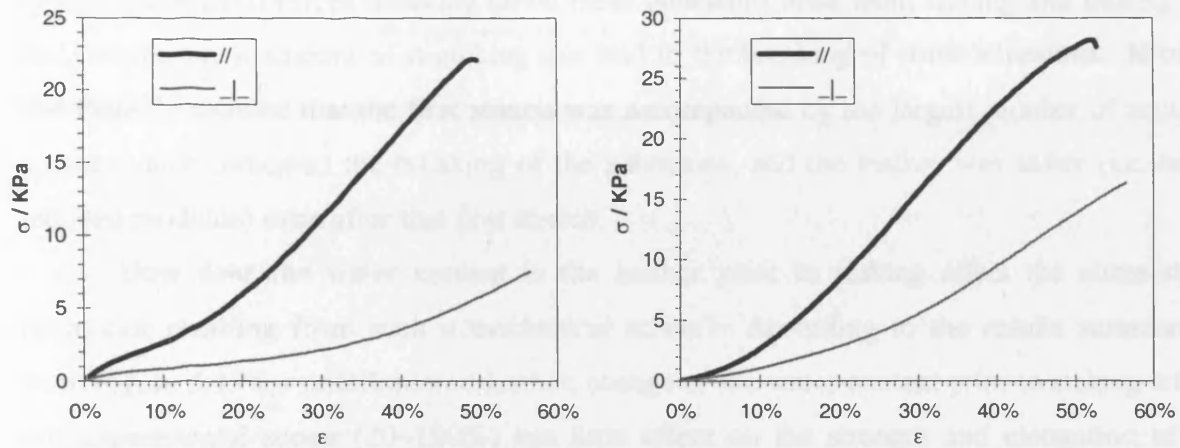


(h) Left -- control samples; Right -- test samples whose water content prior to staking is 100.7%

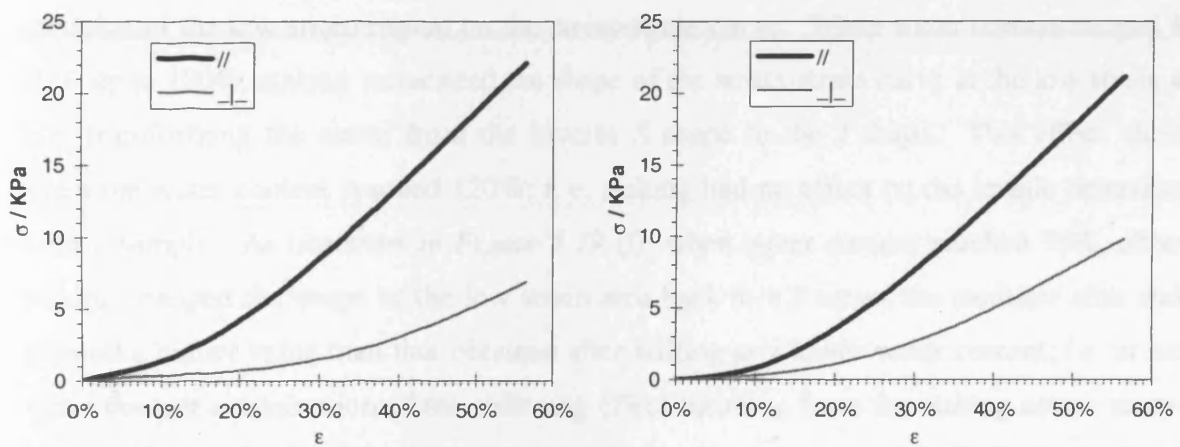


(i) Left -- control samples; Right -- test samples whose water content prior to staking is 120.7%.

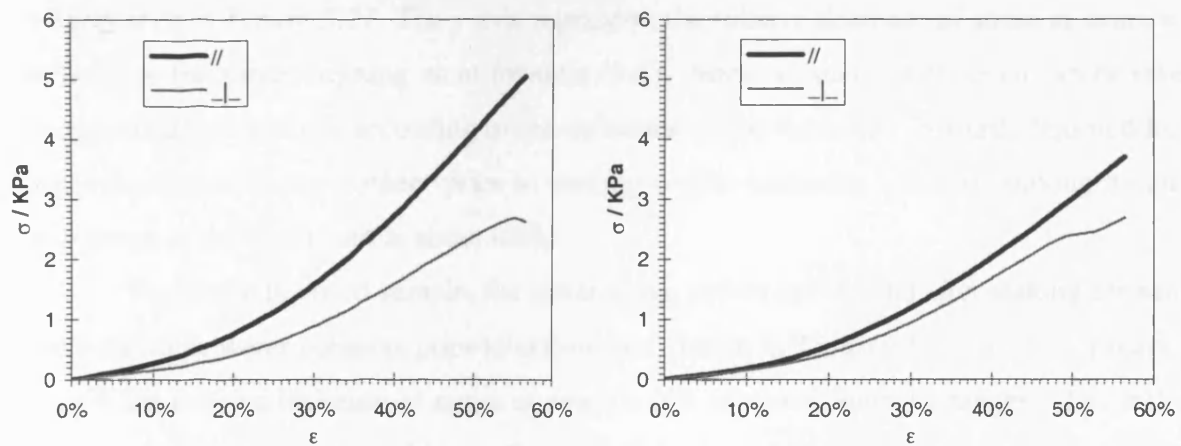
Figure 5. 19 Influence of water content prior to staking on the stress - strain curves of unfatigued leather.



(a) Left -- control samples; Right -- test samples whose water content prior to staking is 14.59%



(b) Left -- control samples; Right -- test samples whose water content prior to staking is 30.51%



(c) Left -- control samples; Right -- test samples whose water content prior to staking is 103%.

Figure 5.20 Influence of water content prior to staking on the stress -strain curves of fatliquored leather.

typical mechanical forces breaking down these adhesions arise from staking and milling. In fact, even a small amount of stretching can lead to the breaking of some adhesions. Kronick and Page^[82] showed that the first stretch was accompanied by the largest number of acoustic pulses, which indicated the breaking of the adhesions, and the leather was softer (i.e. had a reduced modulus) even after this first stretch.

How does the water content in the leather prior to staking affect the stress-strain behaviour resulting from such a mechanical action? According to the results summarised from *Figure 5.19* for unfatliquored leather, change of the water content prior to staking within our experimental scope (20~120%) has little effect on the strength and elongation of the leather sample. However the change showed a clear influence on the shape as well as the modulus of the low strain region on the stress-strain curve. When water content ranged from 20% up to 100%, staking influenced the shape of the stress-strain curve at the low strain area, i. e. transforming the curve from the inverse *S* shape to the *J* shape. This effect vanished when the water content reached 120%; i. e. staking had no effect on the tensile behaviour of such a sample. As observed in *Figure 5.19 (f)*, when water content reached 75%, although staking changed the shape of the low strain area back to a *J* curve, the modulus after staking showed a higher value than that obtained after staking at a lower water content; i.e. at such a water content a diminution of the softening effect resulting from the staking action started to appear. From the low strain region moduli, the water content which leads to the most mechanical softening effect on leather ranges between 35% and 50%. This pattern can be clearly seen in *Figure 5.21*. The y axis represents the relative decrease of stress at strain = 3%, which has the same meaning as in formula (5-1). Stress at such a low strain can be taken as proportional to modulus according to the definition of the modulus. For unfatliquored leather, the influence of water content prior to staking on the softening effect of staking assumes a maximum at water content is about 40%.

For the fatliquored sample, the stress-strain curves before and after staking for samples with different water contents prior to staking are shown in *Figures 5.20 (a)~(c)*. *Figure 5.22* shows the relative decrease of stress at strain = 3% as water content changes. The influence of water content on the staking softening effect is not as prominent as that observed in unfatliquored leather, and this influence begins to disappear above a water content of 103%. In contrast to unfatliquored leather, within the experiment scope of water contents, no peak is observed, and the softening effect of staking on such leather as the water content changes does not show such a very clear trend. This pattern can be explained as follows. For any kind of leather, when its chemical structure is fixed – which includes the chemical bonds formed

between collagen molecules and various tanning agents and chemicals, there is a potential maximum softness limit for this leather. Both fatliquoring and/or mechanical softening can lead to a change towards the direction of the softness limit. For fatliquored leather, the fatliquor has already delivered some softening effect on the leather. Further mechanical softening will therefore be expected to be less marked than in the case of unfatliquored leather. This trend is in accordance with what was interpreted as fatliquor shielding in the *DSC* results. On the other hand, the changes in the mechanical softening effect as the water content alters is more scattered, which suggests that the structure of the leather is much less sensitive to water content changes compared with the unfatliquored leather. This pattern confirms the conclusion of the *DSC* experiment that the interaction between water and collagen molecules is stronger for unfatliquored leather than that in fatliquored leather.

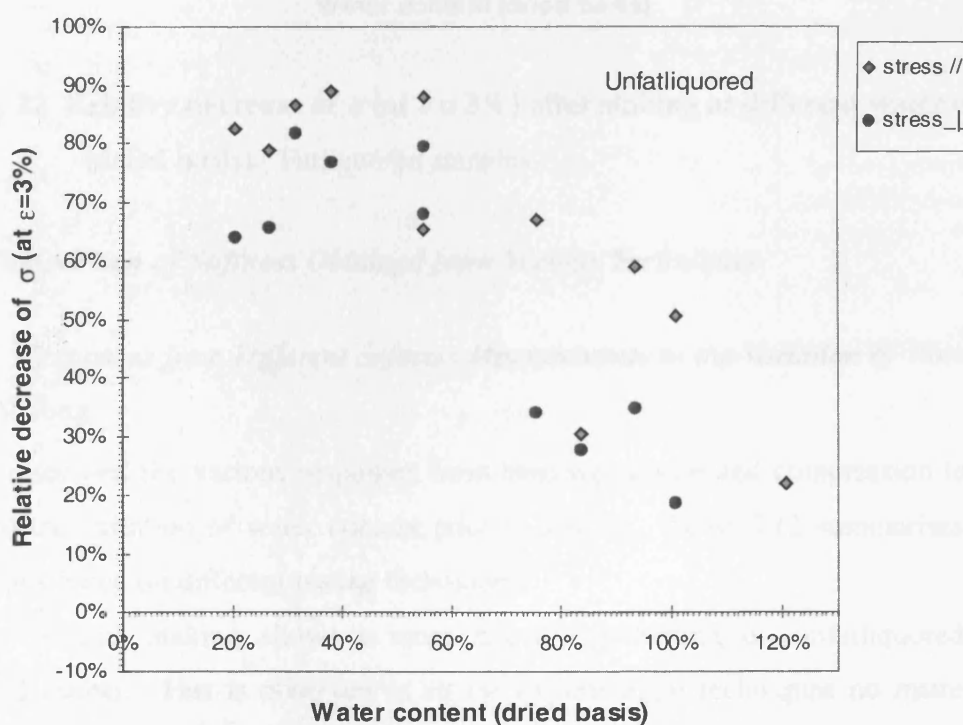


Figure 5. 21 Relative decrease of σ (at $\epsilon = 3\%$) after staking at different water content (dried basis). Unfatliquored samples.

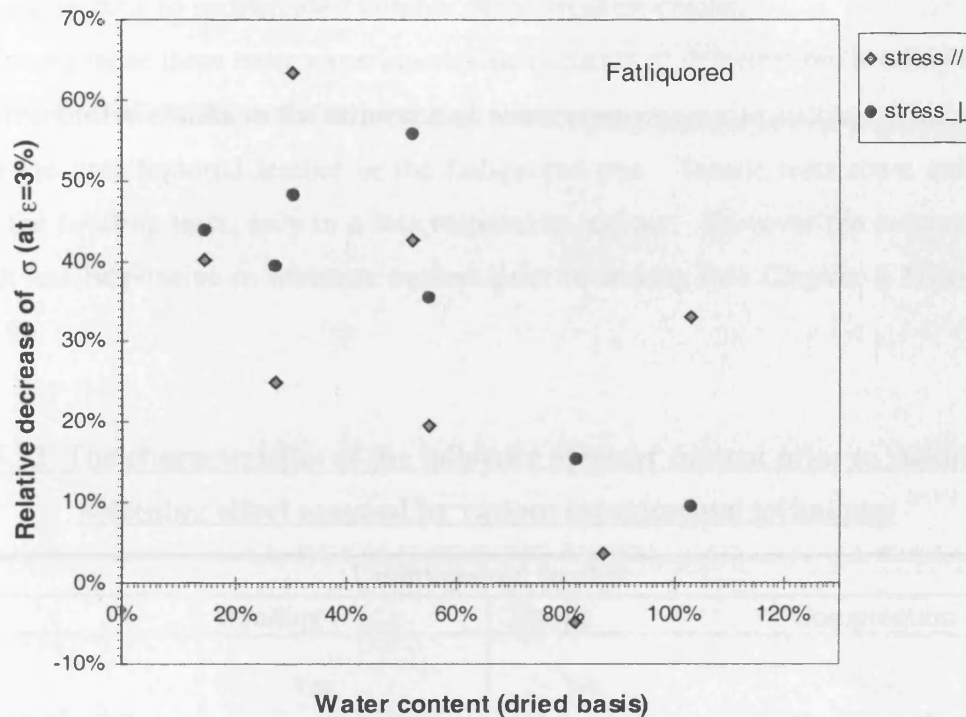


Figure 5.22 Relative decrease of σ (at $\epsilon = 3\%$) after staking at different water content (dried basis). Fatliquored samples.

5.4.3 Comparison of Softness Obtained from Various Techniques

5.4.3.1 Responses from Different Softness Measurements to the Variation of Water Content Prior to Staking

We have discussed the various responses from bending, tensile and compression testing (see 4.3.3) to the variation of water content prior to staking. Table 5.12 summarises the main observations based on different testing techniques.

In general, staking shows a more effective softening on unfatliquored than on fatliquored leather. This is observed in all the experimental techniques no matter whether bending, tensile or compression. This observation is consistent with the work of Kronick *et al* where tensile testing and acoustic emission were applied to study the effect of staking on fatliquored and unfatliquored chrome tanned crust leather^[49]. In their model, parallel bunches of fibrils are organised into fibres; and where these are mutually parallel and close together they form into cohesive domains. Crazes are more easily created within the cohesive domains for fatliquored leather because fatliquor added before drying has penetrated and stayed within the cohesive domains during process of drying, weakening the adhesions within these

domains and leading to an increased number of the weakest cracks.

Among these three basic experimental assessments of deformation, bending tests yield the most responsive results to the influence of water content prior to staking. This is the case for either the unfatliquored leather or the fatliquored one. Tensile tests show quite similar trends to the bending tests, only in a less responsive manner. However the compression test was much less responsive to moisture content prior to staking (see *Chapter 4 Figure 4.8 and Figure 4.9*).

Table 5.12 The characteristics of the influence of water content prior to staking on its softening effect assessed by various experimental techniques

Unfatliquored leather			
	Bending	Tensile	Compression
Influence of water content prior to staking on the softening effect	Yes. Maximum influence at ~30% Clearly responsive.	Yes. Maximum influence at ~40% Clearly responsive.	Yes. No peak influence in the experimental range, influence diminishes as water content increases. Less responsive (more scattered)
fatliquored leather			
Influence of water content prior to staking on the softening effect	Yes. No peak influence in the experimental range, influence diminishes as water content increases. Clearly responsive	Yes. No peak influence. Less responsive.	No

The observations that water content shows a similar influence on softening as assessed in both bending and tensile experiments and that this is more pronounced than that in the compression test, lead to a consideration of the different responses of the leather structure when different types of deformation are applied. Kronick's model ^[49] of cohesive domains and accompanying crazes which form on stretch can well explain the effects of staking on tensile behaviour, but thus not appear to be able to explain why the change of water content prior to staking influenced the effects of such a mechanical treatment on bending, tensile and compression differently.

Basically, the structure of leather can be simply viewed as a network composed of fibre bundles (see 1. 2. 2. 2) interwoven together with joining points as crosslinking hinges. When a certain kind of deformation force is applied, the initial strain will be caused mainly by

- i) elastic unbending of the construction units (in various structure levels);
- ii) restorable slippage of some adhesion points.

Although both deformation modes occur in bending, tensile and compression tests, the direction of the deformation (or the forms the microstructural deformation assumes) will be different, especially in compression.

If leather is cut perpendicularly to its grain surface and the fibre net is envisaged on a lateral section, the deformation of leather (low strain region) in the different types of test is schematically proposed in *Figure 5.23*. This figure does not show exactly what is happening inside the leather during various deformations, however, it is an abstract model to simplify, describe and implement the concepts and procedure of various deformations.

Figure 5.23 (a) represents the lateral section of the network before deformation. *Figure 5.23 (d)* shows the situation when the sample is under bending. The net is compressed (longitudinally, i.e. along the x axis) above the neutral axis, and is stretched along the x axis below the neutral axis. *Figure 5.23 (b)* shows the situation when the network is under tension. Structural units unbend to produce elastic deformation and restorable slippage at adhesion points may occur (along the x axis). *Figure 5.23 (c)* indicates the compressive deformation along the z axis and the restorable slippage at adhesion points along such a direction.

When the concept of “adhesion point” is used, the meaning is the same in both bending and tensile deformation since both kinds of deformation take place along the same x axis direction, although bending involves compression along this axis. However the concept may involve different meanings in compression because deformation and slippage occur along the z axis.

Adhesions can form within all the hierarchical structural levels inside leather, i.e. among tropocollagen molecules, fibrils, fibres or fibre bundles, and subsequently the freedom of movement of the adjoining constructive units will be reduced. Such a restriction may occur longitudinally between the ends of the structural units (*ends adhesions*) or between two relatively parallel adjoining structural units (*lateral adhesions*).

Considering the three dimensional structure of leather, these different adhesions and their contributions to different deformation types are illustrated schematically in *Figure 5.24*.

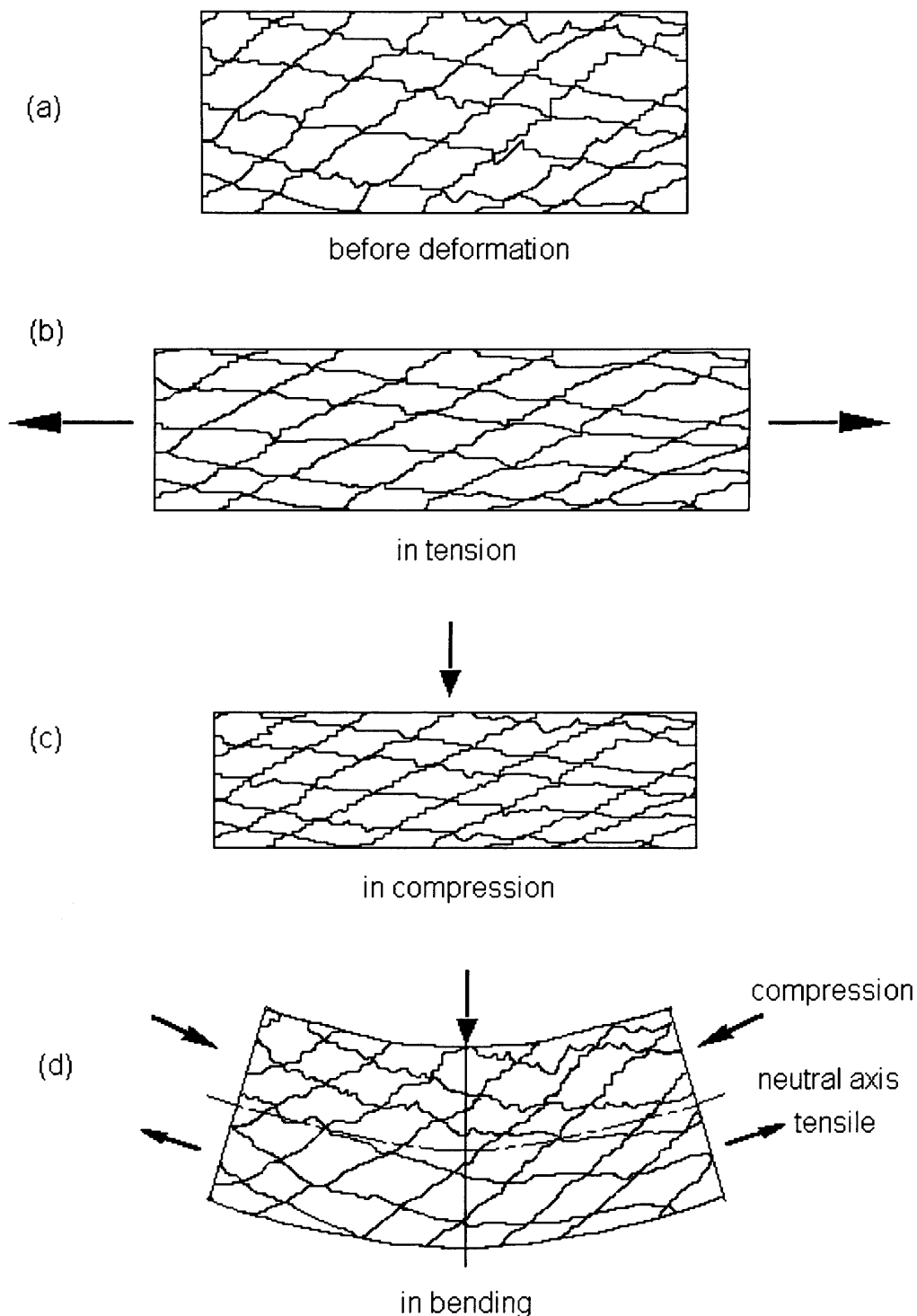


Figure 5.23 Scheme of fibre network deformation during different types of tests.

In *Figure 5.24*, the x axis identifies the direction of tensile strain and the z axis is the direction of lateral compression. The circular dot “o” represents the ends adhesion point and

the solid dot “•” signifies a lateral adhesion point. The former only contribute to some types of deformation; e. g. point a_1 contributes mainly to tensile and/or bending deformation, and point a_2 contributes mainly to the compressive deformation. The lateral adhesions (e. g. point b) contribute to all types of deformation.

The water content prior to staking showed an influence on the staking softening effect which, compared with bending and tensile tests, showed a much less responsive result (e. g. for unfatiguated leather) or little influence (e. g. for fatiguated leather) in the compression tests. Therefore it is reasonable to deduce that during the course of staking, the interaction between collagen molecules and water assumes a certain type of pattern.

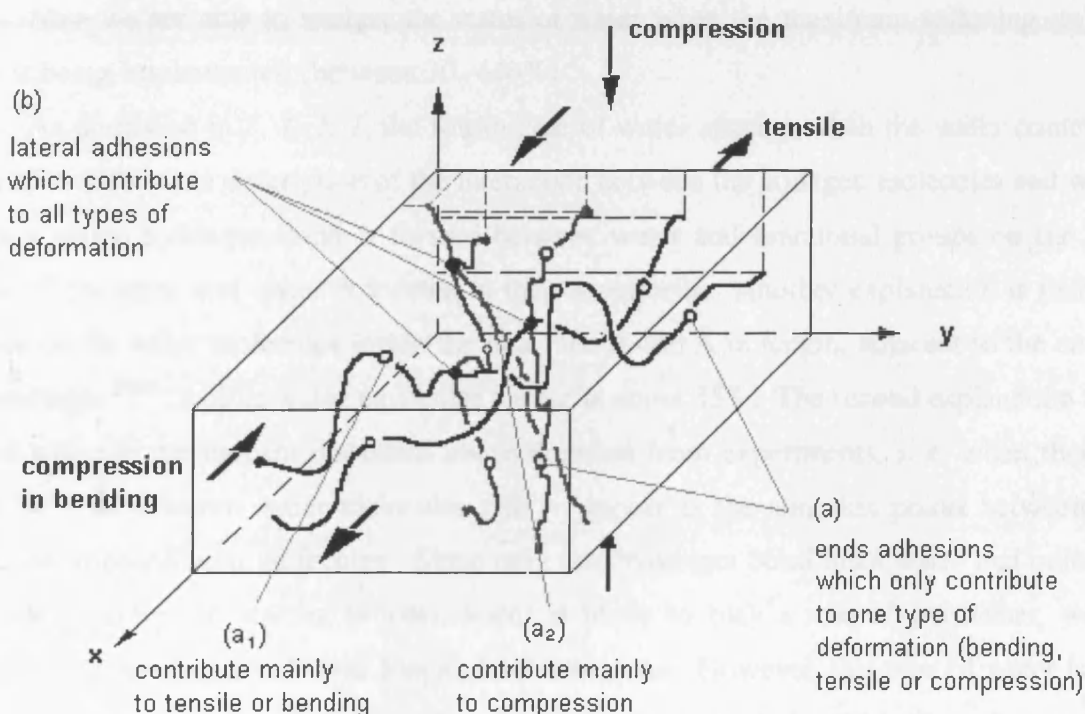


Figure 5.24 Scheme of 3-dimensional network.

Indubitably, staking can make leather softer. Staking opens up fibre (bundles) or even finer levels of structure perhaps down to that of the tropocollagen molecules to some degree. On the other hand, water undoubtedly has interactions with all hierarchical structural levels inside leather. The question is how the existence of water will influence the softening effect of staking? From what was observed from the different mechanical tests, it is reasonable to deduce that, only the opening up of ends adhesions will be facilitated or influenced by the existence of water. The existence of water has little influence in facilitating the opening up of lateral adhesions. Indeed as a natural biological material, leather has its own characteristic

structure. The orientation of tropocollagen molecules, fibres or fibre bundles along x and y axes in the grain layer is much more abundant than that along z axis, thus leading to more ends adhesions along x and y axes than along the z axis. If water interaction mainly influences the ends adhesions, its softening effect would be easily characterised in bending and tensile tests since these two methods predominantly involve longitudinal deformations (tensile or compression) along either x or y axis. While in compression, the deformation primarily comprises a lateral closing together of the fibres (bundles). Although some destruction of ends adhesions along the z axis may be involved at the same time, the structural units concerning these ends adhesions can hardly hold their original straight shape as the compression goes on. Thus compression tests are less responsive to the water influence.

Now we are able to analyse the status of water when the maximum softening staking effect is being implemented (between 30 ~ 40%).

As discussed in 5. 4. 1. 1, the fourth type of water appears when the water content is about 25 ~ 50%. One description of the interaction between the collagen molecules and water is that a single hydrogen bond is formed between water and functional groups on the side chains of collagen, and water is located in the microfibrils. Another explanation is that the fixation of the water molecules inside the hole, about 400 Å in length, adjacent to the end of tropocollagen^[105], mobile water molecules appear at about 35%. The second explanation is in accord with the mechanism discussed above deduced from experiments, i. e. when there is about 30 ~ 40% water, water molecules start to appear at the adhesion points between the “ends” of tropocollagen molecules. Since only one hydrogen bond links water and collagen molecules, during the staking process, water is likely to play a role of plasticiser, which facilitates the opening up of these longitudinal adhesions. However, this type of water is not completely free water (see 5. 4. 1. 1). So when the sample was balanced back to the standard testing conditions (when the water content is 26%), removal of the difference of water between 26% and 30~40% should be more difficult than the free or bulk water. In fact, within the range of our experiments, removal of water can be divided into two distinctive steps^[114]: the first step is the removal of unbound water at a constant evaporation rate and the second is the removal of bound water which starts at about 70% water content. According to water evaporation speed the second step can be further divided into three substages: 70 ~ 50%, 50 ~ 9% and below 9%. In the region of 50 ~ 9%, most inter-fibril water has left leather, and the water located at the “gaps of ends” begin to evaporate. Experimental results showed that staking produced the most softening effect while water content is about 30 ~ 40%. This is in good accord with the prediction^[114] that staking is easier at water content of 35%. Actually,

the final softening effect is a comprehensive result of the two opposite effects: more water makes staking easier and meanwhile the evaporation of water when leather is balanced back makes fibrils re-stick and shrink. At water contents between 30 ~ 40%, the staking action gives its full play to the softening effect. Indeed when water content is reduced to 27%, high rate shrinkage ends^[114]. Therefore, at the optimum water content (30 ~ 40%), on the one hand there just enough water acting as plasticiser during staking and leads to its maximum softening effect. On the other hand, while the sample is balanced back to the standard test conditions there is not sufficient surplus water to assist fibrils to overcome the internal friction to completely re-stick together.

For fatliquored leather, the amount of water has no influence on the lateral opening up of the fibrils (see *Figure 4.9 (b)*). The average softening effect shown from the compression tests is 25%. Fatliquor fills up the voids between the fibrils. The existence of water in the “gaps of ends” is of little importance due to the small amount of fibrils oriented along the *z* axis.

5. 4. 3. 2 Comparison Between Different Softness Measurements and Hand Grading.

The three measuring techniques have shown the relationship between the basic deformation types (tension and compression along the three axes) of leather. Softness assessed by different experimental techniques reflects different types of deformation occurring within the structure of leather. Therefore, it would not be sensible to judge the softness of leather from the results of one single measuring technique. Softness is a comprehensive deformation response of the material to external forces. In hand grading, all these basic deformations must be involved. Experienced tanners are able to give a judgement on such a comprehensive concept from their accumulated knowledge of leather. So softness resulting from hand grading is a comprehensive assessment which involves various deformation responses to the various forces acting on leather during handling.

From the results of softness measurement on BLC samples (*Figure 5.14*), we can see the difference from various test techniques of how the results agree with those obtained from hand grading. The parameter $S_e/t^{1.5}$ from the bending test and *CI* from the compression test show relatively good agreement with the hand grading results. Stress at strain=3% from tensile test does not show such a good agreement with hand grading results. Sample No. 6 arouses particular attention. This sample showed easy deformation in both tensile and bending tests, but when felt, it showed less “softness” than the other samples. The reason is likely to be due to the greater thickness of this sample (see table 4. 3), the influence of which on the softness cannot be excluded during the assessment of hand feeling. Another reason

may be that deformations reflected in bending and tensile tests do not provide a complete description. In contrast, the *CI* values obtained from the compression tests reveal a good correlation with the hand grading. Therefore any type of deformation obtained from the various testing techniques could be related to that which occurs in hand grading. As for how much each type of deformation will contribute to the subjective judgement and what form it will take is not yet clear. It may be an idea to build up a model to simulate the process (an approach being taken by Su et al^[125], and also finding application in defining the objective handle of fabric in textile industry^[88]). However this type of approach is outside the range of this research. In practice, the design of the ST300 Softness Tester (see 1. 2. 3. 4) produces a quantitative value which is in good agreement with the hand feeling.

CHAPTER 6

STAKING OPTIMISATION AND SIMULATION

6. 2 Introduction

The main purpose of vibratory staking is to soften leather. However the degree of softening that can be attained is expected to be influenced by parameters such as the staking frequency, the staking depth (the amplitude) and the number of times a piece of leather passes through the staking machine. Some parameters (e.g. amplitude) are adjustable according to the design of the staking machine. There is no published work on how the magnitude of such parameters affects the softening effect on leather and what is the optimum combination of various parameters for giving full play to softening. In this chapter results from an orthogonal experiment that was applied to gain more information in this area are described.

6. 2 Experimental

6. 2. 1 Material and Instrument

The material used in the orthogonal experiment was an unfatliquored crust leather which was toggle dried after tanning. Samples for dynamic testing were strips, 100 mm × 25 mm. Sample locations were from all over the hide. Staking simulation test samples were cut as rectangular sheets, width 150 mm, of various lengths (in the range 400 ~ 600 mm). The dynamic testing machine is described in 2. 2. 1, 2, *Chapter 2*. All the experiments were carried out in the conditioning room, i.e. temperature 20°C and relative humidity 65%.

6. 3 Results

6. 3. 1 Orthogonal Experiment

6. 3. 1. 1 Design of the Orthogonal Experiment

In scientific experiments and production practice, it is often the case that for a given observation there are several factors which have influence on it. Alteration of each factor may have influence on the observation target value. Some of these factors might have stronger influence than the others. In statistics, analysis of variance (ANOVA) provides an effective method for identifying the effect of each factor^[126,127].

Different status of each factor is called level. Obviously, for a multiple-factor and multi-levelled system, certain number of tests are required before drawing a conditional statistical conclusion. The orthogonal experimental design table offers a way to design the minimum number of tests required and the combinations of the tests to enable such a statistic conclusion to be drawn.

In these staking softening experiments, the main factors considered were:

- (A) frequency of the staking head,
- (B) depth (amplitude) of staking, and
- (C) duration of staking.

Therefore, if three levels are assigned to each factor, for the strip strain cycling experiment the factors and levels table is obtained as listed in table 6. 1.

Table 6. 1 Factors and levels

Factors \ Levels	1	2	3
A (frequency, Hz)	2	10	20
B (upper-limit, mm) (in terms of strain %)	2 (2.9%)	4 (5.7%)	6 (8.6%)
C (cycles)	20	60	120

Considering that interactions between the factors possibly exist and affect the target value (softening effect), we adopted the orthogonal experimental table $L_{27}(3^{13})$ in which interactions between any 2 of the 3 factors were included. Here $L_{27}(3^{13})$ means that the table is able to accommodate 13 3-levelled factors, and the total number of test combinations is 27. The standard $L_{27}(3^{13})$ table is shown in table 6. 2 which contains 27 rows and 13 columns, giving a total number of tests 135.

6. 3. 1. 2 Results

With the experimental design mentioned above, 135 sample strips from all over one side of the crust leather were mixed in a random way and divided into 27 groups, each of which contained 5 tests. The target value is the relative decrease of bending force (F) at a bending depth $d = 3$ mm, i. e.

$$\text{Relative decrease of } F (\%) = \frac{F_{\text{before stretching}} - F_{\text{after stretching}}}{F_{\text{before stretching}}}$$

The experimental results, ANOVA table and the 2-factor tables are given in table 6. 3.

Table 6. 2 $L_{27}(3^3)$ table

	A	B	C	A×B	A×C	B×C	Blanks' column							Results
	1	2	5	3	4	6	7	8	11	9	10	12	13	
1	1	1	1	1	1	1	1	1	1	1	1	1	1	
2	1	1	2	1	1	2	2	2	2	2	2	2	2	
3	1	1	3	1	1	3	3	3	3	3	3	3	3	
4	1	2	1	2	2	1	1	2	3	2	2	3	3	
5	1	2	2	2	2	2	2	3	1	3	3	1	1	
6	1	2	3	2	2	3	3	1	2	1	1	2	2	
7	1	3	1	3	3	1	1	3	2	3	3	2	2	
8	1	3	2	3	3	2	2	1	3	1	1	3	3	
9	1	3	3	3	3	3	3	2	1	2	2	1	1	
10	2	1	1	2	3	2	3	1	1	2	3	2	3	
11	2	1	2	2	3	3	1	2	2	3	1	3	1	
12	2	1	3	2	3	1	2	3	3	1	2	1	2	
13	2	2	1	3	1	2	3	2	3	3	1	1	2	
14	2	2	2	3	1	3	1	3	1	1	2	2	3	
15	2	2	3	3	1	1	2	1	2	2	3	3	1	
16	2	3	1	1	2	2	3	3	2	1	2	3	1	
17	2	3	2	1	2	3	1	1	3	2	3	1	2	
18	2	3	3	1	2	1	2	2	1	3	1	2	3	
19	3	1	1	3	2	3	2	1	1	3	2	3	2	
20	3	1	2	3	2	1	3	2	2	1	3	1	3	
21	3	1	3	3	2	2	1	3	3	2	1	2	1	
22	3	2	1	1	3	3	2	2	3	1	3	2	1	
23	3	2	2	1	3	1	3	3	1	2	1	3	2	
24	3	2	3	1	3	2	1	1	2	3	2	1	3	
25	3	3	1	2	1	3	2	3	2	2	1	1	3	
26	3	3	2	2	1	1	3	1	3	3	2	2	1	
27	3	3	3	2	1	2	1	2	1	1	3	3	2	

An F test was applied in the ANOVA table. The hypothesis (H_0) is:

$$\sigma_i^2 = \sigma_e^2 \quad \text{or} \quad \mu_i = \mu_e$$

where σ_i^2 and μ_i are the variance and average value of the population for each scheme respectively, and σ_e^2 and μ_e are the random variance and random average value of the population. If the ratio of the test statistics of estimated variances, F_i ,

$$\frac{SS_i / \nu_i}{SS_e / \nu_e}$$

is greater than $F_{\alpha}(\nu_1, \nu_2)$, then the hypothesis H_0 is refused and, otherwise we accept H_0 . Here ν_1, ν_2 are the degree of freedom of the numerator and denominator, and α is the confidence level.

Table 6.3 Orthogonal Experiment Design Table ($L_{27}(3^{13})$) and ANOVA Table

Target Value is: F decrease (%) @ d=3mm

	A	B	C	(AB)1	(AB)2	(AC)1	(AC)2	(BC)1	(BC)2	BL9	BL10	BL12	BL13	Σ	Σ	Remarks
	1	2	5	3	4	6	7	8	11	9	10	12	13	Σx_i	Σx_i^2	
1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.074	0.038	each row contains five experimental results
2	1	1	2	1	1	2	2	2	2	2	2	2	2	-0.011	0.014	
3	1	1	3	1	1	3	3	3	3	3	3	3	3	0.311	0.070	
4	1	2	1	2	2	1	1	2	3	2	2	3	3	0.617	0.122	
5	1	2	2	2	2	2	2	3	1	3	3	1	1	1.086	0.303	
6	1	2	3	2	2	3	3	1	2	1	1	2	2	1.124	0.328	
7	1	3	1	3	3	1	1	3	2	3	3	2	2	2.309	1.141	
8	1	3	2	3	3	2	2	1	3	1	1	3	3	2.145	0.968	
9	1	3	3	3	3	3	3	2	1	2	2	1	1	2.487	1.272	
10	2	1	1	2	3	2	3	1	1	2	3	2	3	-0.134	0.071	
11	2	1	2	2	3	3	1	2	2	3	1	3	1	-0.408	0.060	
12	2	1	3	2	3	1	2	3	3	1	2	1	2	-0.113	0.024	
13	2	2	1	3	1	2	3	2	3	3	1	1	2	0.593	0.139	
14	2	2	2	3	1	3	1	3	1	1	2	2	3	1.041	0.360	
15	2	2	3	3	1	1	2	1	2	2	3	3	1	1.110	0.477	
16	2	3	1	1	2	2	3	3	2	1	2	3	1	1.805	0.715	
17	2	3	2	1	2	3	1	1	3	2	3	1	2	2.157	0.979	
18	2	3	3	1	2	1	2	2	1	3	1	2	3	1.757	0.646	
19	3	1	1	3	2	3	2	1	1	3	2	3	2	-0.283	0.029	
20	3	1	2	3	2	1	3	2	2	1	3	1	3	-0.147	0.082	
21	3	1	3	3	2	2	1	3	3	2	1	2	1	-0.378	0.072	
22	3	2	1	1	3	3	2	2	3	1	3	2	1	0.478	0.198	
23	3	2	2	1	3	1	3	3	1	2	1	3	2	0.746	0.122	
24	3	2	3	1	3	2	1	1	2	3	2	1	3	0.878	0.192	
25	3	3	1	2	1	3	2	3	2	2	1	1	3	1.492	0.496	
26	3	3	2	2	1	1	3	1	3	3	2	2	1	2.244	1.029	
27	3	3	3	2	1	2	1	2	1	1	3	3	2	1.718	0.648	
													Σ =	24.70	10.59	
T ₁	10.1	-1.09	6.95	8.19	8.57	8.598	8.01	9.32	8.49	8.13	7.15	8.51	8.5	T _i -- the sum of the results under level i		
T ₂	7.81	7.67	8.85	7.63	7.74	7.702	7.66	7.08	8.15	8.09	8.67	8.43	8.24			
T ₃	6.75	18.1	8.89	8.88	8.39	8.4	9.03	8.3	8.05	8.49	8.89	7.76	7.96			
T ₁ ²	103	1.18	48.3	67.2	73.5	73.93	64.2	86.8	72.1	66	51.1	72.4	72.2			
T ₂ ²	61	58.9	78.4	58.2	59.9	59.33	58.7	50.2	66.5	65.4	75.1	71.1	67.9			
T ₃ ²	45.6	328	79.1	78.8	70.4	70.56	81.5	68.9	64.9	72	79	60.2	63.4			

Total number of tests $N = 135$ Number of tests under each level: $n = 45$ Correction term: $CT = [(\sum \Sigma x_i)^2]/N = 4.52$ $SS_{iA} = \sum (T_{iA}^2)/n - CT$ $SS_{i(AB)} = SS_{i(AB1)} + SS_{i(AB2)}$ SS_i is the square sum of variance for factor A, B, C, AxB, AxC, or BxCThe random square sum of variance: $SS_e = SS_0 - \Sigma SS_i$ Where: $SS_0 = \sum \sum (x_i)^2 - CT = 6.08$ $\Sigma SS_i = 4.46$ Therefore: $SS_e = 1.61$ **ANOVA Table**

	SS_i	ν	SS/ν	F_i	$F_{(0.05)}$	$F_{(0.01)}$
A	0.1339	2	0.0669	4.49	3.09	4.82
B	4.1071	2	2.0535	138	3.09	4.82
C	0.0548	2	0.0274	1.84	3.09	4.82
AB	0.026	4	0.0065	0.44	2.46	3.51
AC	0.0323	4	0.0081	0.54	2.46	3.51
BC	0.0578	4	0.0144	0.97	2.46	3.51
bl	0.0529	8	0.0066	0.44	2.03	2.69
e	1.6109	108	0.0149			
Sum	6.0757	134				

AB two elements Table

	A1	A2	A3	Sum
B1	0.37	-0.65	-0.81	-1.09
B2	2.83	2.74	2.1	7.67
B3	6.94	5.72	5.45	18.1
Sum	10.1	7.81	6.75	24.7

AC two elements Table

	A1	A2	A3	Sum
C1	3	2.26	1.69	6.95
C2	3.22	2.79	2.84	8.85
C3	3.92	2.75	2.22	8.89
Sum	10.1	7.81	6.75	24.7

BC two elements Table

	B1	B2	B3	Sum
C1	-0.34	1.69	5.61	6.95
C2	-0.57	2.87	6.55	8.85
C3	-0.18	3.11	5.96	8.89
Sum	-1.09	7.67	18.1	24.7

A1B3C3

6. 3. 2 Influence of Frequency, Strain and Numbers of Stretching on Softness

Although some conclusion could be drawn from the orthogonal experiment, it is necessary to examine the trend of the influence of each factor on the target. So more extension experiments for each factor were added. *Figure 6.1*, *Figure 6.2* and *Figure 6.3* show the influence trend of stretching frequency, strain applied and the number of total cycles on the softening effect respectively.

6. 3. 3 Staking Simulation

Staking simulation experiment was carried out on a small scale staking device installed on Dartec (see 2. 2. 1. 2 *Figure 2. 6*). A typical load vs. time result is shown in *Figure 6.4*. The containing lines for all wave crest values and the trough values are drawn to show the changing trend of the maximum and minimum forces in each cycle.

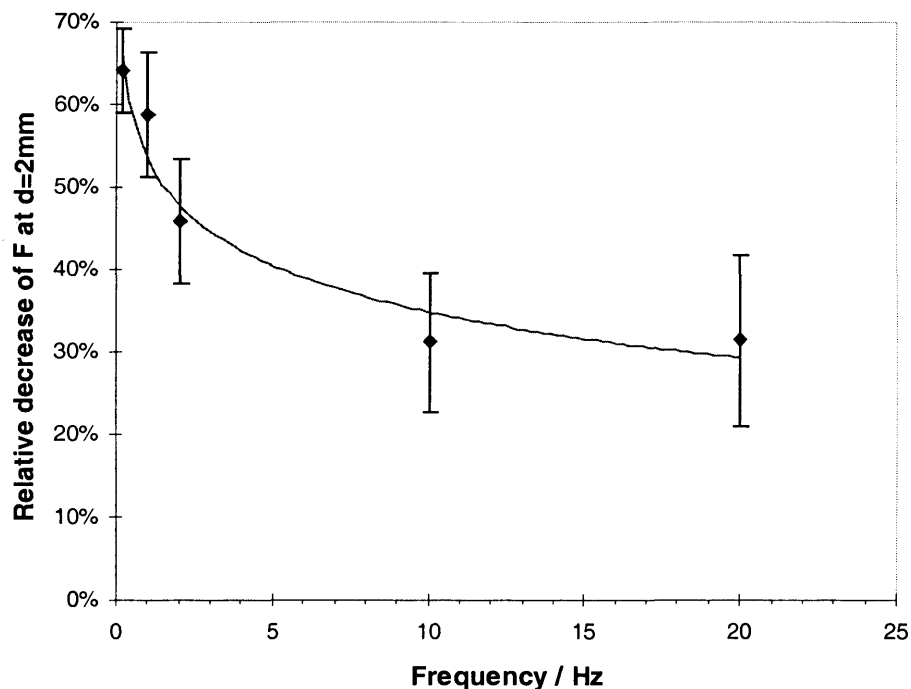


Figure 6.1 Influence of stretching frequency on the softening effect on a leather strip.

(upper-limit = 6mm (strain = 8.6%), number of cycles = 120)

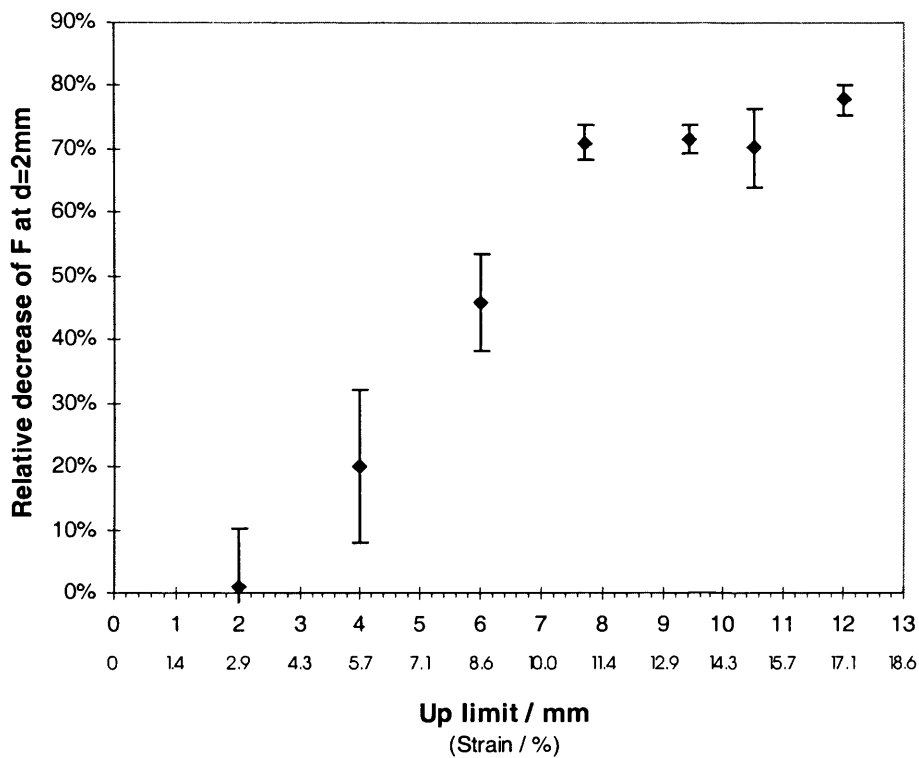


Figure 6.2 Influence of stretching upper-limit (strain) on the softening effect of a leather strip. (the first three points: frequency = 2 Hz, number of cycles = 120; next three points: frequency = 1 Hz, number of cycles = 200; the last point: frequency = 0.5 Hz, number of cycles = 200)

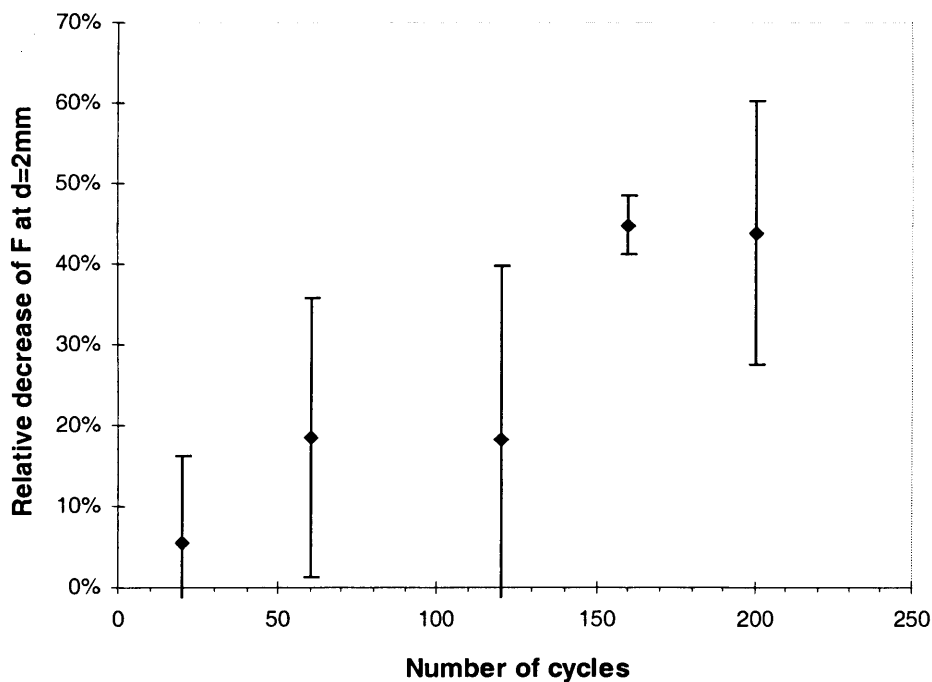


Figure 6.3 Influence of number of cycles on the softening effect of a leather strip. (frequency = 10 Hz, upper-limit = 4 mm (strain = 5.7%))

6. 4 Discussion

6. 4. 1 Statistical Conclusions and Discussion

Comparing the values contained in the column F_i and column $F_{(0.01)}$ from the ANOVA table, when $F_i > F_{(0.01)}$, we refuse H_0 under confidence level 0.01. In other words, we believe under the same confidence level that the corresponding factor in the most left column has significant influence on the target value. Otherwise the influence is not significant. Therefore, from the ANOVA table in table 6.3, the following statistical conclusions can be drawn:

- 1) Interactions between each pair of factors can be omitted, i. e. frequency, upper-limit or number of cycles play an independent role in contributing to the softness of leather.
- 2) From the influence of the three main factors, factor **A** and factor **C** do not have significant influence on the softness.
- 3) Factor **B**(i. e. upper-limit) influences the softness significantly.
- 4) Considering that the larger the object target value, the better, so a higher level of upper-limit is suggested in obtaining a better softening effect.
- 5) Based on 4) and the two element tables in table 6. 3, a combination of $A_1B_3C_3$ should be recommended to obtain an optimum softening effect in this leather strip stretching experiment.

When statistical conclusions are drawn, we must at the same time consider their practical meaning.

The statistical conclusion indicates that frequency and number of cycles do not have significant influence on the softness of leather strip. If this is an unconditional case, from a practical point of view, certainly a fewer number of cycles would be more efficient and energy saving. However, this cannot be applied without considering the conditions under which experiments were carried out. The range of the number of cycles in the experiment was between 20 and 120. Therefore it is in this range that the number of cycles does not have significant influence on the softening effect. Furthermore, according to the two element tables that contain factor **C**, when factor **C** changes from level 1 to level 2, a positive influence emerges on the target value. So we might well say that when the number of cycles is above 120, it's influence on further softening is no longer significant. This phenomenon can be explained by model of Kronick's^[49]. Crazes created in one stretch (strain less than about 60%) tend to close again if allowed to relax, but they are no longer internally cohesive. So

these cracks will open more easily on the next deformation. In our experiment, the repeated deformation (stretching) is carried out in a more continuous way, not allowing crazes to develop to their full extent before the next deformation circle. However, after a certain number of stretch cycles (here we may say 120), the effect on the structure of leather would be similar to that when allowing the sample to relax for a sufficient time. More cycles would add little softening effect after all the possible cracks have been opened.

The statistical conclusions show that the frequency does not have significant influence on the target value either. Still we also need to consider the frequency range used when this conclusion was drawn. From the extended frequency test, frequency has a more influence on the softness (*Figure 6.1*) below the frequency range used in the orthogonal experiment. Therefore the influence of this factor cannot be completely neglected and it is better to select a lower frequency value to obtain a better result. In fact, lower frequency means longer time for the crazes to develop and longer relaxation between two stretch cycles, which will result in a better softening effect.

Factor **B** (upper-limit or strain) contributes significantly to the softening effect on the leather strip. This is very clear from both the statistical conclusion and the extended range of upper-limit results (*Figure 6.2*). However there seems to be a turning point at about upper-limit = 7.51 mm (strain = 10.7%) above which an increase of the upper-limit does not influence the softening effect as greatly as before this point. This may be explained as follows: when the strain is below a certain value, application of such a strain will force the adhesions between fibre or fibre bundles to open up during the procedure of stretching. This effect becomes greater while the strain increases until a certain critical value is reached. Fibres and fibre bundles have been straightened to their full extension and after this point, further stretching can only increase the stiffness of these structural units which will counteract the further opening up of voids.

The best combination of $A_1B_3C_3$ suggests that a lower frequency together with a higher stretch strain and a relatively higher number of cycles will lead to a better softening effect for this strip test. This conclusion might find its use in the tannery where the staking process is carried out.

6. 4. 2 Discussion of the Simulation Test

The staking simulation experimental results (*Figure 6.4*) show how the total staking force changes as the staking process goes on.

The line containing wave crests shows that in the first 5 stretch cycles the maximum force required to stretch the strip sample to its maximum upper limit decreases rapidly and after further 15 cycles or so the maximum force decreases much less distinctively and levels off as more cycles applied. The line containing troughs indicates that there is a certain degree of set as early as after the first three cycles, which levels off after further cycles are applied. From this we can suggest that the opening up of adhesions inside the leather happens at a rather early stage during the cyclic stretching procedure. However for those “elastic” deformations, although they cannot be restored completely in each cycle, the rate of diminution of the forces required is rather slow.

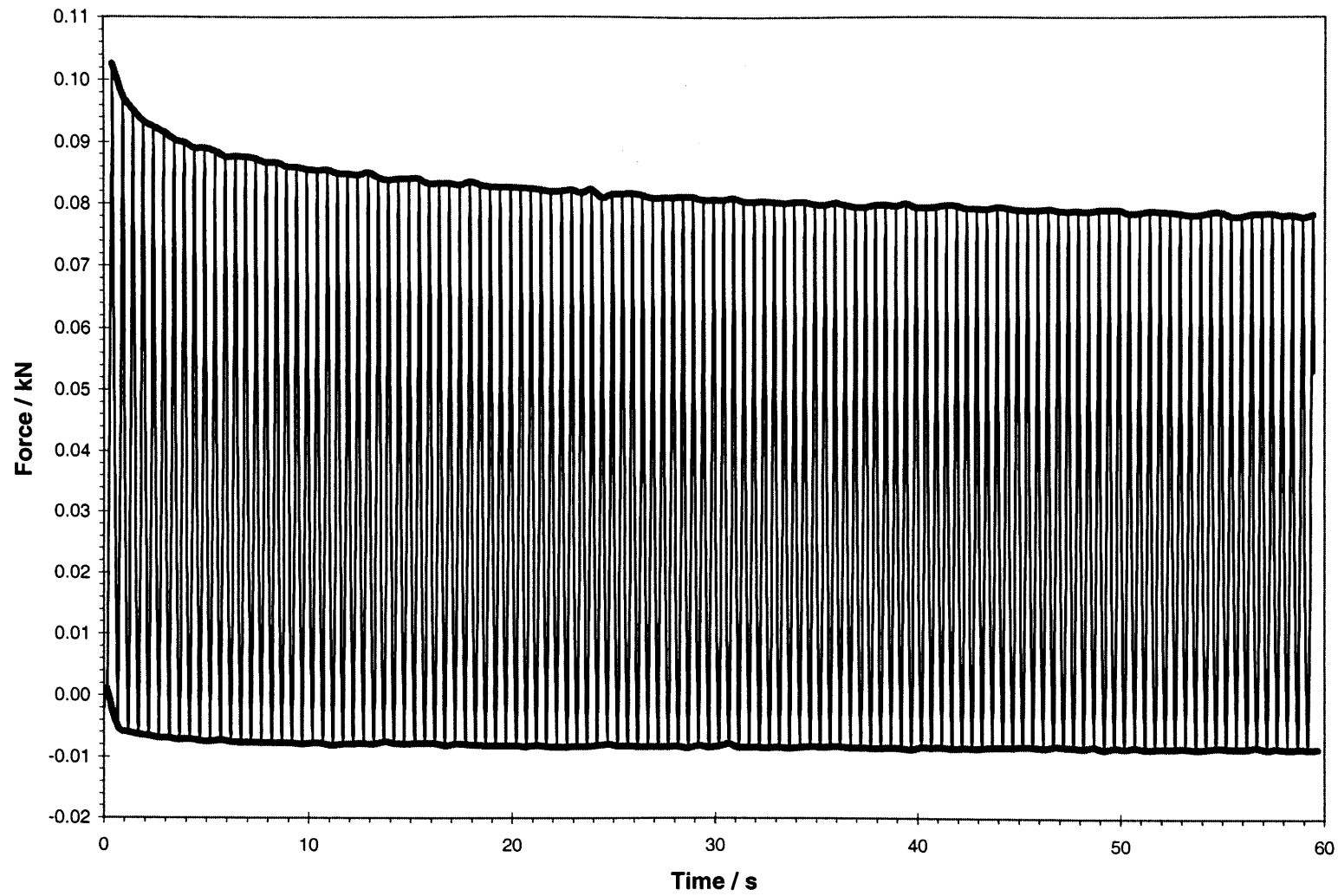


Figure 6. 4 (a) Simulation of the staking process. (frequency = 2 Hz, depth = 2 mm, cycles = 120)

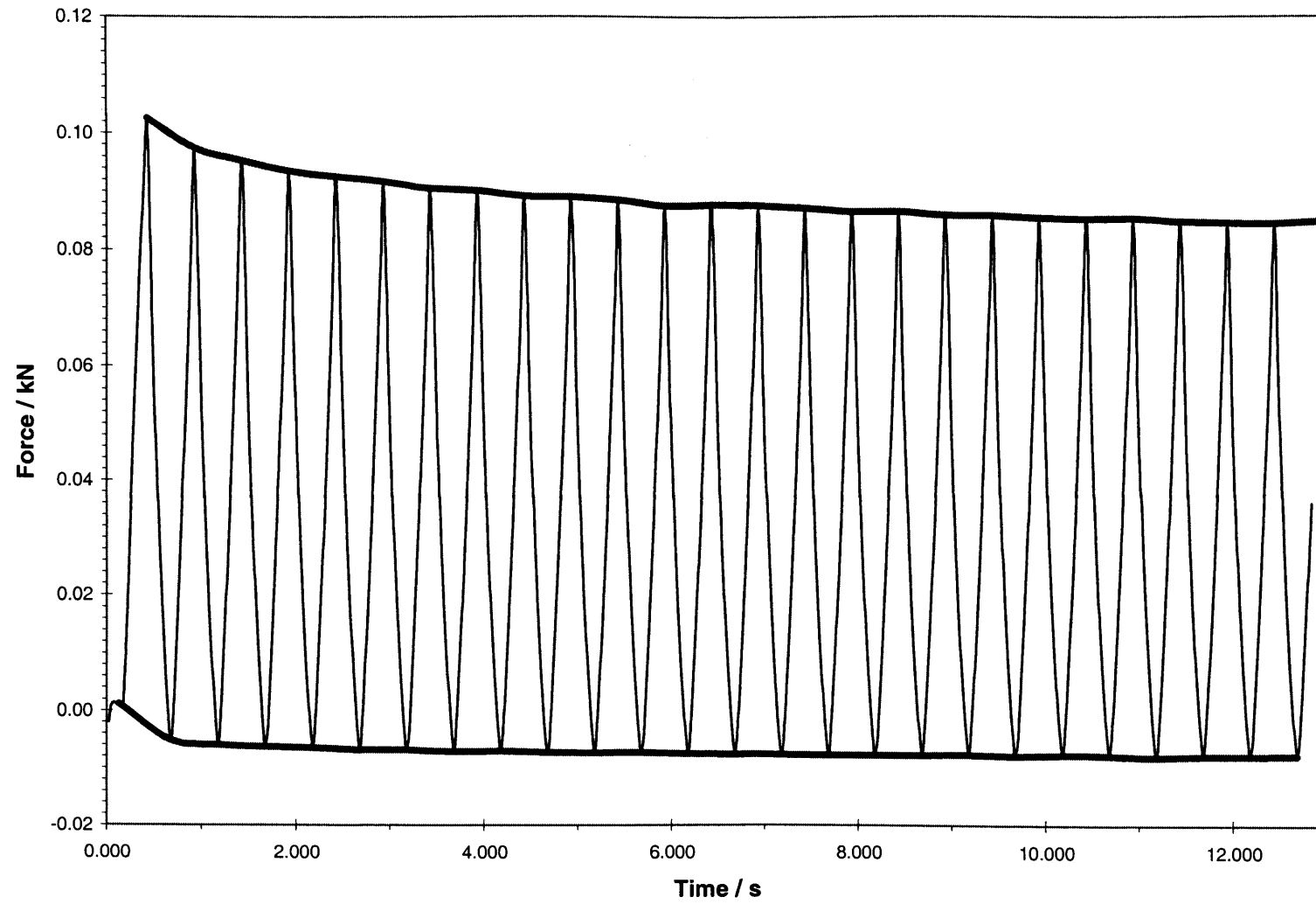


Figure 6. 4 (b) Simulation of the staking process. (frequency = 2 Hz, depth = 2 mm, cycles = 25)

CHAPTER 7

CONCLUSIONS

7.1 Conclusions

Three-point bend testing using a universal testing machine with a sensitive load cell can be used to characterise the bending behaviour of chrome tanned leather. The amount of force, F , required to bend such a leather increases in a linear way with increasing sample width w , which is in accordance with the standard theory of beam bending. The bending force, F , increases in a non-linear form with increasing sample thickness, t . Departure of the F vs. t relationship from the standard theory of beam bending is due to differences in stiffness between the grain and corium layers. The Williams theory of the bending of multi-laminated structures can be successfully applied to leather to account for different stiffnesses of the grain and corium strata. F is approximately proportional to the actual bending length, l , raised to a power between -2 and -3. Departure from the standard bending beam theory (for which $F \propto l^{-3}$) is mainly due to the relatively large deflections used during bending.

An empirical equation based on the results of the three-point bend testing can be obtained and used to relate results to subjectively judged softness. Best fit to an actual bending result can be achieved by adjusting two parameters, S_e and α , in the equation. S_e has a meaning equivalent to the bending stiffness in the standard theory. However S_e/t^n is the best parameter for judging the softness of leather where t is the thickness of sample and n is an approximate index in the power function describing the relationship between bending force F and sample thickness t , ($F \propto t^n$). The value of n depends on the type of leather being evaluated.

Compression index is a useful parameter when it is required to relate compression results to subjectively judged softness.

The compression behaviour of leather has many similarities to soft solid foams but there is an important difference in that the initial linear region is much less pronounced. The compression behaviour of leather may be described by a model in which four compressive stages are included. In most cases the compressive strain increases in a linear form as the sample thickness decreases during the first and the last compression stages. Generally, the relationship between the compressive stress and the sample thickness in the second and third compressive stages are related by a power function, although exceptions exist.

Energy absorbed on compression cycling is also a useful measure in relating instrumental measurement of compression to subjective evaluation.

Freezable water is identified in a differential scanning calorimetry (DSC) spectrum when water content is about 55% for an unfatliquored sample and 50% for a fatliquored one. DSC results show that water has a stronger interaction with collagen molecules in an unfatliquored leather than in a fatliquored one.

In wet blue leather, two states of freezable water can be detected in DSC. The first belongs to mobile water which interacts with collagen molecules by one hydrogen bond. This water produces a broad melting peak in DSC and its melting point is between -6°C and -10°C. The second type of water shows similar characteristics to bulk water and is manifested in DSC by a sharp melting peak at about 0°C.

The influence of water content prior to staking on the mechanical softening effect can be clearly shown in bending and tensile tests, but is not readily evident from compression tests. This influence of water content on staking effectiveness is mainly due to (a) adhesions becoming plasticised by water and so becoming harder to break; (b) adhesions re-forming on drying when the moisture content rises to levels where freezable water can exist. (i.e. at this level hydration of collagen fibre surfaces becomes great enough for adhesions to form). A maximum softening effect can be obtained in the staking process when moisture content is about 30 ~ 40%.

Softness assessed by different experimental techniques represents different modes of deformation occurring within the structure of leather. It is concluded that subjectively judged softness is a comprehensive tactile response based on the overall deformation response of the material to externally imposed forces in various directions. Softness measured by one instrumental method needs to be used in conjunction with the results of other instrumental methods to give the best instrumental parameter representing perceived softness.

Certainly parameters separately measuring bending stiffness (e.g. S_e/t'') and compressibility (e.g. CI or ΔE) need to be used. Probably some measure of resistance to tensile deformation also needs to be used although tensile stress at low strains may not be the most appropriate.

Among the factors involved in staking (frequency, amplitude and number of cycles), the amplitude plays the most significant role in obtaining the maximum softening effect although the other factors are important in particular frequency. Interactions between each pair of factors can be neglected. A combination of low frequency, higher strain and relatively

long staking time leads to a maximum softness by staking.

7.2 Recommendations

- (1) In instrumentally assessing the softness of leather the industry must separately assess resistance to bending, compression and tensile forces. No single measure is sufficient but all are important.
- (2) In order to obtain optimum softness on staking, a leather must be conditioned to a moisture content of 30 ~ 40% (dry leather basis).
- (3) Leather should not be conditioned to more than 50% moisture content since this will reducing staking efficiency.
- (4) Vibratory staking should be carried out at 1 Hz with a maximum amplitude of 10% strain, and for 150 cycles. In order to save energy no more than 150 cycles need be applied. There is no need for a staking machine to impose more than 10% strain.

7.3 Suggestions for Further Work

- (1) Build up a model based on observations from various physical tests to simulate the subjective softness assessment. This could be progressed by applying fuzzy logic theory to computer analysis.
- (2) Apply transmission electron microscopy (refer to *Figure 1.3*) with image analysis and relate the microstructural changes occurring during the staking to the softness of leather.
- (3) More work on staking simulation could be done using the pins and holes geometry in order to verify the results obtained with strips.
- (4) It would be very interesting to use acoustic emission during the multiple strain cycling of strips in order to confirm the effects on adhesion rupture.
- (5) Electron microscopy should be used to visualise the formation of cracks/crazes in the fibres during mechanical action.
- (6) Computer modelling (e.g. finite element method) may be useful in understanding how staking machine design affects the strain produced in the leather.
- (7) The work presented in this thesis could be extended to cover more types of leather.

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Appendix I**Process History of Wet Blue Leather**

Initial material: wet salted domestic ox hide

Process	Processing details
<u>Liming</u> [#]	
Dirt soak	200 wt% water at 26°C. Run 60 min. Drain
Main soak	170 wt% water at 26°C. Run 60 min. Drain. Repeat.
Lime	160 wt% water at 26°C. 2.5 wt% sodium sulphide. 5 wt% lime. Run 90 min. Run for 10 min. every 30 min. for 12 hours. Drain
White lime	150 wt% water at 22°C. 5 wt% lime. Run 15 min. Run for 10 min. every 120 min. for 24 hours. Drain. Empty drum.
Flesh split	2.2 - 2.4 mm backbone, 2.6 - 2.8 bellies.
<u>Chroming</u> ^{##}	
Wash	90 wt% water at 35°C. Run 10 min. Drain.
Delime	70 wt% water at 35°C. 3 wt% ammonium sulphate 0.4 wt% sodium metabisulphate. 1 wt% bate (PBW1). Run 60 min. Drain.
Wash	100 wt% water at 21°C. Run 10 min. Drain.
Tan	20 wt% water at 21°C. 6 wt% sodium chloride. 1 wt% sodium formate. Run 10 min. 2.2 wt% sulphuric acid (77%) Run 120 min. until pH=2.9~3.4. 8wt% chrome powder (42% basic). Run 60 min. 0.5 wt% tanbase. Run 10 hours whereby pH=3.6~3.8. Wash. Empty drum.
Sam	Sam & package

[#] Weight is based on the unfleshed wet salted hide.^{##} Weight is based on lime split pelt weight.

Appendix II**Simple Fatliquoring and Neutralising Process**

Process	Processing details
<u>Wash</u>	200 wt% water at 35°C. Run 10 min. Drain. Repeat.
<u>Neutralise</u>	150 wt% water at 35°C. 1 wt% sodium bicarbonate. Run 30 min. 1 wt% sodium bicarbonate. Run 30 min. Subsequent additions of sodium bicarbonate were added to achieve pH 5-5.5 Drain.
<u>Wash</u>	200 wt% water at 60°C. Run 10 min. Drain Repeat.
<u>Fatliquor*</u>	150 wt% water at 60°C. Run 10 min. 6 wt% Remsynol ESI. Run 45 min. Adjust pH to 3.5 with formic acid. Run 30 min. Drain.
<u>Dry</u>	Horse up for overnight. Toggle dry

* Without this stage for unfatliquored leathers.

Appendix III **Deduction of the Standard Theory of Beam Bending**

The element ABCD becomes A'B'C'D' after bending, *Figure 1*. The neutral axis O-O undergoes no strain during bending, only becomes bent in shape (O'-O'). Suppose the element is bent such that the local radius of curvature is R then, if plane sections are assumed to remain plane, an element at a distance y from the neutral axis has a strained length ds' given by:

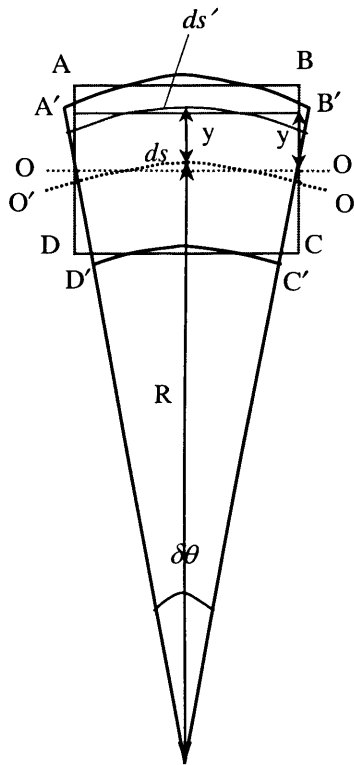


Figure 1

$$\begin{aligned} ds' &= (R + y) d\theta \\ ds &= R d\theta \end{aligned}$$

So, the strain of the element at y is:

$$\epsilon = (ds' - ds) / ds = y / R \quad (1)$$

For an ideal elastic material subject to a transverse force applied in the middle of a beam supported at each end (see *Figure 3.1*), the resistance to bending deformation is described by equation

$$F = E \frac{4dwt^3}{l^3} \quad (2)$$

where F — force applied to bend the beam to a depth d .
 l — distance between the two supporting points.
 w — width of the beam.
 t — thickness of the beam.
 E — Young's modulus.

Two basic assumptions are made in the deduction of equation (2):

(1) The extension behaviour of the material can be described by Hooke's law, i.e.

$$\epsilon_x = \frac{\sigma_x}{E} \quad (3)$$

(2) Deformation is by pure bending (see *Figure 3.2*), i. e.

$$\sigma_y = \sigma_z = \tau_{xy} = \tau_{xz} = \tau_{yz} = 0 \quad (4)$$

and

$$\sigma_{x_{lat}y} = E\epsilon_{x_{lat}y} = \frac{Ey}{R} \quad (3a)$$

or:

$$\frac{1}{R} = \frac{M_r}{EI_c} \quad (3b)$$

where σ_i is the internal stress along the i axis, τ_{ij} is the shear force on the ij plane, y is the distance from the xz plane, R is the curvature at the point concerned, M_r is the resultant internal moment and I_c is the second moment of the cross sectional area of the beam with respect to the neutral axis parallel to the z axis.

When the bending deflexion is small (see *Figure 3.3*), in addition to the above two assumptions, an approximation is made.

Since:

$$\frac{dy}{dx} \ll 1$$

therefore

$$\tan \theta = \frac{dy}{dx} \approx \theta$$

$$\frac{1}{R} = \frac{d\theta}{ds} \approx \frac{d(\frac{dy}{dx})}{ds}$$

$$ds = \sqrt{1 + (\frac{dy}{dx})^2} dx \approx dx$$

$$\frac{d\theta}{ds} = \frac{d^2y}{dx^2} = \frac{1}{R} \quad (4)$$

Thus, two linear differential equations are given by:

$$\left\{ \begin{array}{l} \frac{d\theta}{ds} = \frac{M}{EI} \end{array} \right. \quad (5)$$

$$\left\{ \begin{array}{l} \frac{d^2y}{dx^2} = \frac{M}{EI} \end{array} \right. \quad (6)$$

A free-body diagram of the entire beam is shown in *Figure 3.4 (b)*. For convenience, the left-hand end of the beam is chosen as the origin of the coordinate system. Since the loading is discontinuous at $x = l/2$, it will be necessary to integrate and solve two sets of equations simultaneously. If counter-clockwise moments are positive, for $0 \leq x \leq l/2$,

$$\sum^+ M = M - \frac{1}{2}Fx = 0$$

$$M = \frac{Fx}{2}$$

$$EI\theta = \int \frac{F}{2}x dx = \frac{F}{4}x^2 + C_1 \quad (7)$$

$$EI y = \frac{F}{12}x^3 + C_1x + C_2 \quad (8)$$

Similarly, for $l/2 \leq x \leq l$, we have

$$\sum^+ M = M - \frac{1}{2}Fx + F(x - \frac{l}{2}) = 0$$

$$M = -\frac{F}{2}(x - l)$$

$$EI\theta = \int -\frac{F}{2}(x - l) dx = -\frac{F}{4}(x - l)^2 + C_3 \quad (9)$$

$$EI y = -\frac{F}{12}(x - l)^3 + C_3x + C_4 \quad (10)$$

Since the deflection of each support must be zero, two boundary conditions are

$$y_{x=0} = 0 \quad y_{x=l} = 0$$

These conditions yield, from equation (8) and (10), respectively,

$$C_2 = 0 \quad C_4 = -C_3 l \quad (11)$$

There are two additional boundary conditions. Since the beam itself is continuous, equation (8) and (10) must give the same value for y at their only common point, at which $x = l/2$. This condition yields

$$C_1 = -C_3 \quad (12)$$

Also, since the deflection curve is smooth, equations (3-7) and (3-8) must give the same value at $x = l/2$. Thus,

$$C_1 = -\frac{Fl^2}{8} + C_3 \quad (13)$$

Equation (11), (12) and (13) yield

$$C_1 = -\frac{Fl^2}{16}$$

$$C_2 = 0$$

$$C_3 = \frac{Fl^2}{16}$$

$$C_4 = -\frac{Fl^3}{16}$$

Finally, the deflection will be a maximum when θ is zero, i. e. $x_{\max} = x|_{\theta=0}$. Hence, from equation (7), we have

$$\frac{F}{4}x_{\max}^2 + \left(-\frac{Fl^2}{16}\right) = 0$$

$$x_{\max} = \pm \frac{l}{2}$$

Only the second root is applicable, i. e. $x_{\max} = l/2$, and substitution of this root in equation (8) yields

$$\begin{aligned} y_{\max} &= \frac{1}{EI} \left(\frac{F}{12} x^3 + C_1 x + C_2 \right) \Big|_{x=x_{\max}} \\ &= -\frac{Fl^3}{48EI} \\ d &= |y_{\max}| = \frac{Fl^3}{48EI} \end{aligned} \quad (14)$$

For a rectangular bar, width w and thickness t as shown in *Figure 2*, the second moment of the cross sectional area about its horizontal centroidal axis I is given by

$$I = \int_{\text{cross section}} y^2 da = \frac{wt^3}{12} \quad (15)$$

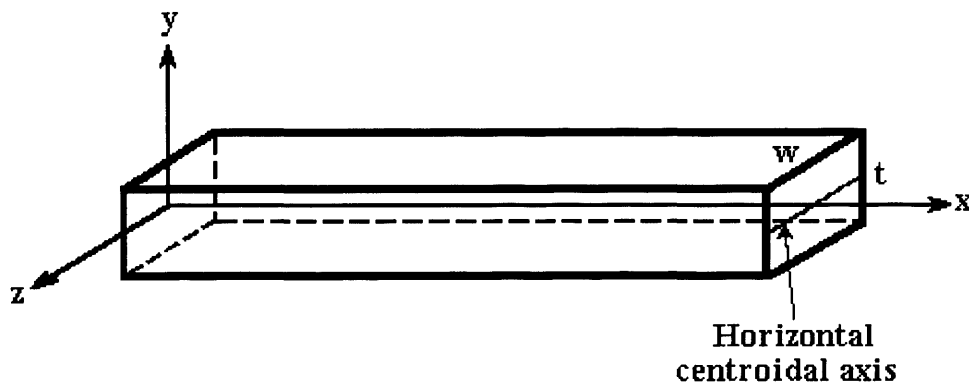


Figure 2

Therefore:

$$F = \frac{4Edwt^3}{l^3} \quad (2)$$

Appendix IV

Newton Approaching Method and the Logic Flow of the Programme

For the empirical equation as follows

$$F = S_e \cdot \frac{\alpha \cdot d^\alpha}{l^{2\left[1+\frac{\alpha^3}{1+2\alpha^3}\right]}} \quad (1)$$

and series of experimental data obtained from the bending test, bending force F_{expi} at bending depth d_i (i equals 1, 2, ..., n):

Table 1

F_{expi}	d_i
F_1	d_1
F_2	d_2
$\vdots$	$\vdots$
F_n	d_n

find S_e and α in equation (1) to satisfy the following condition:

$$\Psi(S_e, \alpha) = \sum_{i=1}^n \left[F_{\text{expi}} - F_{\text{equ}_i}(S_e, \alpha, d_i) \right]^2 = \text{minimum} \quad (2)$$

Here F_{expi} and F_{equ_i} are the experimental bending force and theoretical bending force at $d = d_i$ obtained from equation (1) respectively.

The S_e and α that satisfy the equation (2) should make equation (1) produce the best fit to the experimental bending curve.

Suppose that at the k th point (i.e. when $d = d_k$), there is $F_{\text{exp}_k} = F_{\text{equ}_k}$. Then at point k the relationship between S_e , F_{equ_k} and α is certain and can be expressed as:

$$S_e = \frac{F_{\text{exp}_k} l^{2\left[1+\frac{\alpha^3}{1+2\alpha^3}\right]}}{\alpha d_k^\alpha} \quad (3)$$

Substitute S_e in equation (2) for the above expression:

$$\Psi(\alpha) = \sum_{i=1}^n \left[F_{\text{expi}} - \left(\frac{d_i}{d_k} \right)^\alpha \right]^2 \quad (4)$$

To find the minimum value for equation (4) means to find the solution, α , for the following equation:

$$f(\alpha) = \frac{d\Psi(\alpha)}{d\alpha} = 0 \quad (5)$$

The discrimination of equation (5) can be computerised according to the Newton method in numerical analysis.

Suppose that the root, ξ , of equation $f(\alpha) = 0$ on (a, b) exists, $\alpha_1, \alpha_2, \dots, \alpha_n$, are the stepwise approximation of ξ .

If (i) $f(\alpha)$, $f'(\alpha)$ and $f''(\alpha)$ are continuous on $[a, b]$, (ii) $f(a) \cdot f(b) < 0$ and (iii) the signs of $f'(\alpha)$ and $f''(\alpha)$ do not change on $[a, b]$, then,

(1) when $f(a) \cdot f''(\alpha) > 0$,

$$\alpha_1 = a - \frac{f(a)}{f'(a)} \quad (6)$$

$$\alpha_n = \alpha_{n-1} - \frac{f(\alpha_{n-1})}{f'(\alpha_{n-1})} \quad (n = 2, 3, \dots) \quad (7)$$

(2) when $f(a) \cdot f''(\alpha) < 0$,

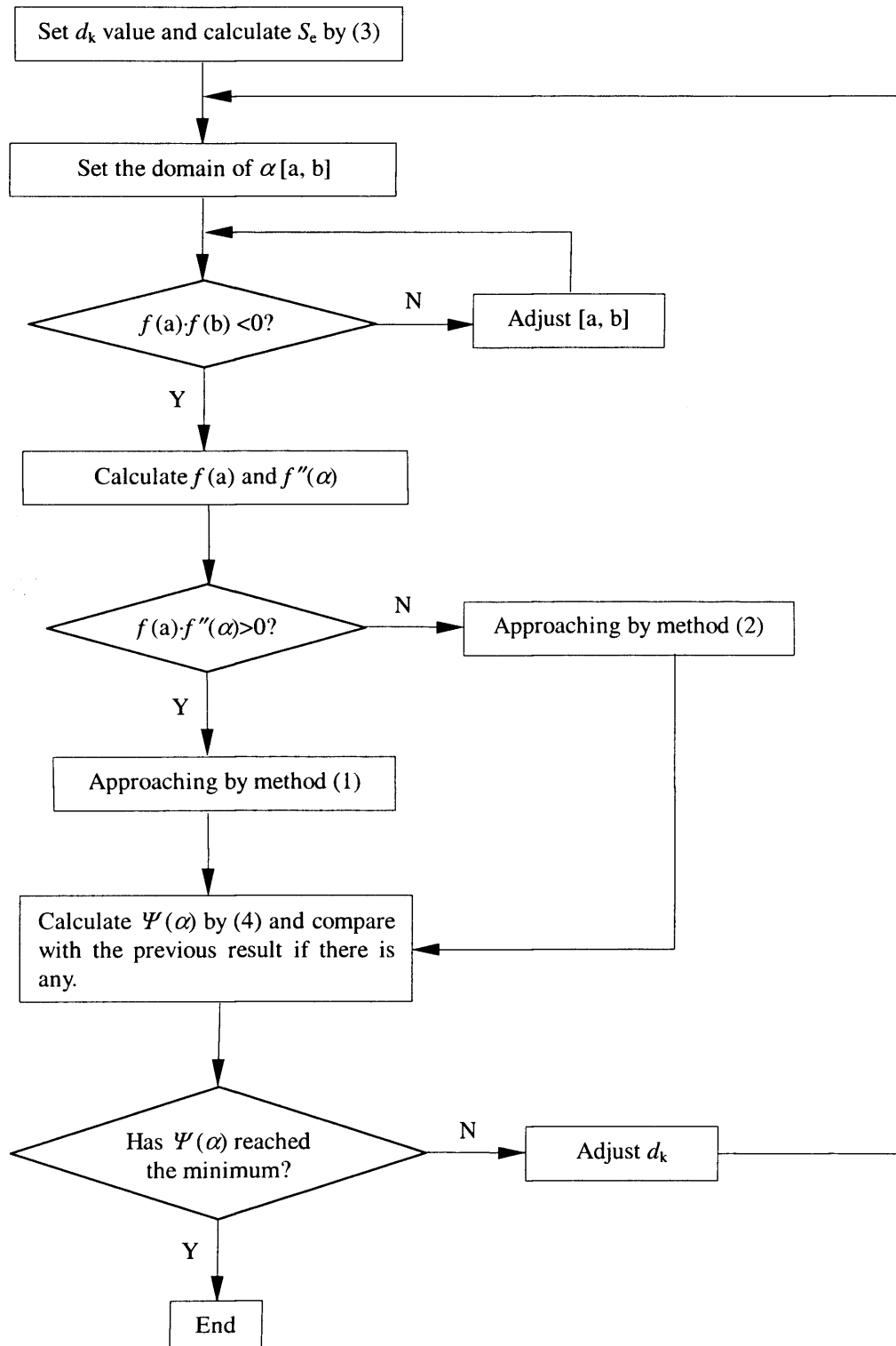
$$\alpha_1 = b - \frac{f(b)}{f'(b)} \quad (8)$$

$$\alpha_n = \alpha_{n-1} - \frac{f(\alpha_{n-1})}{f'(\alpha_{n-1})} \quad (n = 2, 3, \dots) \quad (9)$$

The error is: $|\alpha_n - \xi| \leq \frac{M_1}{2m_1} |\alpha_{n-1} - \xi|^2 \leq \frac{M_1}{2m_1^3} |f(\alpha_{n-1})|^2 \quad (10)$

Here M_1, m_1 are the maximum and minimum value of $|f'(\alpha)|$ on $[a, b]$.

The logic flow of the data simulation is presented as follows:



Appendix V

Deduction of the Equation of Calculating Water Content from DSC

Definitions of water content on a dry basis, η_d , and water content on a wet basis, η_w , are as follows:

$$\begin{aligned}\eta_d &= w_w / w_{ds} \\ \eta_w &= w_w / w_{ws}\end{aligned}$$

Here η_d and η_w are the water content on dry and wet basis of sample, %; w_w , w_{ds} and w_{ws} stand for the weight of water, dry sample and wet sample respectively.

Because $w_{ws} = w_{ds} + w_w$

Therefore $w_{ds} = \frac{w_{ws}}{1 + \eta_d}$

For a given DSC spectrum, according to its definition, freezable water content on a dry basis should be represented by the equation:

$$\begin{aligned}\text{Freezable water content (dry basis)} &= \frac{\text{Water(freezable)}}{w_{ds}} \\ &= \frac{\sum \Delta H_i / \Delta H_0}{w_{ws} \left(\frac{1}{1 + \eta_d} \right)} \\ &= \frac{\sum \Delta H_i}{\Delta H_0} \frac{1 + \eta_d}{w_{ws}}\end{aligned}$$

Here $\sum \Delta H_i$ is the sample's endothermic enthalpy from the DSC curve, J/g, ΔH_0 is the standard fusion enthalpy of pure water, 333.4 J/g.